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# Assessment of the boundary line approach for predicting $N_2O$ emission ranges from Australian agricultural soils

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# **Abstract**

This study aimed to assess the feasibility of predicting ranges in N<sub>2</sub>O emission with a boundary line approach using a few key driving factors. Intact soil cores (9 cm dia. and ~20 cm in depth) were collected from pasture, cereal cropping and sugarcane lands and incubated at various temperature and moisture conditions after addition of different forms of mineral nitrogen (NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub>). The pasture and sugarcane soils showed greater N<sub>2</sub>O production capacity than the cropping soils with similar mineral N and organic C contents or under similar temperature and water filled pore space (WFPS%), and thus different model parameters need to be used. The N<sub>2</sub>O emission rates were classified into three ranges; low (< 16 g  $N_2O/ha/day$ ), medium (16 –160 g  $N_2O/ha/day$ ) and high (> 160 g  $N_2O/ha/day$ ). The results indicated that N<sub>2</sub>O emissions were in the low range when soil mineral N content was below 10 mg N/kg for the cropping soils and below 2 mg N/kg for the pasture and sugarcane soils. In soils with mineral N content exceeding the above thresholds, the emission rates were largely regulated by soil temperature and WFPS and the emission ranges could be estimated using linear boundary line models that incorporated both temperature and WFPS. Using these key driving factors (land use, temperature, WFPS and mineral N content), the boundary line models correctly estimated the emission ranges for 85% of the 247 data points for the cropping soils and 59% of the 271 data points for the pasture and sugarcane soils. In view of the fact that  $N_2O$  emissions from soil are often very variable and difficult to predict and that the soil and environmental conditions applied in this study differed substantially, the above results suggested that, in terms of accuracy and feasibility, the boundary line approach provides a simple and practical alternative to the use of a single emission factor and more complex process-based models.

# **Key Words**

Greenhouse gas, nitrous oxide, boundary line model.

# Introduction

Three types of modelling approaches of varying complexity are available for estimating regional or national scale N<sub>2</sub>O emissions. The simplest and coarsest is the emission factor approach that estimates an annual loss of N<sub>2</sub>O as a fixed percentage of fertiliser N applied (IPCC 2006), which does not account for the effects of climate, soil type, cropping regime, and management practices on N<sub>2</sub>O emissions. The most complex approach is the process-based models, which generally require large amounts of input data and need to be calibrated under different climatic, soil and cropping systems. In the middle of the complexity spectrum are the empirical models, where N<sub>2</sub>O emissions are estimated as a function of a number of key driving factors (Conen et al. 2000; Roelandt et al. 2005). The relationships between the N<sub>2</sub>O emission rate and the driving factors are often restricted to the experimental conditions under which they were derived. In recognition of the large spatial and temporal variability and the difficulties in prediction of N<sub>2</sub>O emissions from soil, Conen et al. (2000) used soil temperature, WFPS, and mineral N content and a boundary line approach to predict  $N_2O$  emissions in three ranges: low (< 10 g  $N_2O$ -N/ha/day), medium (10 – 100 g  $N_2O$ -N/ha/day) and high (> 100 g N<sub>2</sub>O-N/ha/day). Conen et al. (2000) found that the prediction accuracy of this approach was comparable to those of the process-based models (Frolking et al. 1998). Given the small number of parameters required, this technique raises the prospect for large-scale application. However, the major drivers for N<sub>2</sub>O production may differ in different regions or ecosystems. The objective of this study was to test and, if necessary, modify the boundary line model of Conen et al. (2000) for spatial prediction of N<sub>2</sub>O fluxes.

## Methods

Intact soil cores were collected from eight different locations in southern Queensland (including 1 sugarcane, 3 cereal croping and 4 pasture sites) by driving PVC tubes (35 cm length and 10.5 cm i.d.) about 25 cm below the soil surface and pulling out with a hydraulically driven sampling rig. Mean annual temperature for the sites ranged from 14.4 to 20.7°C, and mean annual rainfall from 517 to 1706 mm. The basic properties in

the 0-20 cm depth were: pH (1:5 in water), 5.0-7.2, clay, 6-63%, TOC, 5-55 mg/kg, TON, 0.38-5.4 mg/kg, and bulk density, 0.73-1.61 g/cm<sup>3</sup>.

Following a pre-incubation at room temperature ( $\sim$ 22°C) and field moisture for 5-10 days in the laboratory, each soil core was applied with zero or 130 mg N as NH<sub>4</sub><sup>+</sup> and/or NO<sub>3</sub><sup>-</sup> on the soil surface. Water was then added gradually using a fine sprayer to bring soil moisture content to different water filled pore space (WFPS). After equilibrating for several hours, initial soil samples were destructively taken to measure soil mineral N and water contents in 0 – 10, 10 – 20 and > 20 cm depths. The remaining soil cores were covered with a cap that had a hole in the middle and incubated at 5, 10, 15 and 25°C for 3 days. Gas samples were taken daily from the head space before and after sealing the cap with a rubber septa for 30 – 60 minutes and later analysed for N<sub>2</sub>O and CO<sub>2</sub> concentrations with a gas chromatograph equipped with ECD and TCD detectors. The soil cores were destructively sampled after the incubation and determined for mineral N and water content in 3 depths as described before.

# Results

# Classification of soils

Under the same temperature, or similar WFPS, mineral N, DOC and TOC contents, the pasture and sugarcane soils generally had higher emission rates than the cropping soils (data not presented). The pasture soil cores had living plant roots, which could supply bio-available C to microbes from root exudates and fine root turnover and thus enhance N<sub>2</sub>O production capacity. Thus, separate model parameters should be developed for the cropping soils and the pasture and sugarcane soils.

# Boundary lines of the emission ranges

Figure 1 shows that  $N_2O$  emissions generally fell in the low range if mineral N content was below 10 mg N/kg for the cropping soils and below 2 mg N/kg for the pasture and sugarcane soils, regardless of soil temperature and WFPS values. The difference in the mineral N threshold values between the cropping soils and the pasture/sugarcane soils could be related to the difference in their  $N_2O$  production capacities as discussed above.

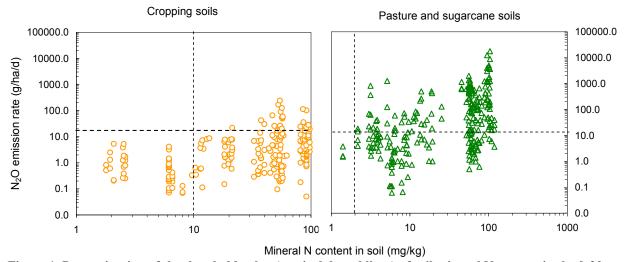


Figure 1. Determination of the threshold value (vertical dotted lines) of soil mineral N content in the 0-20 cm layer below which  $N_2O$  emission rates were limited to the low emission range.

For soils with mineral N content above the threshold values,  $N_2O$  emission rates varied substantially, presumably controlled primarily by other factors. To further assess the effects of these factors on the magnitude of  $N_2O$  emissions, the observed emission data were arranged into low (< 16 g  $N_2O/ha/d$ ), medium (16 to 160 g  $N_2O/ha/d$ ) and high (> 160 g  $N_2O/ha/d$ ) emission ranges. The distribution of the data points in each emission range in relation to soil temperature and WFPS is shown in Figure 2. Similar analyses were conducted using other possible regulating factors such as TOC, DOC, clay content and pH in various combinations with temperature and moisture content (WFPS%, w/w% or v/v%). These alternative analyses resulted in no significant improvement compared to the results shown in Figure 2. This suggested that temperature and WFPS were the main driving factors for soils with high mineral N content, although their effects might be interactively affected by other factors.

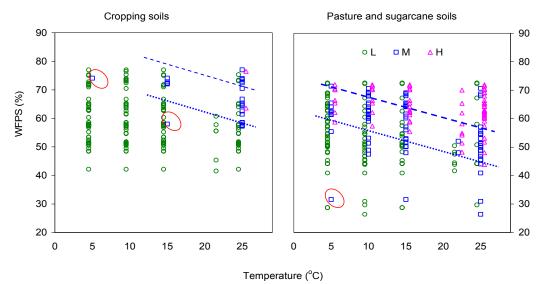


Figure 2. Distribution of  $N_2O$  emissions in the low (<16 g  $N_2O/ha/d$ ), medium (16 to 160 g  $N_2O/ha/d$ ) and high (>160 g  $N_2O/ha/d$ ) ranges in relation to temperature and WFPS in soils where mineral N was presumably not limiting. The dotted and dashed lines represent the boundaries between the low and medium, and between the medium and high ranges respectively. Horizontal separation of the data points at the same temperature into low, medium and high ranges were for clear illustration only.

Figure 2 shows that  $N_2O$  emissions at lower temperature/WFPS combinations were mostly in the low range, whilst the high emissions tended to occur at higher temperature/WFPS combinations. However, there was no clear cut-off point for the boundary conditions between the low and medium or between the medium and high ranges, further indicating the complex relationships between  $N_2O$  emissions and the regulating factors. After removing one or two outlier data points (in red circles in Figure 2), a linear regression analysis using only the data in the medium emission range of each land use type indicated that there was a complementary effect between temperature and WFPS on  $N_2O$  emission rates. This was consistent with the findings of Conen *et al.* (2000). The trend line of this relationship could be described by:

WFPS (%) + 0.76 T (
$$^{\circ}$$
C) = 84 for the cropping soils. (1)

WFPS (%) + 0.71 T (
$$^{\circ}$$
C) = 69 for the pasture and sugarcane soils.

By mathematically treating WFPS as the dependent variable in the regression analysis, the lower and upper boundary lines of the medium emission range could be estimated by vertically shifting the trend line down and up, respectively, by a magnitude of the residual standard error of WFPS.

For the cropping soils, the boundary line below which  $N_2O$  emission was limited to the low emission range was given by:

WFPS 
$$(\%) + 0.76 \text{ T } (^{\circ}\text{C}) = 78$$
 (3)

when T  $\geq$ 10°C. N<sub>2</sub>O emissions from the cropping soils were generally in the low emission range at <10°C (Figure 3). The boundary line separating the medium and high emission ranges was given by: WFPS (%) + 0.76 T (°C) = 90

WFPS (%) + 
$$0.76 \text{ T}$$
 (°C) = 90 (4)  
For the posture and suggressine soils, the boundary lines between the law and medium emission ranges and

For the pasture and sugarcane soils, the boundary lines between the low and medium emission ranges and between the medium and high emission ranges were given, respectively, by:

WFPS (%) + 0.71 T (
$$^{\circ}$$
C) = 63, and (5)

WFPS (%) + 0.71 T (
$$^{\circ}$$
C) = 75 (6)

Therefore, with the knowledge of land use, temperature, WFPS and mineral N content in the upper 20 cm soil, the N<sub>2</sub>O emission rate from a soil can be estimated as summarised in Table 1.

Table 1. Summary of the boundary line model for predicting N<sub>2</sub>O emission ranges.

Land use	Mineral N (mg/kg)		Temperature (T °C) and WFPS (%)	Flux ranges (g N <sub>2</sub> O/ha/d)
	≤ 10	or	$T \le 10 \text{ or WFPS} + 0.76 \text{ T} \le 78$	< 16 (L)
Cropping	> 10	and	$T > 10$ and $78 < WFPS + 0.76$ $T \le 90$	16 - 160 (M)
	> 10	and	T > 10 and WFPS + 0.76 T > 90	> 160 (H)
Pasture or	$\leq 2$	or	$T < 5 \text{ or WFPS} + 0.71 \text{ T} \le 63$	<16 (L)
sugarcane	> 2	and	$T \ge 5$ and $63 < WFPS + 0.71 T \le 75$	16 - 160  (M)
	> 2	and	$T \ge 5$ and WFPS + 0.71 T > 75	> 160 (H)

(2)

Altogether 247 and 271  $N_2O$  emission measurements (mean values within the first 3 days) were available for the cropping soils and for the pasture and sugarcane soils, respectively. On average across all emission ranges, the percentage of correct predictions for the above models was 85 for the cropping soils and 59% for the pasture and sugarcane soils. Considering the contrasting land uses, soil properties and climate conditions in the sampling regions, as well as the wide ranges of temperature, WFPS and mineral N forms and amounts applied in the incubation experiments, accurately predicting  $N_2O$  emissions from all the soils presents a challenge for any modelling approach. The boundary line model requires information for only a few input factors and thus has the potential to be used in large-scale predictions.

### Conclusion

In terms of accuracy and feasibility, the boundary line modelling approach provides a practical alternative to the use of a single emission factor and more complex process-based models. Similar to the calibration of process-based models, the accuracy of prediction may be improved by adjusting the gradient and intercept of the boundary lines for a specific site. Such adjustment would reflect the impacts of other regulating factors not considered in the model.

# Acknowledgement

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# Bioenergy residues as soil amendments: climate-relevant C and N dynamics during decomposition

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# **Abstract**

It is not clear how an expanding bioenergy sector will affect land use and what could be the environmental consequences. Probably the increased bioenergy production will lead to higher input of its by-products to the soil as amendments or fertilizers. However, it is still unclear how these novel by-products of bioenergy production will influence microbial transformation processes in soil, and thereby its greenhouse gas balance and organic matter stocks. In this laboratory incubation study, we compared the greenhouse gas dynamics after application of different bioenergy by-products into an agricultural soil. Ten by-products were selected from different bioenergy sectors: anaerobic digestion (manure digestates), first generation biofuel residues (rapeseed meal, distilled dried grains with solubles), second generation biofuel residues (non-fermentables from hydrolysis of different lignocellulosic materials) and pyrolysis (biochars). These by-products were added at the same N rate (150 kg N/ha) to a moist (80% water filled pore space) sandy soil and incubated at 20 °C for 60 days.

After 60 days, first generation biofuel residues had emitted more than 80% of added C as CO<sub>2</sub>. Around 60% was emitted in the case of second generation biofuel residues and 40% with digestates. Biochars were the most stable residues with the lowest CO<sub>2</sub> loss (between 0.5 and 5.8 % of total added C). Regarding N<sub>2</sub>O emissions, addition of first generation biofuel residues led to the highest total N<sub>2</sub>O emissions (between 2.5 – 6.0% of added N). Second generation biofuel residues emitted between 1.0-2.0% of added N, whereas anaerobic digestates led to emissions lower than 1% of added N. The two biochars used in this study led to negative N<sub>2</sub>O emissions, i.e. lower than N<sub>2</sub>O emitted from the blank soil. We conclude that, at least in the short term, the effects of biofuel residues on the combined greenhouse gas balance of the soil ranges from beneficial (biochar) via mixed (digestates, second generation biofuels) to manifestly adverse (first generation biofuels). These effects are relevant and should be taken into account in life cycle analyses of biofuel production and assessment of the environmental impact of biofuels and bioenergy.

# **Key Words**

Biofuels by-products, nitrous oxide, carbon dioxide, soil amendments, mineralization.

# Introduction

In spite of the large number of studies analysing the benefits of biofuels on the greenhouse gas balance, only a few studies take into account the contribution of residues from biofuel production. Farrell *et al* (2006) underlined the importance of considering the fate of by-products on net energy and GHG calculations. They considered that by-products of ethanol production have a positive economic value and displace competing products that require energy to make. However, large amounts of residues could represent a serious environmental problem leading to elevated GHG emissions if inappropriate management options are selected. The physico-chemical characteristics of the different bioenergy residues vary widely depending on the original biomass and the method used for energy production. But generally speaking, these materials still have a high concentration of C (usually the most recalcitrant fractions). Moreover, they contain a wide range of nutrients that must be recycled in a environmental benign way. It is likely that the intensification of bioenergy production will lead to an increased use and higher input of these by-products to the soil as amendments or fertilizers.

To our knowledge there is a limited number of studies that measure greenhouse gas relevant dynamics such as C mineralization and N<sub>2</sub>O emissions after application of bioenergy residues to soil (Moller and Stinner 2009; Spokas *et al.* 2009), and most of them are focused on biogas residues or biochar. No literature is available comparing the main different bioenergy chains and evaluating how the application of N-enriched bioenergy residues will influence microbial transformations processes in soil and thereby the emissions of

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greenhouse gases. The aim of this paper is therefore to compare C and N climate relevant gases emissions during decomposition in soil of residues generated by different bioenergy sectors.

# Methods

Soil and residues used in the incubation experiment

A sandy agricultural soil (Typic Endoaquoll with 75% sand, 23% silt, 2% clay) (USDA, 1999) was selected for the incubation experiments and sampled from the 10-30 cm layer at the experimental farm 'Droevendaal', outside Wageningen, the Netherlands (51°59'N, 5°39'E). Air-dried soil was sieved (< 2 mm) and stored (15°C) until the beginning of the experiment. Ten organic residues from bioenergy production were selected: residues from anaerobic digestion (cow manure digestate (CMD) and pig slurry digestate (PSD)); first generation biofuel residues (rapeseed meal (RSM) from biodiesel production, dried distillers grains with solubles (DDGS), and two different yeast concentrates (YC1 and YC2) from bioethanol production); second generation biofuel residues (non-fermentables from enzymatic hydrolysis of potato peels (NFPP) and non-fermentables from enzymatic hydrolysis of wheat straw (NFWS); commercially available green waste biochar (GBC) and poultry manure biochar (PBC), both produced by continuous slow pyrolysis at 550 °C. The residues were freeze-dried (except the biochars), ground and sieved (< 0.5 mm) before application to avoid a moisture or particle size effect. Their chemical characteristics are shown in Table 1.

# Soil incubations

The incubation experiment was carried out with 500 g (based on oven-dry weight) soil in 1 L glass jars at 20 °C. Before the start of the incubation, the soil was adjusted to ca. 60 % of water holding capacity (WHC) and pre-incubated at 20 °C for 7 days. Subsequently the different organic residues were thoroughly mixed and water was added to adjust moisture to 80% of water filled pore space. The jars were covered by a woven black polyethylene cover, to allow gaseous exchange, but retard evaporation. The incubation jars were maintained in a climatic room with a constant temperature (20 °C) and air humidity (40%). The soil moisture was gravimetrically adjusted 2 times a week with de-ionized water for each individual jar. During the incubation experiment we evaluated  $CO_2$  and  $N_2O$  emissions when the different bioenergy residues were applied. The experiment, consisting of 11 treatments: a control (unfertilized soil) and ten bioenergy byproducts, was laid out as a randomized block design with five replicates per treatment and lasted 60 days. All the residues were applied at a rate of 150 kg N/ha, corresponding to 50 mg N/kg soil based on a plough layer of 25 cm.

Table 1. Main chemical properties of the bioenergy by-products used in the experiment.

Table 1. Main	memmean p.	oper ties	or the k	ordenergy b	y prou	ucts uscu	in the ca	per intent.		
Residue type	Residue	TOC	TN	TOC/TN	pН	EC	WSC	WSN	$NH_4^+$	$NO_3$ + $NO_2$
		(%)	(%)			(dS/m)	(g/kg)	(g/kg)	(mg/kg)	(mg/kg)
Anaerobic	CMD	41.7	3.2	13.2	9.03	16.80	48.8	4.3	166	4.2
digestion	PSD	37.9	4.4	8.7	8.52	19.77	38.7	11.6	5361	2.5
First generation	RSM	45.9	6.0	7.7	6.15	2.54	74.4	2.4	180	13.4
biofuels	DDGS	48.4	5.4	8.9	5.02	5.40	111.1	4.4	151	2.0
	YC1	48.5	6.2	7.8	4.22	8.36	202.5	12.8	1153	1.9
	YC2	47.4	4.7	10.0	4.05	8.39	220.0	8.7	274	1.5
Second	NFWS	44.8	1.3	34.2	5.82	3.50	135.3	2.0	196	18.0
generation	NFPP	46.5	3.6	12.9	5.59	2.75	44.3	2.8	292	38.2
biofuels										
Pyrolysis	GBC	86.3	0.3	345	6.55	0.12	0.1	0.0	17	0.4
	PBC	37.0	1.2	29.8	10.25	10.32	0.5	0.0	2	1.8

Measurements of  $N_2O$  and  $CO_2$  emissions

Fluxes of  $N_2O$  and  $CO_2$  were measured 26 times over a period of 60 days. Gas fluxes were analysed daily during the first six days, decreasing the sampling frequency to four times, three and twice a week subsequently. Changes in the concentration of  $N_2O$  in the headspace of the jars after closing the lid were determined with a photo-acoustic infrared analyser (Innova air Tech Instruments, Ballerup, Denmark) which was directly attached to the jars by two Teflon tubes and needles through septa. The gas analyser was fitted with optical filters to measure selectively concentrations of  $N_2O$ ,  $CO_2$  and water vapour. To prevent a strong accumulation of  $CO_2$  in the headspace of the jars, which may interfere with the  $N_2O$  measurements, a soda lime trap was installed in the tube at the inlet to the gas monitor (Velthof *et al.* 2003).  $CO_2$  emissions were measured following a similar setup, but without the soda lime filter and after a separate closing period. The concentration of  $N_2O$  and  $CO_2$  were measured 30 min after closing the jar.

# Statistical analysis

The impact of the different characteristics of biofuel residues on CO<sub>2</sub> and N<sub>2</sub>O losses was determined by redundancy analysis (RDA) using Canoco 4.5 for windows software package. Significance of the ordination axes was calculated by the Monte-Carlo permutation test.

# **Results and discussion**

Application of the bioenergy by-products to the soil resulted in an immediate increase of soil respiration. The highest CO<sub>2</sub> and N<sub>2</sub>O fluxes were produced during the first week of incubation. Biochars were the exception with very low respiration rates through the whole incubation period. In the case of green-biochar, respiration was never significantly different than that of the control soil (data not shown). The relative amounts of total C evolved as CO<sub>2</sub> after 60 days differed significantly among residue categories and decreased in the order: first generation biofuel by-products> second generation biofuel by-products> manure digestates> biochars (Table 2). First generation biofuel residues resulted in almost complete decomposition during the experiment, contributing little or nothing to soil organic matter stocks. Conversely, second generation biofuel residues led to a buildup of C comparable to anaerobic digestates. Finally, biochars were by far the most recalcitrant residues, showing therefore the highest C sequestration potential. N<sub>2</sub>O emissions followed a similar pattern, with highest losses for first generation biofuel residues. Biochars led to negative (although not statistically significant) N<sub>2</sub>O emissions.

Table 2. Percentages of CO<sub>2</sub>-C and N<sub>2</sub>O-N emitted respect to C and N added with biofuel by-products in soil and total C remaining after 60 days incubation.

Residue type	Residue	CO <sub>2</sub> -C emitted respect to	$N_2O$ -N emitted respect to	C remaining in
		added C (%)	added N (%)	soil
				(g C/kg soil)
Anaerobic digestion	CMD	$38 \pm 9$	$0.2 \pm 0.1$	$0.41 \pm 0.06$
	PSD	$42 \pm 5$	$0.8 \pm 0.1$	$0.25 \pm 0.02$
First generation	RSM	$94 \pm 11$	$5.0 \pm 1.3$	$0.02 \pm 0.04$
biofuels	DDGS	$91 \pm 12$	$2.5 \pm 0.7$	$0.04 \pm 0.05$
	YC1	$107 \pm 16$	$6.0 \pm 2.7$	$-0.03 \pm 0.06$
	YC2	$81 \pm 12$	$2.9 \pm 0.6$	$0.10 \pm 0.06$
Second generation	NFWS	$62 \pm 5$	$1.1 \pm 0.3$	$0.65 \pm 0.09$
biofuels	NFPP	$75 \pm 13$	$1.9 \pm 0.4$	$0.16 \pm 0.09$
Pyrolysis	GBC	$0.5 \pm 0.2$	$-0.10 \pm 0.03$	$17.17 \pm 0.04$
•	PBC	$6 \pm 2$	$-0.06 \pm 0.05$	$1.40 \pm 0.03$

Mean  $\pm$  std error (n=5)

Figure 1 shows the redundancy analysis (RDA) ordination plot. The results of RDA indicated that 96.3 % of the total variance within the investigated parameters was explained by the first and second ordination axis with the different characteristics of the residues as environmental variables. High species-environment correlation (0.984, P=0.002) revealed a strong relation between greenhouse gas emissions and residues characteristics. Total concentration of N in the residue seems to be the most critical factor, highly correlated with both CO<sub>2</sub> and N<sub>2</sub>O emissions. Samples from different bioenergy chains clearly grouped with respect to the first ordination axis (x axis), showing their different behaviour with respect to N<sub>2</sub>O and CO<sub>2</sub> emissions. The biochars (GBC and PBC) were the resides positioned at the right of the diagram indicating the lowest C and N losses and highest C sequestration potential. Digestates (PSD, CMD) exhibited lower than average emissions, followed by second-generation biofuels (NFPP, NFWS) which were positioned just in the middle. First generation biofuel by-products (RSM, DDGS, YC1, YC2) produced the most adverse impact (high emissions, low C sequestration) and all of them showed higher than average emission values.

# Conclusion

With this study we highlight the importance of considering the by-products of bioenergy production on net greenhouse gas balance calculations. Biofuel by-products vary enormously in chemical composition and, when used directly as soil-amendments, they lead to very different climate relevant dynamics. Whereas some may lead to elevated  $N_2O$  emissions and contribute little to soil organic matter, others may increase soil organic matter stocks with little  $N_2O$  emission. These dynamics need to be taken into account in life-cycle analyses in the future in order to reach a truly integrated assessment of the climate impact of biofuel production.

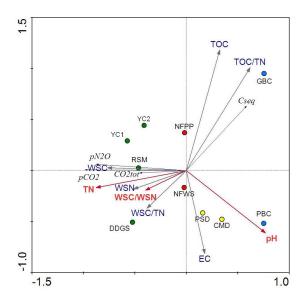


Figure 1. Redundancy analysis (RDA) ordination diagram depicting the residues characteristics responsible for differences in  $\mathrm{CO}_2$  and  $\mathrm{N}_2\mathrm{O}$  emissions among the biofuel by-products. The length of the arrows indicates the significance for sample differentiation. Arrows point in the direction of by-products with above average signal. Color legend: green represents first generation biofuel residues, red for second generation residues, yellow for digestates and blue for biochars. pCO2 and pN2O represent the percentages of C and N emitted as  $\mathrm{CO}_2$  and  $\mathrm{N}_2\mathrm{O}$  respectively. Cseq refers to amount of C remaining in soil after 60 days. For biofuel residues abbreviations see the methods section.

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# Brazilian greenhouse gas emissions: the importance of agriculture and livestock

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# **Abstract**

Tthe aims of this study were (i) to update estimates of the GHG emissions for the Brazilian territory, (ii) estimate the sinks to provide calculations of the GHG net emissions to the 1990-2005 period, (iii) to calculate the actual and estimated shares of agriculture and livestock activities, and (iv) to discuss in the light of the new figures and patterns the best mitigation options for Brazil. Total emissions in CO<sub>2</sub>-eq increased by 17% during the 1994-2005 period. CO<sub>2</sub> represented 72.3% of the total, i.e. a small decrease, in favour of non-CO<sub>2</sub> GHG, in relation to 1994 when its share was 74.1%. The increase of all GHG excluding LUCF was 41.3% over the period 1994-2005. CAIT-WRI estimated a higher increase (48.9%) that classified Brazil at the 69th position. Using our estimates Brazil will fall to the 78th position. But in both cases Brazil increased in clearly lower values than the tendency calculated for China and India, two major emitters, with increases of 88.8% and 62.1%, respectively. Besides effort to curb emissions from the energy and deforestation sectors, it is now a top priority to implement a national program to incentive mitigation efforts concerning the agricultural and livestock sectors.

# **Key Words**

Soil, livestock, CO<sub>2</sub>-equivalent (CO<sub>2</sub>-eq), inventory, land use change and forestry.

# Introduction

It is widely recognized that the Land Use, Land-Use Change and Forestry (LULUCF) is a key sector of Climate Change. The agricultural sector alone is responsible for about 14% of total global anthropogenic GHGs emissions and is expected to have high emission growth rates, driven mainly by population and income increases. Deforestation is responsible for an additional 17%, setting the total contribution of the LULUCF sector to nearly one third of the current total global emissions (IPCC 2007). Brazil is one of the top world greenhouse gas (GHG) emitters and a majority of Brazil's GHG emissions, which contribute to global warming, come from burning linked to deforestation of the Amazon biome, and not from fossil fuels which are the main culprit in most countries. Brazil suffered and still regularly suffers pressure to curb destruction of the Amazon rainforest. The latest official Brazilian data on GHG emissions and sinks were published in 2004 in the report entitled "Brazil's Initial National Communication to the United Nation Framework Convention on Climate Change" (Brazil 2004). The second part of this report included the first GHG inventory but included only the period from 1990 to 1994. This report showed that the sub-sector "Forest conversion" from the bulk LULUCF Sector was the main contributor in 1994, representing 55% of the total GHG sources, which totalised 1728 Mt CO<sub>2</sub>-eq (CO<sub>2</sub> equivalent), and nearly 82% of the sole emissions of CO<sub>2</sub>. This last percentage is reduced to 75% when considering the net result, which includes a CO<sub>2</sub> sink of 251 Mt. The agricultural sector is now facing a crossroads of issues linked with food security, rural livelihoods, environmental sustainability, bio-energy, climate change adaptation and mitigation, in a context of important and difficult negotiations for a future regime for LULUCF under the United Nation Framework Convention on Climate Change in a post-2012 international agreement. Our understanding is that the main focus of the majority of the National Inventories is on GHG emissions. However, in Brazil we do include sinks in our net GHG emissions. The sinks are mainly due to carbon fixation in soils and phytomass resulting from advanced agricultural management practices, reforestation and land abandonment. Thus, the objectives of this paper are (i) to update estimates of the GHG emissions for the Brazilian territory, (ii) to estimate the sinks to provide calculations of the GHG net emissions to the 1990-2005 period, (iii) to calculate the actual and estimated share of agriculture and livestock activities, and (iv) to discuss the best mitigation options for Brazil in light of the new figures and patterns.

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# Methods

Actual and recent data and forecasted values (from 2005 to 2020) were obtained from two main internationally recognized sources: i) Climate Analysis Indicators Tool (CAIT) from the World Resources Institute (WRI 2009), available on line at <a href="http://cait.wri.org">http://cait.wri.org</a>; ii) Emission Databases for Global Atmospheric Research (EDGAR) from the Netherlands Environmental Assessment Agency (http://www.mnp.nl/edgar/model/). Specifically for Brazil, data of the CAIT from WRI were derived from individual sectors. For the CO<sub>2</sub> emission, fossil fuel emissions for the period 1971-2005 were obtained from IEA (2007). The emissions from cement manufacture and gas flaring were included for the year 1980 and subsequent years. CO<sub>2</sub> emissions for the period 1950-2000 were calculated from Houghton (2003). Finally CH<sub>4</sub> and N<sub>2</sub>O emissions each 5 years for the period 1990-2005 were estimated using EPA (2006).

Concerning the EDGAR database, two principal databases were used. Data for the years 1990 and 1995 were derived from the EDGAR 3.2 database (Olivier et al. 2002) that provides global annual emissions per country of Kyoto Protocol greenhouse gases CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O<sub>5</sub>, and F-gases (HFCs, PFCs and SF<sub>6</sub>). Data for the year 2000 were obtained from the EDGAR 3.2 Fast Track 2000 dataset that incorporated updated values from EDGAR 3.2. Most data in EDGAR derived from IEA, FAO and UN databases. Emissions for the LULUCF sectors were calculated and updated for the years 2000 and 2005 using the same methodologies described in the background reports of the BINC. Details of the different methodologies are provided in each report, but they are all based on steps proposed by the Revised 1996 Guidelines for National Greenhouse Gas inventories. The estimates of GHG emissions associated with LULUCF sector were updated for the 2000-2005 time period according to data availability. The LULUCF sector was subdivided into the following two broad sub-sectors: Land-use change and Forestry, and Agriculture. The former represented the GHG emissions and removals due to deforestation of the native vegetation, changes in forest and other woody biomass stocks, abandonment of managed areas, and from soils. The agriculture sub-sector represented the emissions of GHG from the enteric fermentation, manure management, rice cultivation, field burning of agricultural residues, and agricultural soils. Agricultural soils include the emissions produced by the use of synthetic N fertilizers; organic N applied as fertilizer (e.g., animal manure, compost, sewage sludge, rendering waste); urine and dung deposited on pasture, range and paddock by grazing animals; crop residues, including from N-fixing crops. The GHG emissions from the agriculture sub-sector were estimated based on the procedures and parameters adopted in the Brazil's Initial National Communication. GHG emissions estimates associated with the Forest sub-sector for the 1990-1994 period were derived from the use of remote sensing, which mapped for this period the land cover situation in the main Brazilian biomes (Amazônia, Cerrado, Mata Atlântica, Caatinga, and Pantanal).

The CO<sub>2</sub> emissions from soils were estimated according to the approach proposed by the Revised 1996 Guidelines for National Greenhouse Gas Inventories and adapted by Bernoux *et al.* (2001). The estimate was based on the variations in soil C stocks due to the land-use changes for the time period of 1985-2005, assuming a linear change in C storage. The 20-year period, the soil depth (0-30 cm) and the units of measurement (Mha for land areas and Mg C/ha for soil C) suggested by the IPCC were used in the present study. The calculation was performed by state and more details about the parameters adopted and procedures can be found in Bernoux *et al.* (2001). CO<sub>2</sub> emissions due to the organic soils cultivation were also included, using the same methodology used in the Brazil's Initial National Communication, assuming as organic soils the lowlands cultivated with rice, and adopting the IPCC emission factor. All results are expressed in CO<sub>2</sub> equivalent (CO<sub>2</sub>-eq) using the official global warming potential (GWP) considered for the 1<sup>st</sup> commitment period, i.e. 21 for methane and 310 for nitrous oxide. The latest IPCC assessment report provided revised values (25 for CH<sub>4</sub> and 298 for N<sub>2</sub>O).

# **Results and discussion**

Table 1 presents a tentative proposal for the Brazilian main greenhouse gas (CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O) emissions for the 2005-1990 period based on the above results for LUCF, amended with sectors estimated for the other categories (Energy, Industrial Processes and Waste). The most crucial sector to be estimated is the Energy because of the importance of its share. Our estimate is based on the results calculated for the national carbon balance in the energy sector (MCT 2007). The authors calculated the emission from fossil fuel combustion using both bottom-up and top-down approaches for the 1970-2005 period, and also compared their results to BINC values. They concluded that their results systematically underestimate the values from the BINC in 5%. Therefore, in our calculations, the estimates for the Energy sector for CO<sub>2</sub> and CH<sub>4</sub> derived from their proposed values for the year 2000 and 2005 were corrected by this coefficient (5%). For the other emissions

of the Energy sector (Fugitive emissions, and  $N_2O$  emissions from fossil fuel combustion) a conservative approach was used considering the level unchanged in relation to 1994.

Table 1. Greenhouse gas emissions for 1990-2005 period for the Energy, Industrial Processes, Agriculture, Land

Use Change and Forestry and Waste sectors.

SECTOR	1990	1994	2000	2005	2005-1994	
		Mt CO <sub>2</sub> -eq				
Energy						
Fossil Fuel Combustion	207.4	240.4	324.9	347.0	44.4	
Fugitive Emissions	7.6	7.4	7.3	7.3	-0.5	
Total	215.1	247.7	332.2	354.3	43.0	
Industrial Processes						
Cement Production	10.2	9.3	19.0	14.2	52,5	
Other	6.7	7.5	9.0	14.6	94.2	
Total	19.5	21.3	34.1	36.9	73.6	
Agriculture						
Enteric Fermentation	184.9	196.9	204.8	248.4	26,1	
Manure Management	13.0	13.9	13.2	16.1	15.7	
Rice Cultivation	5.0	5.9	5.0	5.4	-8.4	
Field Burning of Agricultural Residues	4.4	5.0	4.0	4.6	-7.9	
Agricultural Soils	132.1	147.6	155.4	192.9	30.7	
Total	339.4	369.3	382.4	467.4	26.6	
Land Use Change and Forestry						
Forest and Grassland Conversion	919.8	993.5	1051.8	1074.2	8.1	
Emissions and Removals from Soils	110.2	75.6	67.9	65.1	-13.8	
Total	1030.0	1069.1	1119.7	1139.3	6.5	
Waste						
Total	19.2	20.6	22.7	24.4	18.5	
TOTAL	1623.2	1728.0	1891.1	2022.3	17.0	

Cement production is the main contributor of the Industrial Processes. Emissions from this sub-sector were calculated according to the energy inputs in the processes (reported by MCT 2007). The total emissions for the Industrial Processes were estimated in the same manner, and emissions from Other Activities were calculated by difference.  $N_2O$  and  $CH_4$  emissions from cement production were calculated using a linear trend. This last approach was also used in the case of the Waste sector. Table 1 does not include the  $CO_2$  fixation by the phytomass from reforestation and abandoned lands. If these sinks are accounted in the calculations, the net emissions for the Land Use Change and Forestry decreases by about 26%, from 1189.5 to 936.7 Mt  $CO_2$ . Then, the total net emission for 2005, adjusted considering the mentioned removals, would be 1231.5 against 1461.7 Mt  $CO_2$ , which is about 19% lower in relation to the emission only scenario.

Global emissions in CO<sub>2</sub>-eq increased by 17% during the 1994-2005 period. CO<sub>2</sub> represented 72.3% of the total, i.e. a small decrease, in favour of non-CO<sub>2</sub> GHG, in relation to 1994 when its share was 74.1%. The increase of all GHG excluding LUCF was 41.3% over the period 1994-2005. CAIT-WRI estimated a higher increase (48.9%) that classified Brazil at the 69th position. Using our estimates Brazil will fall to the 78th position. But in both cases Brazil increased in clearly lower values than the tendency calculated for China and India, two major emitters, with increases of 88.8%and 62.1%, respectively. It can also be noted that Brazil's increase is lower than those for some Annex 1 country that are submitted to a quota of reduction, e.g. Spain with 55.6% of increase and New Zealand with 45.8%. Brazil also is below the average increase showed by non-Annex I countries, estimated to be 61.3%, but above the world average (28.1%).

# Conclusion

In Brazil most mitigation efforts focused on the energy and LUCF, i.e. mostly reduction of deforestation in the Amazon. The later aspect succeeded since deforestation rates decreased. On the other hand, despite the intensification of ethanol use (increasing percentage of flex fuel cars), the energy sector showed the highest level of increase (+44%). However, it must be recognized that the energy-related programs and measures implemented in the 90's and after have provided a broad range of benefits for the Brazilian economy, and helped lower carbon emissions in relation to was considered business as usual in the yearly 90's. Besides

effort to curb emissions from the energy and deforestation sectors, it is now a top priority to implement a national program to incentive mitigation efforts concerning the agricultural sectors (+27%). These mitigation options should not be only focused on emissions reduction, but also prone enhancement of the carbon sink. Such a program would be easy to implement, because several mitigation strategies have already proved to be efficient, simple to adopt and economically viable.

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# Carbon dioxide emission from peatland in relation to hydrology, peat moisture, humification at the Vo Doi national park, Vietnam

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### **Abstract**

The relationships of CO<sub>2</sub> emission with water table, peat moisture and humification was studied in secondary peat swamp forest floor at the Vodoi national park, Vietnam in order to propose a better water management system to maintain forest growth and restore peat. The recent artificially maintained high water level in the forest floor for most of the year in order to reduce risks of fire has led to bad growth of forest and death of some plants. The results of this study showed that the less humified top 10 cm peat (litter) layer has a major contribution to CO<sub>2</sub> emission from peat surface. The CO<sub>2</sub> release rate from peat oxidation decreased significantly when peat moisture became less than 80% of the water holding capacity. Deep water level in dry season, lower than 25 cm under the peat surface, might decrease the rate of CO<sub>2</sub> emission from peat oxidation and is good for forest-root respiration. Therefore, artificially maintaining a high water level in the dry season is not a good choice to restore peat and forest in the Vo Doi National Park.

# **Key Words**

CO<sub>2</sub> emission, peat oxidation, water table level, peat humification.

# Introduction

Vodoi National Park in the southern Vietnam holds one of the largest areas of intact peatland remaining in the country. The park has a peat area of around 1,150 ha, and a further area of about 2,000 ha where the peat has been burned by forest fires, and which has now been reforested (report of the Camau department of forestry 2003). In order to reduce the risk of further fires, a dike and canal system has been built around the peat area to maintain unnaturally high water levels. Consequently, the peat area was flooded for most of the year. Water table level depth in peat plays an important role in peat accumulation and decomposition dynamics, and thereby also in soil CO<sub>2</sub> emissions, all of which form important components in terrestrial carbon storage and soil-atmosphere greenhouse gas dynamics (Rieley and Page 2005). Appropriate water management may improve vegetation growth rate on peat, and thus increase the potential for peat accumulation in comparison to decomposition carbon losses. The objective of this study was to measure the rate of CO<sub>2</sub> emission from peatland in the Vodoi area in relation to the water table level, peat moisture content, and the degree of peat humification.

# **Materials and Methods**

Water table level was measured with an automated water table logger. The logger was installed in a well-developed forest canopy area (October 2006 to July 2008).  $CO_2$  emission was measured during the dry season at five permanent points located in the peat area. At each point, the depth of the water table level was recorded and peat moisture content above the water table was determined at 10 cm intervals up to the soil surface. For the measurement of the rate of  $CO_2$  emission, a round aluminium chamber (with a diameter of  $CO_2$  emission was calculated from concentration increase in the closed chamber detected by EGM-4 infrared gas analyzer. In another experiment, the  $CO_2$  emission rate from the peat surface in the absence of plant root respiration was examined. For that, four intact peat columns of 60-cm diameter and 80-cm depth were put into plastic tanks of the same diameter and 1 m height for measuring  $CO_2$  emission. Water in tanks was filled up to the surface by using water collected from the same sampling site. Water level in tanks was adjusted to different levels by withdrawing water through an outlet at the bottom of tanks. Measurement of  $CO_2$  emission at each water level was conducted only one week after the water level was adjusted in order to stabilize moisture of peat above the water level.

The relationship between peat moisture and CO<sub>2</sub> flux from peat decomposition, without live roots, was measured at depths of 0-10cm, 10-20cm and 20-30cm. For this purpose, peat samples collected from each

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depth were put into air-tight boxes of 160cm diameter and 10 cm height. The peat was packed in the boxes to 5 cm thick layer. CO<sub>2</sub> respiration was measured by infrared gas analyzer after the peat material reached: water holding capacity, 80%, 60%, 40% and 20% of the water holding capacity. There were four replicates for each moisture level.

The degree of peat humification at different depths was assessed by collecting peat samples at 10 cm intervals in a peat profile from the soil surface, and analysing them for humic compounds and fulvic compounds by the Kononova method (Sokolov 1965) and for ash and organic matter contents.

### Results

# Peat humification status

The peat contained 90-94% organic matter. The top litter layer was 5-10 cm deep and contained lower levels of humic and fluvic compounds and a lower ratio of humic to fulvic compounds than deeper peat layers, indicating that the top litter layer was less humified than the deeper peat horizon (Table 1). However, the peat just above the underlying mineral soils also had relatively low levels of humic and fulvic compounds, suggesting that proximity to the underlying mineral soil retarded humification.

Table 1. The degree of peat humification.

Sample depth	OM	Humic+fulvic matters	Humic matter	Fulvic matter	Humic - fulvic ratio
(cm)	(%)	(%)	(%)	(%)	
0-10 (litters)	92.1	23.2	14.6	8.6	1.7
10-20	93.4	38.8	33.1	5.7	5.8
20-30	94.0	42.8	37.0	5.8	6.4
30-40	93.0	39.4	33.5	5.9	5.7
40-50	92.8	27.5	23.6	3.9	6.0
50-60	87.2	18.3	13.0	5.3	2.5
60-65	76.5	18.5	16.6	2.0	8.4

# Peat water table level and moisture

The fluctuation of water table level during observed period from 10/2006 to 7/2008 showed that in the peat area was below the peat surface from February to May (from the middle to the end of the dry season), and the depth of water table level below the ground surface in dry season fluctuated by years and depended on how it was artificially maintained (Figure 1). At the deepest water level in 2006, peat above the water table had a moisture content of 70-82%, which is about 80-100% of its water holding capacity.

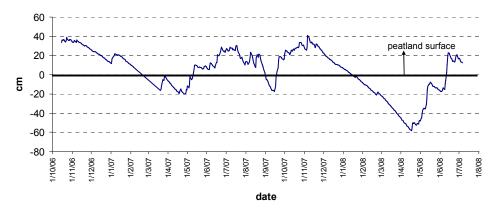


Figure 1. Water table level at the study site in Vodoi National Park.

Relationship between rate of peat oxidation and peat humification and moisture

The rate of  $CO_2$  release from peat – that is, from decomposition and faunal activity but excluding root respiration – was significantly higher in the less humified top 10 cm (litter layer) than in the more humified deeper peat layers, irrespective of the moisture content (Figure 2). The highest  $CO_2$  release rate from peat decomposition and faunal activity was found in the top 10 cm litter layer at a moisture content of 67-85% w/w (from the water holding capacity of 80%). By contrast, the rate of  $CO_2$  release via decomposition and faunal activity in more humified peat material below the litter layer was very low, being less than 0.02 mg  $CO_2$ /g/h at water content ranging from 60% to 100% of the water holding capacity, *i.e.* higher than 50%

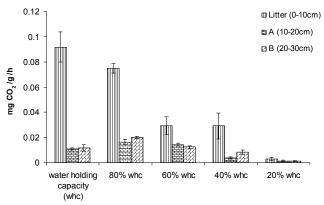


Figure 2. Relationship of CO<sub>2</sub> release from peat at various depths and peat moisture conditions.

moisture (w/w). The  $CO_2$  release rate was even less at moisture content  $\leq 40\%$  of the water holding capacity. As the water table level in the forest floor did not sunk deeper than -30 cm below the soil surface and the peat moisture content above the water table was over 80% of the water holding capacity, we conclude that the near surface litter layer played the major role in  $CO_2$  emission from peat materials in Vodoi National Park.

# Gaseous CO<sub>2</sub> losses from peat

Root respiration, peat decomposition and faunal activity all contributed to  $CO_2$  release from peat. The overall rate of  $CO_2$  release, including all the aforementioned components, ranged from 0.8 g  $CO_2/m^2$ /hr when the water table was near the peat surface to 1.8 g  $CO_2/m^2$ /hr when the water table was around -30 cm from the peat surface (Figure 3). Moisture of peat above water level when that ranged within 0-30 cm below ground surface was 80-100% peat water holding capacity. As mentioned above, this is the optimal range of moisture for peat oxidation. The figure 3 also showed the increasing tendency of  $CO_2$  release with depth of water level. The reason might relate to better aerobic condition which favour peat oxidation and root respiration.

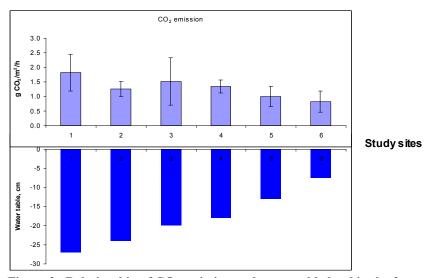


Figure 3. Relationship of CO<sub>2</sub> emission and water table level in the forest floor.

Comparing CO<sub>2</sub> emission from the peat surface in natural condition and in experiment with intact cut peat columns which killed tree roots can help to identify what factor mainly contributes to CO<sub>2</sub> emission from peat surface when water level descends. The rate of CO<sub>2</sub> emission in the absence of living roots, CO<sub>2</sub> considered to be from peat oxidation, was around 0.15-0.27 g/m²/hr, much less than the rate in natural conditions (Figure 4). When the water table level went down lower than 25 cm, CO<sub>2</sub> release became less. It was also observed that when the water level was lower than 25 cm, the top-layer peat became a dryer. Thus lowering water level might make the top-layer dryer and reduce peat oxidation. Therefore, the period of low water level in peat area in the dry season may be beneficial for the peat ecosystem because it can enhance forest-root respiration and reduce oxidation of top peat material. It was also observed that many specimens of *Melaleuca cajuputi*, lianas and the grass *Stenechleana palustrie* are either growing poorly or have died in areas flooded all year round.

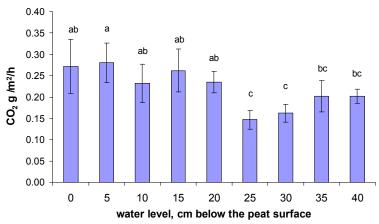


Figure 4. CO<sub>2</sub> release from peat surface at different water levels in the absence of living tree roots.

# **Conclusions**

- CO<sub>2</sub> release rate from peat oxidation decreases with increasing peat humification degree. Top organic material (0-10 cm) has major contribution to CO<sub>2</sub> emission from the peat surface because of low humified degree and frequent exposure to the air in the dry season.
- The rate of CO<sub>2</sub> emission from peat surface relates to water level: high CO<sub>2</sub> emission at low water level in dry season might mainly come from root respiration, not from peat oxidation. Therefore, maintaining an artificially high water table level in the dry season to reduce the fire risk disturbs the natural hydrology of peatland and leads to high moisture of peat above the water table, high CO<sub>2</sub> loss from peat oxidation and bad conditions for tree-root respiration, which may badly affect forest growth.

# Acknowledgements

We would like to thank the RESTORPEAT project for financial and technical support, and the administrators of Vodoi National Park for access to the site and other facilities, and their support.

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# Climatic impacts on greenhouse gas emissions in rice paddy fields

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# **Abstract**

Greenhouse gas emissions from rice paddy fields may be influenced by climatic or soil environment conditions. In this study, we investigated greenhouse gas emissions associated with climatic impacts. Experiments were conducted in Thailand and Japan. Emissions of CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O in rice paddy fields were continuously measured using the relaxed eddy accumulation method. As factors affecting greenhouse gas emissions, air temperature, humidity, soil temperature, soil redox potential and net irradiance were measured as well. This paper presents the behaviour of greenhouse gas flux in Thailand and Japan.

# **Key Words**

Rice paddy field, CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O, net irradiance, soil temperature.

# Introduction

Global warming is an important issue for humans. A major attributor of global warming is increases in greenhouse gases. Carbon dioxide ( $CO_2$ ), methane ( $CH_4$ ) and nitrous oxide ( $N_2O$ ) are considered as major greenhouse gases. The global warming potential in  $CH_4$  and  $N_2O$  are 21 times and 296 times respectively, so that  $CH_4$  and  $N_2O$  are important gases. Anthropogenic greenhouse gas emission for  $CH_4$  and  $N_2O$  accounts for 70% and 46% in the total greenhouse gas emission (IPCC 2001). Methane emission from paddy field makes up 29% of the total of  $CH_4$ . Also  $N_2O$  emission from agricultural land makes up 52% of the total of anthropogenic  $N_2O$ . So, greenhouse gas emissions from rice paddy fields are considered as one of the most important emission sources. Methane emission from rice paddy fields is high in a flooded field, but decreases in a drained field. Nitrous oxide emission from rice paddy fields is little in flooded, but increases sharply in drained fields. It is reported that the factors affecting  $CH_4$  and  $N_2O$  emissions are soil temperature, soil redox potential, net irradiance and organic matter (Hou *et al.* 2000). Since the area in rice cultivation spread from the tropical region to the cool-temperate region, it is expected that those factors vary in each climate zone. The objective of this study was to investigate climatic impacts on greenhouse gas emissions in rice paddy fields.

# Methods

Field experiments were conducted at an experimental field for rice plants, Kasetsart University, Kamphaengsaen, Thailand and a rice farming field, Hiratuka, Japan. Gas fluxes (CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O) were continuously measured with 20 min intervals using the relaxed eddy accumulation method (McInnes and Heilman 2005) developed recently. Gas concentration (CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O) was analysed by a photoacoustic field gas-monitor (model 1412, Innova Air Tech Instruments, Denmark). Air temperature, humidity, soil temperature, soil redox potential and net irradiance were also continuously measured with 5 min intervals.

### Results

In Hiratuka, CO<sub>2</sub> flux started to increase in the afternoon and reached a maximum in the midnight (Figure 1). In Thailand, CO<sub>2</sub> flux reached a maximum in the daytime, but the temporal change in CO<sub>2</sub> flux was the opposite variation relative to Hiratuka. CO<sub>2</sub> flux increased with the decrease in the net irradiance in Hiratuka, which indicates the respiration of rice plants was more active during the night. CH<sub>4</sub> flux in Hiratuka was lower than in Thailand during an anthesis period. In Thailand, CH<sub>4</sub> flux started to increase in the early morning with the net irradiance increasing and reached a maximum, but the temporal change in CH<sub>4</sub> flux in Hiratuka was smaller than in Thailand (Figures 2 and 4). The behaviour of N<sub>2</sub>O flux in two sites was similar to CH<sub>4</sub> flux in Thailand (Figure 3). Soil surface temperature was strongly influenced by net irradiance in Thailand (Figures 4 and 5). It is expected that the rapid rise of soil temperature in Thailand stimulated the activities of soil microorganisms and as a result, larger flux of CH<sub>4</sub> and N<sub>2</sub>O occurred.

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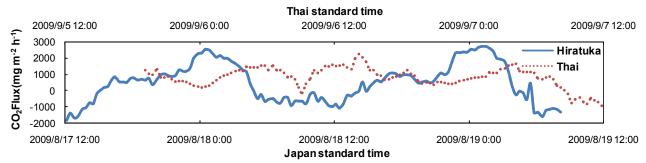


Figure 1. Temporal changes in CO<sub>2</sub> flux during anthesis.

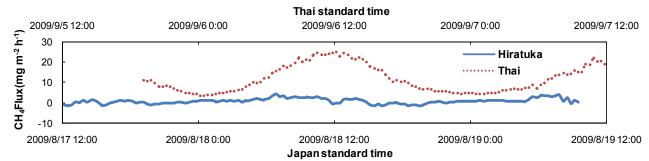


Figure 2. Temporal changes in CH<sub>4</sub> flux during anthesis.

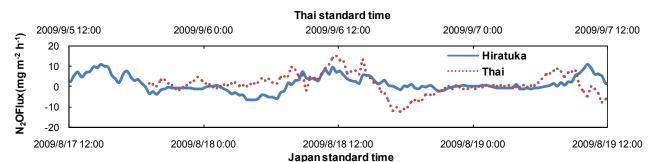


Figure 3. Temporal changes in N<sub>2</sub>O flux during anthesis.

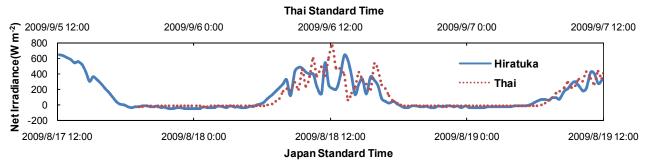


Figure 4. Temporal changes in net irradiance during anthesis.

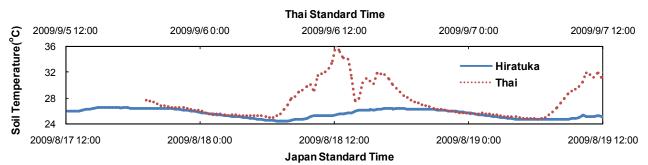


Figure 5. Temporal changes in soil surface temperature during anthesis.

# **Conclusions**

The study showed the behaviours of  $CO_2$ ,  $CH_4$  and  $N_2O$  flux are affected by net irradiance in anthesis. Specifically, the impacts of the net irradiance to greenhouse gas flux in Thailand was stronger than in Hiratuka, so it is possible that the net irradiance is one of the important factor affecting greenhouse gas emission in the tropical region.

# Acknowledgements

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# Comparison of different approaches for estimating carbon budgets in a managed grassland in Hokkaido, Japan

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### **Abstract**

We estimated carbon (C) budgets of the fertilizer and manure plots established in a grassland of reed canary grass for two years in Southern Hokkaido, Japan. In the manure plot, beef cattle manure was applied at a rate of 43 - 44 Mg fresh matter (5.8 - 7.7 MgC/ha/yr), and a supplement of chemical fertilizer was also added to equalize the application rate of mineral nitrogen to that of the fertilizer plots. The harvesting of grass was carried out twice a year. The net ecosystem production (NEP) was estimated by biometric and micrometeorological approaches. The net biome production (NBP) was estimated as NEP + Manure application - Harvest. In addition, we measured changes in soil organic carbon (SOC) within the top 30 cm layer. All approaches showed that the manure application can increase C sequestration and is necessary to prevent the loss of C from the grassland. However, the meteorological NBP (-2.2 and 3.0 MgC/ha/yr in the fertilizer and manure plots, respectively) was higher than biometric NBP (-3.6 and 0.3 MgC/ha/yr) and changes in SOC (-4.3 and 1.3 MgC/ha/yr). This suggests that the meteorological method could possibly overestimate the NEP.

# **Kev Words**

Net ecosystem production, net biome production, soil organic carbon sequestration, grassland.

# Introduction

Carbon dioxide (CO<sub>2</sub>) concentrations in the atmosphere have increased at an annual rate of 1.9 ppmv from 1995 to 2005 (IPCC 2007). An understanding of the carbon (C) cycle through soil-plant ecosystems is essential to predict the effect of an increase in CO<sub>2</sub> on the earth. The net gain or loss of C from an ecosystem is defined as the net ecosystem production (NEP). NEP is estimated as the gain in C by plant (net primary production, NPP) minus C loss by heterotrophic respiration (RH). Recently, micrometeorological methods (e.g. eddy covariance, Bowen ratio/energy balance method) have been widely applied for measuring the NEP without any disturbance. However, the measurement using only meteorological methods is not sufficient to explain seasonal and yearly changes in C budgets or to forecast the change in the source or sink of C. A comparison with different approaches such as biometric method and direct soil sampling is considered to be helpful in estimating annual flux and understanding C stock and flow. The C budget in managed grasslands includes C input through manure application and C output through crop harvest and grazing as well as NEP. This budget, taking abiotic process into account, is defined as the net biome production (NBP), and is thought to be equal to changes in SOC (Schulze *et al.* 2000). In the non-grazing grasslands, the NBP is estimated using the following equation.

NBP = NEP + Manure application - Harvest

(1)

In Japan, livestock husbandry has been depending on enormous amounts of imported feed, and livestock excreta are in surplus. Therefore manure should be efficiently and appropriately returned to crop fields for an environmental-friendly agro-ecosystem, and it is expected to sequester the applied manure C in soils (Janzen *et al.* 1998). The objectives of this study were therefore to compare different approaches for estimating carbon budgets in a managed grassland, and to clarify the effect of manure application on C budgets.

# Materials and methods

Study site

This study was conducted for two years in a managed grassland located on the Shizunai Experimental Livestock Farm, Field Science Center for the Northern Biosphere of Hokkaido University in Southern Hokkaido, Japan (42°26'N, 142°29'E). The mean annual precipitation is approximately 1365 mm and the mean annual temperature is 7.9 °C. The dominant species of the grassland are reed canarygrass (Phalaris arundinacea L.) and meadow foxtail (Alopecurus pratensis L.). The soil is classified as Thaptic Melanudands (Soil Survey Staff 2006).

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Two experimental plots were set up on the study site, one for application of farmyard manure (manure plot), and the other for chemical fertilizer (fertilizer plot). The application rate of manure was 43 - 44 Mg fresh matter (5.8 - 7.7 MgC/ha/yr). At the manure plot, supplement of chemical fertilizer was also given to equalize the application rate of mineral nitrogen to that of fertilizer plot (164 - 184 kgN/ha/yr). The harvesting of grass was carried out twice a year; in late June and in mid August.

# Biometric approach

The above-ground and below-ground biomass was measured by using a harvest method to estimate the NPP. Heterotrophic respiration from soil organic matter (RHs), dead plants (RHI) and manure (RHm) was measured by using the static closed chamber method. The biometric NEP was estimated using the following equation (Shimizu *et al.* 2009).

Biometric 
$$NEP = ANPP + BNPP - RHs - RHI - RHm$$
 (2)

The biometric NBP was estimated as the C budget of a field taking into account the harvest and manure applications as equation (1).

# Micro-meteorological approach

The net ecosystem CO<sub>2</sub> exchange was measured continuously by an eddy-covariance method to estimate the meteorological NEP. The eddy covariance system, which consisted of a sonic anemometer (CSAT3, Campbell Scientific) and an open-path infrared gas analyzer (LI-7500, LI-COR), was installed at each plot with instruments to measure other meteorological variables. The eddy covariance data were post-processed on half-hourly basis following general procedures including half-hourly block averaging, the planar fit coordinate rotation (Wilczak *et al.* 2001), corrections for high-frequency spectral losses due to path-length averaging and horizontal separation between the sonic anemometer and the gas analyzer and for low-frequency spectral losses due to the block averaging (Massman 2000; 2001), corrections to sensible heat flux due to water vapour flux, and the density correction (WPL correction) (Webb *et al.* 1980). As quality control of the eddy covariance data, 10-Hz raw data were examined by quality control tests proposed by Vickers and Mahrt (1997). We did not apply u\*-correction. Missing and rejected half-hourly CO<sub>2</sub> fluxes were filled by non-linear gap filling method. The meteorological NBP was estimated using equation (1).

# Changes in SOC

The SOC stocks within the top 30 cm layer were measured in October 2006 and August 2008 to estimate changes in SOC. Sixteen soil cores (5 cm internal diameter) were collected from each plot at 0-15 cm and 15-30 cm depth. The soil samples were air-dried and weighted. A portion of the air-dried sample was dried at 105°C for 24 h to measure bulk density. The C content of air-dried sample was measured using N/C analyzer (SUMIGRAPH NC-1000, Sumika Chemical Analysis Service). SOC concentration (gC/kg) was converted to SOC content with depth (MgC/ha within specified depth) using measured soil bulk density.

# Statistical analyses

Uncertainties were calculated using the following equation. Uncertainty (%) =  $\{(\text{two-sided }95\% \text{ confidence interval}) / 2\} / \text{Means} \times 100$  (3)

# Results and discussion

The biometric NEP in 2005 and 2006 were 2.1±0.8 and 1.2±0.6 MgC/ha/yr for the fertilizer plot, and -1.5±1.1 and -0.9±0.9 MgC/ha/yr for the manure plot, respectively. The meteorological NEP in 2005 and 2006 were 2.6 and 3.6 MgC/ha/yr for the fertilizer plot, and 0.9 and 2.2 MgC/ha/yr for the manure plot, respectively. Both biometric and meteorological NEP were greater in the manure plot than in the fertilizer plot. However, the meteorological NEP were 0.5 - 3.1 MgC/ha/yr larger than the biometric NEP (Figure 1). Two-year averages of the biometric NBP in the fertilizer and manure plots were -3.6±1.3 and 0.3±1.6 MgC/ha/yr, respectively (Table 1). Two-year averages of the meteorological NBP in the fertilizer and manure plots were -2.2 and 3.0 MgC/ha/yr, respectively (Table 1). Changes in SOC within the top 30 cm layer were -4.3±12.5 and 1.3±10.3 MgC/ha/yr, respectively. All approaches show that the C was lost in fertilizer plot, but gained in manure plot. This result indicates that the harvest consumes the C, and that manure application is necessary to prevent the loss of C from the managed grassland. The C sequestration rate estimated by the difference between the fertilizer and manure plots ranged from 3.9 to 5.4 MgC/ha/yr. Jarecki and Lal (2003) have also reported that manure application increases C input to soil and consequently enhances SOC concentration. However, Poulton (1996) stated that the manure applications at the rate of 3 MgC/ha/every 4 years over many decades in a grassland at Rothamsted Experimental Station did not change SOC levels appreciably, because the SOC content of the grassland soil might have reached a steady state. In

this study, the site might not be carbon saturated, thereby manure application may enhance SOC sequestration in soils.

The meteorological NBP was the highest among three approaches. We used open-path eddy covariance method for meteorological approach. Some studies have reported that the NEP measured by the open-path system might be systematically overestimated compared with the closed-path system (Anthoni *et al.* 2002; Hirata *et al.* 2007). Hirata *et al.* (2007) measured the NEP in a northern Japan larch plantation forest using open- and closed-path eddy covariance methods, and found that the NEP from open-path system was 3.9 - 4.3 MgC/ha/yr larger than that from closed path system. Recent studies have indicated that the heat flux from surface heating of an open-path instrument produced incomplete WPL correction (Ono *et al.* 2007). The literature values of biometric and meteorological NEP were plotted on Figure 1. The NEP from closed-path system was closer to the biometric NEP than that from open-path system. This suggests that meteorological method, especially open-path eddy covariance method, could possibly overestimate the NEP.

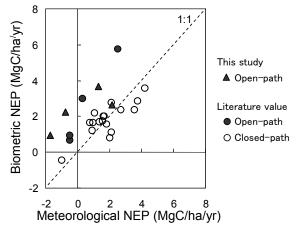


Figure 1. Biometric net ecosystem production (NEP) compared to meteorological NEP. Literature values are referred to Barford *et al.* (2001), Law *et al.* (2001), Ehman *et al.* (2002), Curtis *et al.* (2002), Gough *et al.* (2008), Hirata *et al.* (2008) and Kominami *et al.* (2008).

Table 1. Annual net biome production (NBP) and the changes in soil organic carbon (SOC) (MgC/ha/yr). Data represent means  $\pm$  (uncertainties/100×means).

	Fertilizer plot	Manure plot
Biometric NBP		
2005	-3.3 (1.0)	-0.4 (1.2)
2006	-3.9(0.7)	0.1 (1.1)
Average	-3.6 (1.3)	0.3 (1.6)
Meteorological NBP		
2005	-2.8	2.8
2006	-1.5	3.2
Average	-2.2	3.0
Changes in SOC		
0 - 15 cm	-1.8 (6.6)	1.8 (5.0)
15 - 30 cm	-2.5 (7.8)	-0.5 (6.6)
0 - 30 cm	-4.3 (12.5)	1.3 (10.3)

# Conclusion

Carbon budgets in a managed grassland were measured using three different approaches. All approaches showed that manure application is necessary to prevent the loss of C from the grassland. However, meteorological approach could possibly overestimate the NEP.

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# Comparison of the ability of the nitrification inhibitors DCD and DMPP to reduce nitrification and $N_2O$ emissions from nitrogen fertilisers

**Helen Suter**<sup>A</sup>, Deli Chen<sup>A</sup>, Huilin Li<sup>A,B</sup>, Robert Edis<sup>A</sup> and Charlie Walker<sup>C</sup>

# **Abstract**

Nitrification of applied nitrogen fertilisers leads to losses of nitrogen (N) as nitrate (NO<sub>3</sub><sup>-</sup>) or as the greenhouse gas nitrous oxide (N<sub>2</sub>O). Nitrification inhibitors can be used to suppress the ammonia oxidizing bacteria involved in nitrification and hence reduce these losses. The ability of nitrification inhibitors to reduce nitrification is dependent upon both climatic and soil conditions, and different inhibitors respond differently. The ability of two nitrification inhibitors, 3,4-dimethylpyrazole phosphate (DMPP) (1.84 kg/t urea) and dicyandiamide (DCD) (10 kg/t urea) to reduce nitrification from applied fertiliser (100 kg N/ha) in a pasture soil, in small scale (150 g) incubation studies under a range of temperatures (5, 15 and 25°C) was studied. Both products were applied as commercially prepared granular urea products. The comparable ability of the 2 inhibitors to reduce nitrification, as measured by NO<sub>3</sub><sup>-</sup> formation, were similar across all treatments, with neither effective in the topsoil and both causing reduced NO<sub>3</sub><sup>-</sup> formation in the subsoil. N<sub>2</sub>O emissions were reduced by both inhibitors. DMPP was applied at a lower concentration than DCD and performed almost, and equally as well in many cases.

# **Key Words**

3,4-dimethylpyrazole phosphate; Dicyandiamide, nitrification rates; incubation studies.

#### Introduction

Nitrification of applied nitrogen fertilisers leads to losses of nitrogen (N) as nitrate (NO<sub>3</sub>) or as the greenhouse gas nitrous oxide (N<sub>2</sub>O). These losses mean that plant use efficiency of nitrogen fertilisers is low. Reducing nitrification losses can be achieved with the use of nitrification inhibitors that suppress the activity of the autotrophic ammonia oxidizing bacteria (AOB). Nitrogen is then retained in the ammonium (NH<sub>4</sub><sup>+</sup>) form for longer making is available to plants and reducing the risk of leaching losses. Many nitrification inhibitors with differing modes of action have been tested in cropping systems and have shown variable reductions in nitrification, N<sub>2</sub>O emissions and influence on crop yields (Chen et al. 2008; Hatch et al. 2005; Li et al. 2008; McCarty 1999; Yu et al. 2007). The variability in the response of nitrification to the inhibitor is related partly to climatic conditions, such as moisture and temperature, and partly to the conditions within the soil including the nitrification potential of the soil and fertilizer history (Barth 2006; Kelliher et al. 2008). 3,4-dimethylpyrazole phosphate (DMPP) is one inhibitor that has been reported to work as effectively as DCD at lower concentrations (Zerulla et al. 2001). DMPP is a newer inhibitor and has not been tested in Australian dryland agriculture and knowledge of its viability for high temperature situations is unknown, with studies covering temperatures to a maximum of 30°C (Irigovena et al. 2003). DCD has been extensively used overseas but is considered to be less effective than DMPP (Chaves et al. 2006; Weiske et al. 2001). This paper reports on laboratory studies investigating the effect of temperature on the inhibition of nitrification by DMPP and DCD from urea applications to pasture soils, in small-scale incubation experiments.

# Methods

Soils

Soils were collected from a dairy farm in northern Victoria (S36°25'27", E145°42'26") from the top (0-5cm) and subsoil (5-15 cm), air dried and sieved to <2 mm. Table 1 provides details of the soils used.

# Incubation trials

Soil (150 g) in small vials (15cm x 35 cm<sup>2</sup>) was pre-wetted 2 days prior to commencement of the experiment. Granular urea was applied at a rate of 100 kg N/ha (175 ug N/g soil). DMPP was applied as the commercial product Urea with ENTEC<sup>TM</sup> (1.84 kg DMPP active ingredient/t urea (0.71 µg DMPP/g soil) and DCD was applied as a granular urea product containing 10 kg DCD active ingredient/t urea (3.8 µg DCD/g soil). A

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control treatment (no fertiliser) was included to measure background N transformations. Samples were incubated at 5, 15 and  $25^{\circ}$ C and at 60 % water filled pore space (WFPS). Experiments ran for 70 days with sample aeration and water replenishment at regular intervals. Nitrous oxide (N<sub>2</sub>O) samples were collected in triplicate and analysed using a Hewlett Packard 6890 GC with 2 Porapak Q columns and a carbosorb column with an ECD detector.

Table 1. Selected source and soil properties.

	Dookie –topsoil	Dookie-subsoil
Source site	Northern Victoria	Northern Victoria
Agricultural activity	pasture	pasture
colour	Very dark grey	Brown
Texture		
%clay	21	33
%silt	28	30
%sand	50	37
pН	5.4	5.5
Org C (%)	10.0	2.4
Total N (%)	1.0	0.2
$NH_4^+$ (mg/kg)	35	11
$NO_3$ (mg/kg)	53	33
Nitrifying potential	18	4
(mg/kg/day)		

### Results

Nitrification rates in the control treatments were similar to those observed in the fertilizer treatments under all temperatures in the topsoil, and less in the subsoil (Figure 1). This was due to the high nitrification potential of this soil (Table 1). Addition on the nitrification inhibitors DCD and DMPP had no impact on the formation of NO<sub>3</sub><sup>-</sup> in the topsoil but did reduce the level of NO<sub>3</sub><sup>-</sup> formed in the subsoil, where the nitrification potential of the soil was lower. DCD appeared to perform slightly better than DMPP where inhibition was achieved (subsoil) especially under cooler temperatures.

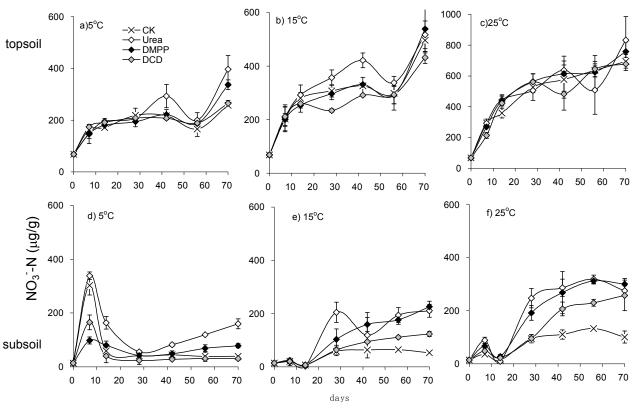


Figure 1. Nitrate (NO<sub>3</sub><sup>-</sup>) formation for the control, urea, urea +DMPP and urea+DCD treatments over 70 days, at temperatures of 5, 15 and 25°C.

Cumulative nitrous oxide ( $N_2O$ ) emissions measured in the urea treatments was greater than in the inhibitor (DCD and DMPP) treatments and in the control under all conditions (Figure 2). DCD and DMPP were both able to reduce the  $N_2O$  emissions over 70 days. The reduction in  $N_2O$  emissions after 70 days with DCD was 81 (5°C), 64 (15°C) and 37% (25°C) in the topsoil, and was 88 (5°C), 86 (15°C) and 44% (25°C) in the subsoil. The reduction in  $N_2O$  emissions after 70 days with DMPP was 65 (5°C), 61 (15°C) and 14% (25°C) in the topsoil, and was 76 (5°C), 74 (15°C) and 31% (25°C) in the subsoil. DCD appeared to perform better than DMPP most noticeably at 5°C. However DCD was applied at a greater application rate (10 kg/t urea) than DMPP (1.84 kg/t urea).

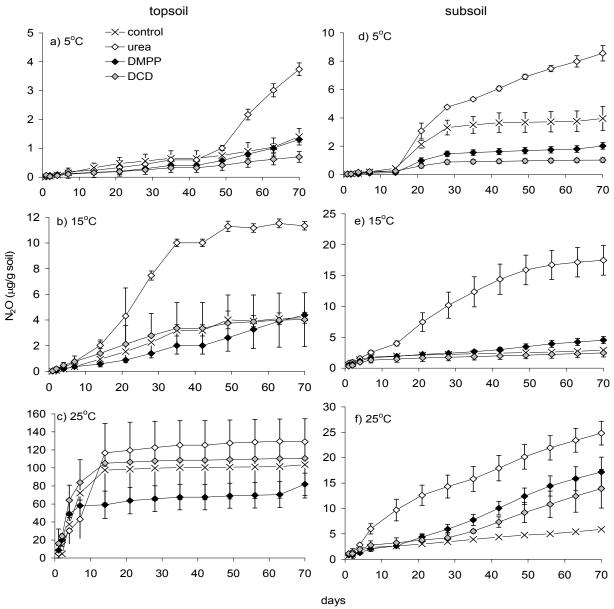


Figure 2. Cumulative nitrous oxide (N<sub>2</sub>O) emissions for the control, urea, urea +DMPP and urea+DCD treatments over 70 days, at temperatures of 5, 15 and 25°C.

## Conclusion

Nitrification rates in the topsoil of the pasture soil were very high and addition of fertiliser made no difference to the level of  $NO_3^-$  produced. Under these conditions neither DMPP nor DCD were able to reduce nitrification rates. In the subsoil both inhibitors were able to reduce the nitrification rate and rate of  $NO_3^-$  formation relative to urea. Emissions of  $N_2O$  were greatest with fertiliser addition and both DMPP and DCD were able to reduce the emissions. Temperature affected how much reduction in  $N_2O$  emissions was observed for both inhibitors.

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# Considerations for making chamber-based soil CO<sub>2</sub> flux measurements

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# **Abstract**

Chamber-based method for making soil  $CO_2$  flux ( $F_c$ ) measurement has two basic system designs: closed-chamber systems (also called transient or non-steady-state systems), and open-chamber systems (also called steady-state systems). For closed systems, air is circulated from a chamber to an infrared gas analyzer (IRGA) and then returned to the chamber.  $F_c$  is estimated from the rate of  $CO_2$  concentration increase inside a chamber that has been deployed on the soil surface for a short period of time. For an open system, fresh ambient air is pumped into or pulled from a chamber, and  $F_c$  is calculated using the air flow rate and the difference in  $CO_2$  concentrations between the air entering and leaving the chamber after the air in the chamber headspace has reached a steady state. In this paper, we will discuss in detail those considerations and requirements in chamber design and in making soil  $CO_2$  flux measurements. Due to the space limit, the discussion will be on the closed-chamber design only.

# **Key Words**

Soil CO<sub>2</sub> flux, Closed-chamber based flux measurement, steady-state soil CO<sub>2</sub> flux system.

# Introduction

Soil  $CO_2$  production is the sum of the respiration from free-living microbes (heterotrophic) and plant roots (autotrophic), and it is strongly temperature dependent. On a seasonal scale, soil  $CO_2$  production will also depend on the soil moisture, soil organic content, growth activity of plants etc. Due to the high resistance to gas transport in the soil, a strong  $CO_2$  concentration gradient exists in the soil and across the soil surface. This gradient, among others, is a major driving force for soil  $CO_2$  efflux. The fundamental requirement for an accurate  $F_c$  measurement is that the deployment of chambers and sensors must have no or minimal disturbance to environment conditions that have impact on soil  $CO_2$  production (soil temperature, soil moisture, radiation, wind speed, plant growth, shading on soil etc.) and  $CO_2$  transport ( $CO_2$  diffusion gradient, chamber pressure equilibrium etc.) across the soil surface.

# Methods for soil CO2 flux measurement

The closed-chamber method is the most common approach used to estimate the fluxes of  $CO_2$  ( $F_c$ ,  $\mu mol/m^2/s$ ) and other trace gases at the soil surface. It is widely used in carbon cycle research, soil sciences, agronomy, and other environmental research areas (*Norman et al.* 1992; *Davidson et al.* 2002).  $F_c$  can be estimated with Eq. 1 using the information of chamber volume (V), soil surface area (S), air temperature (T), atmospheric pressure (P), and the rate of  $CO_2$  concentration increase inside the chamber ( $dC_c/dt$ ,  $\mu mol/mol/s$ ) which has been on the soil surface for a short period of time.

$$F_c = \frac{PV}{RTS} \frac{dC_c}{dt} \tag{1}$$

Where R is the gas constant (8.314 Pa  $\text{m}^3/\text{°}\text{K}/\text{mol}$ ).

Many custom-made closed systems have been described in the literature (e.g. *Savage and Davidson*, 2003; *Irvine and Law*, 2002) and commercial systems are also available. Figure 1 presents a schematic diagram for an automated closed-chamber system (LI-8100, LI-COR Biosciences, Lincoln, NE USA).

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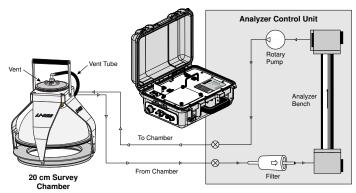


Figure 1. Schematic diagram of the measurement flow path for the Automated Soil CO<sub>2</sub> Flux System (LI-8100, LI-COR Biosciences, Lincoln, NE USA). A 20-cm survey chamber is shown with the control unit. The system can also support measurements with a 10-cm survey chamber and a 20-cm Long-term Chamber.

The concept of chamber-based soil CO<sub>2</sub> flux measurements can at first seem quite simple, because the only items needed for making a measurement are a chamber, a pump, a CO<sub>2</sub> gas analyzer, and a data-logging device. However, we must take many considerations into account in the process of instrument design and making the measurements in order to have accurate flux data. As stated above, soil CO<sub>2</sub> production strongly depends on many environmental conditions. Also, soil CO<sub>2</sub> flux is a physical process driven primarily by the CO<sub>2</sub> concentration diffusion gradient between the upper soil layers and the atmosphere near the soil surface. The fundamental challenge for making accurate soil CO<sub>2</sub> flux measurements is that the deployment of chambers must have minimal or no disturbance to environmental conditions that impact CO<sub>2</sub> production and transport inside the soil profile. The four most important considerations for an accurate measurement are (1) maintaining the chamber-pressure equilibrium with ambient air pressure, (2) ensuring good mixing of the air inside the chamber, (3) dealing with an altered diffusion gradient inside the chamber, and (4) minimizing the disturbance to the environment. Below we will discuss each of these considerations and how we carefully address them.

Maintaining pressure equilibrium between inside a chamber and the ambient air.

Pressure equilibrium between inside a flux chamber and the surrounding air outside the chamber must be maintained during the measurement. A simple open vent tube connecting to the chamber has often been used for the chamber pressure equilibrium (e.g. Hutchinson and Mosier, 1981; Davidson *et al.* 2002). This approach, however, is effective only under calm conditions. Under windy conditions, negative chamber pressure excursion will occur as wind blows over the vent tube's external open end because of the Venturi effect. This will cause a mass flow of CO<sub>2</sub>-rich air from the soil into the chamber, leading to a significant overestimation of soil CO<sub>2</sub> flux. In fact, some researchers (e.g. Conen and Smith 1998) recommended eliminating the vent tube after recognizing the potential problem from the Venturi effect.

Scientists and engineers at LI-COR Biosciences have developed a novel vent design for our chambers. The new vent has a tapered cross section as shown in Figure 2. Conservation of mass requires that the average air flow rate drops as the air enters the vent. According to Bernoulli's equation, as the air flow rate decreases, a major portion of dynamic pressure is converted to static pressure, raising the static pressure with which the chamber equilibrates. This design is radially symmetric to eliminate wind-direction sensitivity. Data from field experiments on differential pressure measurements between inside the chamber and the outside ambient air show that chambers equipped with our newly designed vent always have internal chamber pressure equal to outside the chamber under both calm and windy conditions. Our new vent thus virtually eliminates the Venturi effect. For more details, see our published journal paper (Xu *et al.* 2006).

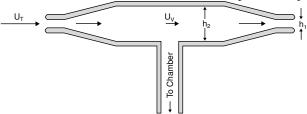


Figure 2. Cross-section view of the new vent design (patent pending).  $U_T$  is the wind speed at the height of the vent.  $U_V$  is the wind speed inside the vent near the vent tubing.  $h_1$  and  $h_2$  is the edge and the central distance between the upper- and the lower-half of the vent.  $U_V$  depends on the ratio of  $h_1$  to  $h_2$ .

# Ensuring good mixing.

Because only a small portion of the chamber air is sent to the infrared gas analyzer to determine  $dC_c/dt$ , good mixing inside the chamber is essential. A mixing fan often has been used in many custom-made soil  $CO_2$  flux systems to achieve good mixing, but using a mixing fan inside a chamber can also cause disturbances in the pressure equilibrium. To eliminate any potential chamber pressure perturbation, a mixing fan is not used on LI-8100 chambers. Good mixing is achieved through both optimal bowl-shaped chamber geometry or a mixing manifold.

# Dealing with altered CO<sub>2</sub> diffusion gradients.

Soil  $CO_2$  flux is driven primarily by the  $CO_2$  diffusion gradient across the soil surface. With the closed-chamber technique for estimating the flux, the chamber headspace  $CO_2$  concentration ( $C_c$ ) must be allowed to rise in order to obtain  $dC_c/dt$ . However, raising  $C_c$  will reduce the  $CO_2$  diffusion gradient across the soil surface inside the chamber, leading to an underestimation of the flux. To overcome this, a new exponential function is derived to fit the time series of  $C_c$  (Eq. 2). With the initial slope ( $dC_c/dt$  at t=0) of the fitted function (Eq. 3), the flux is then estimated at the time of chamber closing, when  $C_c$  is close to the ambient level.

$$C_{c} = C_{s} + [C_{c}(0) - C_{s}]e^{-at}$$

$$\frac{dC_{c}}{dt} = a[C_{s} - C_{c}(0)]e^{-at}$$
(2)

where  $C_s$  is the CO<sub>2</sub> concentration in the soil surface layer communicating with the chamber (µmol/mol), and a is a rate constant (1/s).

From the literature, a linear regression often has been used on the time series of  $C_c$  to determine  $dC_c/dt$ . Our experimental data show that the underestimation of  $F_c$  from the linear approach was systematic and significant, even though the linear regression sometimes gave a very high value for the regression coefficient. Furthermore, the underestimation will be greater for porous soil that has a high conductance to gas transport. Therefore we do not recommend using the linear regression on the time series of chamber  $CO_2$  data to determine the  $dC_c/dt$ .

# Minimizing the disturbance to the environmental conditions.

For a long-term soil  $CO_2$  flux measurement, it is critical to keep the environmental conditions inside the collar as close to the natural conditions as possible. The impact of installation of the long-term chamber on radiation balance, wind field, and precipitation interception should be minimized. This issue was been addressed carefully when we designed the two long-term chambers (8100-101 and 104). Both chambers are parked away from the collar when they are not in the measurement mode. The baseplate of the two long-term chambers is also perforated to minimize the perturbation to the soil environment around the collar.

Also chambers must close and open automatically and slowly. This eliminates the possibility of pushing fresh ambient air into the soil or removing soil air during the chamber closing/opening. Temperature artifacts are minimized by careful consideration of chamber materials and coatings.

# Example of soil CO2 flux measurement over a soybean field in Nebraska

Figure 3 shows an example of diurnal soil  $CO_2$  flux from a soybean field at the University of Nebraska Lincoln Agricultural Experimental Station near Mead, Nebraska USA. The dataset was obtained in the middle of the growing season (July 9 to 19, 2006). The flux value and soil temperature at 5 cm depth were averaged from 16 measurements at different locations with an LI-8100 sixteen chamber multiplexed soil  $CO_2$  flux system. The soil  $CO_2$  flux ranged from 2 to 7  $\mu$ mol/m²/s. The soil  $CO_2$  flux shows a strong diurnal pattern and closely follows the soil temperature variations; this is because microbial respiration increases exponentially with temperature. This flux range of 2 to 7  $\mu$ mol/m²/s was comparable with other soil  $CO_2$  flux data published in the literature obtained from similar agricultural fields in the middle of the growing season. Normally, the soil  $CO_2$  flux from natural ecosystems can vary from less than 1  $\mu$ mol/m²/s to around 10  $\mu$ mol/m²/s, depending on the soil temperature, moisture, soil organic matter, plant canopy size, growing season, etc.

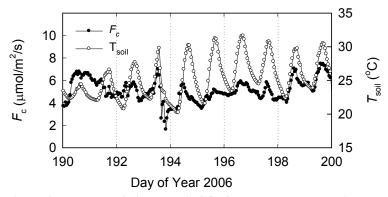


Figure 3. Example of diurnal soil  $CO_2$  flux ( $F_c$ ) measured with a LI-8100 sixteen chamber multiplexed soil  $CO_2$  flux system from a soybean field at University of Nebraska Lincoln Agricultural Experimental Station at Mead. Soil temperature at the depth of 5 cm ( $T_{soil}$ ) is also shown.

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## Contribution of root respiration to soil respiration in a maize field in Southwest China

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#### **Abstract**

Soil respiration, which originates from autotrophic root respiration and heterotrophic microbial respiration in the rhizosphere and the bulk soil, provides the main carbon efflux from terrestrial ecosystems to the atmosphere and is therefore an important component of the global carbon balance. Soil respiration, root biomass and nitrogen content in root in a subtropical maize field of Southwest China over a growing season (June to September) in 2007 were investigated to separate the respective contributions of root and heterotrophic respiration to the total soil respiration, and to reveal the seasonal variations of root respiration coefficient. The rates of soil respiration showed a remarkably high spatial variability and were 779, 611 and 425 mg CO<sub>2</sub>/m²/h near the plant, inter-plants and inter-rows, respectively. The contribution of root respiration to soil respiration varied from 47.26~63.59%, with mean value of 56.38%. The root respiration coefficient was much higher on 23 June (0.09) and 18 July (0.12) and gradually decreased to 4 September (0.05). Root respiration coefficient was positively correlated with root nitrogen content. The root nitrogen content could explain 91% changes of root respiration coefficient during the maize growing season.

#### **Key Words**

Root respiration, soil respiration, root respiration coefficient, root nitrogen content, maize field.

#### Introduction

Soil respiration is a major component of the global carbon cycle, accounting for about 25% of the global carbon dioxide exchange (Bouwmann and Germon 1998). Therefore, soil respiration becomes one of the important research issues in the global carbon cycle (Schimel 1995). Soil respiration originates mainly from root and the associated rhizosphere and soil microorganisms, the partitioning of soil respiration helps to improve our understanding of the environmental changes that drive carbon cycling (Bond-Lamberty *et al.* 2004) and to accurately estimate carbon budgets of ecosystems and turnover rates of soil organic matter (Wang *et al.* 2006). Separating root and heterotrophic respiration from total soil respiration is exceptionally difficult and presents one of the greatest challenges to quantify carbon cycling (Killham and Yeomans 2001). In this study, soil respiration, root mass, nitrogen content in root in a subtropical maize field of Southwest China during the growth season (June to September) in 2007 were investigated to separate the respective contributions of root and heterotrophic respiration to the total soil respiration, and to reveal the seasonal variations of root respiration coefficient.

#### Methods

*Site description* 

The experimental site  $(30^{\circ}26' \text{ N}, 106^{\circ}26' \text{ E})$  is located at the farm of Southwest University, Chongqing, China. The average total annual precipitation was 1105.4 mm, and the annual mean air temperature was  $18.3^{\circ}\text{C}$ . The soil for this study was classified as Purplish in the Second Soil Survey of China. It was developed from purple parent material of Mesozoric sandstone formation. The soil properties are described as follows: clay content, 144.2 g/kg; sand content, 447.4 g/kg; pH (H<sub>2</sub>O), 7.1; total N content, 1.74 g/kg; total P content (as P<sub>2</sub>O<sub>5</sub>), 0.75 g/kg; total K content (as K<sub>2</sub>O), 22.7 g/kg. The selected crop type was Yayu  $2^{\#}$ . It was sown on 22 May and harvested on 12 September in 2007, Plants were planted 40 cm apart in rows. The distance between rows was 50 cm. The field was fertilized with 150 kg N /ha,  $120 \text{ kg P}_2O_5$  /ha and 41 kg K<sub>2</sub>O /ha surface-applied as basal fertilizer before sowing.

#### Soil respiration measurement

Soil respiration rates were measured five times on 23 June, 18 July, 10 August, 21 August and 4 September in 2007. Three measurement positions in the maize field were chosen: near a plant (1-7cm from a plant), inter-plants (8-20 cm from the plant) and inter-rows (20-25cm from the plant) and every position had three

replicates. Soil respiration rates were measured every two hours from dawn to cockshut at clear days. Soil respiration rates were measured using a closed chamber technique. The gas was collected using an stainless steel cylinder (7 cm dia., 7 cm high) which had a white-colored acrylic lids equipped with two ports, one for gas sampling and the other for the attachment of a sampling bag to equilibrate the chamber pressure with the atmospheric pressure. Two days before the sampling, the chamber bases made of stainless steel were inserted into soils at each site, to a depth of 3 cm. During sampling, the stainless steel cylinder was placed over the base and filled with water in the groove to ensure air-tightness. Air sample inside the chamber was taken for every 10 min over a 30 min period by using 20 ml plastic syringes (total of four samples). Air temperature inside the chamber was measured during taking samples. Concentrations of CO<sub>2</sub> were analyzed in the laboratory (within a period of at most 12 hours) using a gas chromatograph equipped with a flame ionization detector and an electron capture detector (Wang and Wang 2003). Soil respiration rate was calculated from a linear regression of the changes in the concentration. Corrections were made for air temperature and pressure. The data deviating significantly from linearity (R<sup>2</sup><0.95) were discarded. Air temperature, wind speed and atmospheric pressure at 2 m height were measured at a climate station in close proximity to the measurement sites. Soil temperatures and moisture contents were measured in parallel with soil respiration.

### Partitioning of root and heterotrophic respiration

Root respiration in this study refers to the combination of rhizosphere respiration and root respiration, and heterotrophic respiration refers to the respiration of soil microbes that are free from roots, *i.e.*, derived from soil organic matter. The CO<sub>2</sub> attributable to roots and microorganisms was apportioned using a regression method (Kucera and Kirkham 1971), in which soil respiration was plotted against total root mass at 0-30 cm depth. The regression line between the two has a *y*-intercept, which estimates the respiration in the absence of roots, *i.e.*, heterotrophic respiration. Root respiration was estimated by the differences between total soil respiration and heterotrophic respiration.

#### Results

#### Root respiration

Soil respiration rates showed a remarkably high spatial variability among the three measurement positions (Table 1). The order of soil respiration was as follows: near the plants>inter-plants>inter-rows. During the growing season in 2007, soil respiration rates from the maize agricultural ecosystem were 778.52, 610.78 and  $425.48 \text{ mg CO}_2/\text{m}^2/\text{h}$  near plant, inter-plants and inter-rows, respectively.

Table 1. Soil respiration rates at the three measurement positions during the maize growing season in 2007 (mg  $CO_2/m^2/h$ ).

Date	Near plant	Inter-plants	Inter-rows
23 June	430.57±48.95	371.82±20.53	310.77±3.81
18 July	$844.11\pm74.46$	$632.83\pm53.64$	$464.01\pm50.00$
10 August	1034.34±141.21	846.47±128.35	644.72±51.75
21 August	972.24±94.15	$737.97 \pm 95.37$	$389.13\pm64.75$
4 September	611.33±115.59	464.81±101.50	$318.78\pm40.55$

Soil respiration increased with the increase of root biomass, the relationships between soil respiration and root mass were established based on the data derived from the measurements conducted on 23 June, 18 July, 10 August, 21 August and 4 September of 2007, respectively (Table 2). The determinant coefficients ( $R^2$ ) between soil respiration and root mass at different observation dates ranged from 0.76 to 0.88 (Table 2).

Table 2. Regression analysis between soil respiration and root biomass on the sampling date during the maize growing season in 2007.

Date	Intercept	Slope	$R^2$	р
23 June	215.11	13.81	0.76	0.002
18 July	290.13	16.70	0.83	0.001
10 August	335.37	7.96	0.88	< 0.001
21 August	281.21	7.83	0.87	< 0.001
4 September	221.67	5.29	0.84	< 0.001

Heterotrophic respiration averaged 268.70 mg CO<sub>2</sub>/m<sup>2</sup>/h, ranging from 215.11~335.37 mg CO<sub>2</sub>/m<sup>2</sup>/h (Table 3). Root respiration varied from 192.73 to 585.60 mg CO<sub>2</sub>/m<sup>2</sup>/h, with mean value of 373.96 mg CO<sub>2</sub>/m<sup>2</sup>/h.

The seasonal variation of the contribution of root respiration to soil respiration presented as a single peak. The contribution was the lowest on 23 June and rose with the increase of root biomass and reached the maximum value on 10 August. This was ascribed to not only the higher soil temperature but also the enhancement of root respiration. Strong photosynthesis provided more nutrients for root in this period, which stimulated the root growth and therefore promoting the root respiration (Kuzyakov and Cheng, 2001). The contribution declined slowly from later August and during the entire maize growing season the average value was 56.38%. Kuzyakov and Larionova (2005) found that the contribution of root respiration to soil respiration is 48%±5% generally in agroecosystems. Hanson *et al.* (2000) summarized that the contribution of root respiration to soil respiration averaged 60.4% for non-forest ecosystems. These values were close to our result. However, Yang and Cai (2006) found that the ratios of root respiration to soil respiration during the soybean growing season fluctuated in the range of 62%~98%, which were much bigger than the values in this paper. Probably the discrepancy was owing to the different experimental methodologies or crop species.

Table 3. Root respiration and heterotrophic respiration on the sampling date during the maize growing season in 2007.

Date	Soil Respiration	Heterotrophic respiration	Root respiration	Ratio of root respiration
	$(mg CO_2/m^2/h)$	$(mg CO_2/m^2/h)$	$(mg CO_2/m^2/h)$	to soil respiration (%)
23 June	407.84	215.11	192.73	47.26
18 July	784.50	290.13	494.37	63.02
10 August	920.97	335.37	585.60	63.59
21 August	634.99	281.21	353.78	55.71
4 September	464.97	221.67	243.30	52.33

#### Root respiration coefficient

In order to correct the influence of soil temperature on soil respiration, we set the value of  $Q_{10}$  as 2. The soil respiration rates measured in different temperatures in our experiment were all corrected into the values in 25 °C according to equation 1. Then we calculated the ratio of root respiration to root biomass, namely root respiration coefficient (Sun *et al.* 2004), which unit is g/g/d and its meaning is how many gram carbon were respired by per gram plant per day.

$$RR_{25} = \frac{RR}{2^{[(T-25)/10]}} \tag{1}$$

Where  $RR_{25}$  is soil respiration rates in  $25^{\circ}$ C, RR is soil respiration rate measured in our experiment, T is the soil temperature when sampling. The value 2 is the temperature coefficient of soil respiration. Accordingly, we could obtain root respiration coefficients on every sampling date (Figure 1), which was much higher on 23 June and 18 July and gradually decreased to 4 September. Gifford (2003) reported that the root respiration coefficients were higher in early growing stage than in later maturing stage, which was consistent with our results.

Root respiration coefficient was positively correlated with root nitrogen content (Figure 2). The root nitrogen content could explain 91% changes of root respiration coefficient in the maize growing season. Ryan (1991), Tjoelker *et al.* (1999) and Sun *et al.* (2004) all reported that there existed the significantly linear correlation between respiration coefficient of different plant organ and its nitrogen content from tree, shrub and crops.

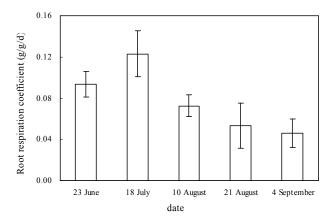


Figure 1. Root respiration coefficients during the maize growing season in 2007.

Figure 2. The relationship between root respiration coefficient and root nitrogen content.

#### Conclusion

The rates of soil respiration showed a remarkably high spatial variability and were 778.52, 610.78 and 425.48 mg  $CO_2/m^2/h$  near the plant, inter-plants and inter-rows, respectively. Hetetotrophic respiration averaged 268.70 mg  $CO_2/m^2/h$ , ranging from 215.11~335.37 mg  $CO_2/m^2/h$ . Root respiration varied from 192.73 to 585.60 mg  $CO_2/m^2/h$ , with mean value of 373.96 mg  $CO_2/m^2/h$ . The contribution of root respiration to soil respiration varied from 47.26~63.59%, with mean value of 56.38%. Root respiration coefficient was much higher on 23 June (0.09) and 18 July (0.12) and gradually decreased to 4 September (0.05). Root respiration coefficient was positively correlated with root nitrogen content. The root nitrogen content could explain 91% changes of root respiration coefficient during the maize growing season.

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## Crop yield and greenhouse gas responses to stover harvest on glacial till Mollisol

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#### **Abstract**

Producing clean renewable energy and reducing climate change are important and interrelated issues. Corn stover is targeted as a potential non-food bioenergy feedstock, especially in the Midwest United States. Crop residue management impacts soil water and temperature dynamics, which in turn can impact many soil processes. Stover harvest is expected to reduce soil cover and has the potential to reduce crop yield and impact carbon dioxide ( $CO_2$ ) and nitrous oxide ( $N_2O$ ) emission. Corn and soybean were grown from 2005 to 2009 in rotation on plots managed without tillage. After corn grain harvest, stover was harvested from 0 of 8 (0%), 4 of 8 (50%), 6 of 8 (75%) and 8 of 8 (100%) rows using a forage harvester with a 76-cm swath. All soybean stubble was returned to the field. Two cycles of stover harvest did not reduce corn or soybean yield or alter  $CO_2$  or  $N_2O$  emission. Thus, these results suggest that harvesting residue will not influence  $CO_2$  or  $N_2O$  emission in the field.

#### **Key Words**

Corn stover removal, nitrous oxide, bioenergy, carbon dioxide.

#### Introduction

Renewable bioenergy is one strategy for addressing the interrelated challenges of reducing dependence on finite, foreign fossil fuel sources while mitigating global climate change. Non-food plant materials such as crop residues and bioenergy crops (herbaceous and woody) are anticipated to serve as bioenergy feedstocks (Biomass Research and Development Board 2008; Perlack et al. 2005). Use of biomass for energy can reduce CO<sub>2</sub> emission when used as a substitute for fossil fuels, but potential risks (e.g., loss of soil quality and productivity) need to be minimized. There are instances of crop yield and soil quality rapidly declines in response to harvesting residue (Blanco-Canqui and Lal 2007; Blanco-Canqui et al. 2007; Wilhelm et al. 1986). Tillage and residue management influence many physical, chemical and biological soil properties (Johnson et al. 2009), thus it can be difficult to predict their impact on emissions (Petersen et al. 2008). Residue absorbs the energy of raindrop impact, increases infiltration, and presents a barrier to evaporation (Flerchinger et al. 2003; Sauer et al. 1996; Unger and Parker 1976). Therefore, residue covered soils may remain wetter and cooler than when a residue layer is absent (Johnson and Lowery 1985; Unger 1988). Harvesting crop residue for bioenergy changes the soil microclimate, soil susceptibility to erosion, organic matter available for microbial activity and C sequestration, and may also change methane (CH<sub>4</sub>) and N<sub>2</sub>O flux. The objectives of this research were to one) assess the impact of corn stover harvest rate on subsequent corn and soybean yield; and two) monitor the CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub> emission from soil with maximum stover harvested or all stover returned.

#### **Material and Methods**

The study site was on the Swan Lake Experimental Farm (45.682° lat and 95.802° long, elevation 357 m), with a mean annual temperature of 5.8°C and mean annual precipitation of 645 mm. Native vegetation for the region is tall grass prairie. The soil series in the experimental area are predominately a Barnes loam (fine-loamy, mixed, superactive, frigid Calcic Hapludoll) and an Aastad loam (fine-loamy, mixed, superactive, frigid Pachic Hapludoll). The experimental area is nearly level with <2% slope. The parent material is glacial till from the Des Moine Lobe deposited during the Wisconsin glaciations. Texture analysis and baseline bulk density, pH, total C, organic C, total N, P (Olsen extract for calcareous soils) and K were determined on soil collected in the fall of 2005 using standard soil protocols (Table 1).

The plot area has been managed without tillage since 1995, primarily in continuous corn. Since 2005, the plots have been in a corn-soybean rotation, with both phases grown each year. All soybean stubble was returned to the field. Stover was harvested from 0 of 8 (0%), 4 of 8 (50%), 6 of 8 (75%) and 8 of 8 (100%) rows using a forage harvester with a 76-cm swath. Harvest rows are shifted across the plot, such that the

Table 1. Base-line texture analysis summary of biomass removal plots at Swan Lake research farm plots, soil

samples collected in the of fall 2005.

Depth	Sand	Clay	Silt	Bulk	$pH_{CaCl2}$	Total	Organic	Total	$P^{b}$	K
				density		C	$C^{a}$	N		
cm	(	%	)	$Mg/m^3$		(	g /kg	)	( mg	(/kg)
0 to 5	43.2	23.5	33.4	1.37	6.06	27.9	27.5	2.43	34.9	178
5 to 10	42.1	24.4	33.4	1.41	6.27	20.9	20.4	1.87	17.2	132
10 to 20	41.5	21.6	36.9	1.44	6.48	21.1	20.6	1.89	15.0	130
20 to 30	39.1	21.6	39.3	1.51	6.73	15.9	14.9	1.39	8.3	142
30 to 60	42.5	20.6	36.9	1.41	7.46	18.3	6.6	0.67	3.9	139
60 to 100	42.7	20.6	36.7	1.58	7.73	25.8	1.3	0.25	3.0	115

<sup>&</sup>lt;sup>a</sup>Organic C determined by the difference between total combustible C and inorganic C as these are calcareous soils. <sup>b</sup> Olsen Phosphorus extraction for calcareous soils.

same rows are not repeatedly harvested. Based on the amount of biomass remaining in the field we estimated that 40 to 90% of the stover biomass was removed when 8 of 8 rows were harvested (data not shown). The dry mass of material harvested was determined. In plots with no stover removal, stover yield was determined by harvesting residue from two 2-m row sections; this stover was returned to the harvest site (except for a small subsample used for moisture determination). The rate of GHG (CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub>) emission was monitored from planting 2008 to planting 2009 in the 0 and 100% residue harvest in both phases of the rotation (corn and soybeans). Samples were collected using closed-vented chambers with anchors driven at least 8 cm into the soil (Hutchinson and Mosier 1981; Johnson *et al.* 2010) using a stratified sampling with weekly sampling during the spring-thaw and after management events (e.g., N-fertilizer application or tillage), and 14-day sampling intervals at other times. The concentration of CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub> were determined by GC-TCD, GC-ECD and GC-FID, respectively (Johnson *et al.* 2010). Treatments were arranged in a randomized complete block design with four replicates. The effect of residue removal on yield and emission was assessed with a mixed model, with replication as a random term and removal rate as a fixed term.

#### **Results and Discussion**

Residue cover at planting was inversely proportional to the amount of corn stover harvested (data not shown). The impact was still noticeable during the next corn phase with there being less protection against erosive forces when the residue was harvested. Harvesting corn stover did not cause an appreciable or consistent impact on corn grain, stover or soybean yields after one or two cycles of corn stover harvest (Table 2). The first year of corn stover harvest depended upon the rotation phase and tillage. Corn (grain and stover) yield in 2007 reflects the impact of harvesting corn stover in 2005, while corn yield in 2008 reflects one cycle of harvesting corn stover (2006). Soybean yields in 2008 and 2009 reflect the impact of two stover harvest events, while yields in 2006 and 2007 reflect only one cycle of stover harvest. Reduced yield after only one cycle of stover harvest has been reported, due to increased evaporation and reduced infiltration (Blanco-Canqui and Lal 2007; Wilhelm *et al.* 1986), but others found no yield differences after repeated silage (Wilts *et al.* 2004) or residue harvest (Barber 1979). Under our experiment conditions, two cycles of harvesting corn stover, did not cause a detrimental impact on crop yields.

During the 2008 cropping season (May/2008 to April/2009), soil respiration was greater during the summer months (June to September) compared to the winter months (November to April) (Fig. 1). In general, the rate of CO<sub>2</sub> emission was unaffected by the returning or harvesting corn stover. At most sampling dates, there was relatively little N<sub>2</sub>O emission. However, N<sub>2</sub>O emission was observed in early spring (2009) when fluxes

Table 2. Corn grain, stover and soybean yield response, 2005 is the baseline yield before treatments.

1 abie	2. Corn	grain, si	tover and	u soybea	n yieia r	esponse,	2005 IS	me basei	ime yieid	before	treatmen	its.	
Rate		Corn grain				Corn	stover			Soybean			
	2005	2006	2007	2008	2005	2006	2007	2008	2005	2006	2007	2008	2009
	(						Mg/ha						)
0	9.5	7.3	7.9	7.5	7.1	5.7	7.9	6.4	3.2	2.7	2.6	3.3	2.3
50	6.8	8.1	7.4	9.7	5.1	5.2	7.4	7.3	3.5	2.9	3.0	3.3	2.2
75	7.4	8.3	8.4	8.2	5.6	5.5	7.8	7.0	3.5	2.7	3.1	3.6	2.6
100	8.5	7.5	5.7	9.1	6.4	5.4	7.5	6.8	3.4	1.9	2.9	2.9	2.5
	$NA^a$	NS	NS	NS	NA	NS	NS	NS	NA	NS	NS	NS	NS

<sup>&</sup>lt;sup>a</sup>NA = not appropriate, NS=not significant at  $P \le 0.05$ 

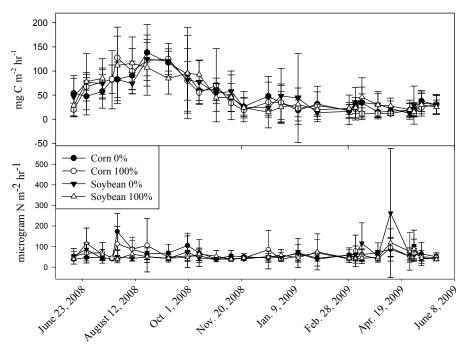


Figure 1.  $CO_2$  - C (top) and  $N_2O$ -N (bottom) measured from May 21, 2008, to April 28, 2009. Each point is the average of four replications with two collars within each plot.

Table. 3. Cumulative GHG gas emission from May/2008 to April/2009 collected from two residue treatments, no rows harvested (0) or all rows harvested (100) from both crops.

	Corn	Corn Soybean		
Removal rates	0	100	0	100
kg C /ha from CO <sub>2</sub>	4230	4110	4260	4230
kgN /ha from N <sub>2</sub> O	5.14	5.01	5.14	4.70

were highly variable and the plots varied in the amount of surface thawing, and standing water in or near the collar. We suspect that application of anhydrous ammonia fertilizer on June 23, 2008, is the reason we observed more  $N_2O$  from corn than from soybean on July 1 and July 15, 2008. Integrated for a full year, there were no differences between crops or residue treatment on the flux of  $CO_2$  or  $N_2O$  (Table 3). Methane flux (consumption and release) were very small with concentrations at or near the detection limit of the gas chromatograph (data not shown).

#### Conclusion

In the short term, harvesting corn stover did not reduce corn or soybean yield. However, reduced soil cover increases the risk of soil erosion. The annual CO<sub>2</sub> and N<sub>2</sub>O emission was not appreciably altered after only two cycles of harvesting corn stover. To assess more fully the impact of stover harvest on climate change also requires measuring changes in soil organic C, but measurable changes in soil organic carbon are slow and have not yet been assessed. The impact of long-term repeated corn stover on crop yield and GHG emission still needs to be studied.

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## Dependency of nitrous oxide emission factors on nitrogen input rates: A metaanalysis

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#### **Abstract**

Rising atmospheric concentrations of nitrous oxide ( $N_2O$ ) can cause global warming and associated climate change. It is typically assumed that there is a linear relationship between  $N_2O$  emission and nitrogen (N) input, and therefore, soil  $N_2O$  emission is often estimated as a proportion of N additions using emission factors (EF). However, a growing body of studies shows non-linear, exponential relationship between  $N_2O$  emission and N input. These studies commonly reported that  $N_2O$  emission abruptly increases at superoptimal level of N additions. Additionally, this rise in  $N_2O$  emission consistently causes EF to sharply increase and also to be directly dependent on N input rate. Meta-analysis revealed that increments in EF per additional unit of N input ranged from 0.0006 to 0.02, and these  $\Delta EF/\Delta N$  input values exhibited significant negative correlation with soil pH (r= -0.793, P < 0.001). Results support the importance of N management based on optimal rates particularly in intensive agricultural systems and low pH soils. It also indicates current IPCC default  $N_2O$  EF methodology could underestimate  $N_2O$  emission from these systems. Additional research efforts are needed to improve  $N_2O$  EF methodology and/or system modelling to capture the observed patterns of linear dependency of EF on N input rates.

#### **Key Words**

Greenhouse gas, ozone layer depletion, Intergovernmental Panel on Climate Change.

#### Introduction

Atmospheric N<sub>2</sub>O contributes to both greenhouse effect (Wang et al. 1976) and ozone layer depletion (Crutzen 1970). A change in the N<sub>2</sub>O mixing ratio from 270 ppb in 1750 to 319 ppb in 2005 caused an increased radiative forcing of  $0.16 \pm 0.02$  W/m<sup>2</sup> in part because N<sub>2</sub>O possesses a relatively high global warming potential (i.e., 298 and 25 times greater than carbon dioxide and methane, respectively; IPCC 2006). Of the entire anthropogenic N<sub>2</sub>O emission (5.7 Tg N<sub>2</sub>O-N/y), agricultural soils provide 3.5 Tg N<sub>2</sub>O-N/y (IPCC 2006). Use of N fertilizers and animal manure is the main anthropogenic N<sub>2</sub>O source and it is responsible for roughly 24% of total annual emissions (Bouwman 1996). Several early reports indicate a linear relationship between N input and N<sub>2</sub>O emission in various agricultural systems (Bouwman 1996). This relationship is adapted for current IPCC Tier I EF methodology (IPCC, 2006) which estimates N<sub>2</sub>O emission based on N additions in managed agricultural areas. However, there is a growing body of evidence indicating a nonlinear, exponential relationship between N input and N<sub>2</sub>O emission (Grant et al. 2006; Zebarth et al. 2008). This nonlinear rise caused EF to increase with N additions, and therefore, N<sub>2</sub>O EF values are not constant but dependent on N input rates (Grant et al. 2006). To date, these contradictory results pattern have not been clearly explained. Thus, the objectives of this study were to compile available data on the subject of direct N<sub>2</sub>O EF in multiple agricultural systems with varying N input rates, to examine the dependency of N<sub>2</sub>O EF on N input rates, and to establish hypotheses to potentially explain these relationships.

#### Materials and methods

Data were acquired by searching existing refereed literature as well as through personal communications with individual data owners. We compiled field data from 20 independent referred studies encompassing 40 experimental site-years worldwide. A complete list of the 20 assessed studies can be found within the caption for Figure 1. Based on this global dataset, direct  $N_2O$  EF were calculated following IPCC (2006) Tier I methodology, and subsequently, the changes in EF as a function of increments in N input ( $\Delta$ EF/ $\Delta$ N input with units/kg N ha) were also calculated. Statistics included Pearson correlation analyses.

#### Results and discussion

*N*<sub>2</sub>*O EF dependency on N input rates* 

This data compilation resulted in a very wide range of N<sub>2</sub>O EF (i.e., 0.0005 to 0.16; Figure 1) revealing inconsistency amongst existing studies as well as when compared to the current IPCC single default value

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for direct  $N_2O$  emissions (i.e., 0.01; IPCC 2006) as previously discussed by other researchers (Grant *et al.* 2006). Variations in N input sources across studies as well as dynamics soil-plant interactions in systems receiving superoptimal N addition rates could partly account for this ample EF variability. Extremely high EF values would likely occur when soil mineral N availability exceeds plant and soil N uptake capacities (McSwiney and Robertson, 2005). This collective evidence supports the critical need for enhancing existent  $N_2O$  estimation methodology for superior accuracy of both field-specific and global budget  $N_2O$  estimations. Furthermore, this meta-analysis also suggests that the pronounced variability in EF values across all assessed experimental site-years is directly associated with varying N input rates (Figure 1, Table 1). As N input (e.g., fertilizer or manure) rates increased, calculated  $N_2O$  EF consistently increased in all studied cases. Based on fitting linear regression models to the existing data, values of  $\Delta$ EF/ $\Delta$ N input (i.e., regression coefficient) ranged from 0.0006 to 0.02 and averaged 0.0074 (Table 1). In addition, the parameter  $\Delta$ EF/ $\Delta$ N input preliminary appears to behave linearly within several studies (Figure 1B). This numerical description of  $N_2O$  emission dynamics across multiple studies had not been previously documented in the existing literature.

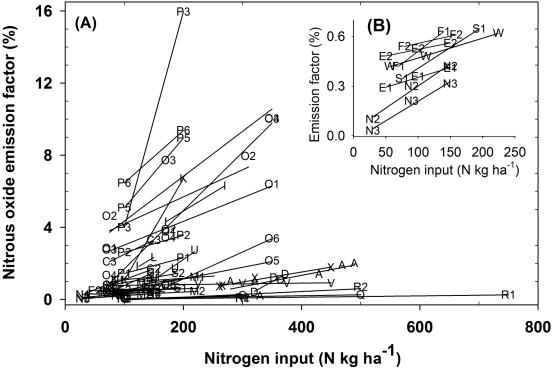


Figure 1. Direct nitrous oxide emission factors as a function of nitrogen (N) input rates across 20 studies. Ranges of N input from (A) 0 to 800 and (B) 0 to 250 kg N/ha. The 20 assessed studies are labelled as A (Hyde *et al.* 2006), C (Zebarth *et al.* 2008), D (Clayton *et al.* 1997), E (Zhang and Han 2008), F (Abdalla *et al.* 2010), G (Hua *et al.* 1997), I (Kilian *et al.* 1998), K (Allen *et al. in press*), L (Sehy *et al.* 2003), M (Mosier *et al.* 2006), N (Ma *et al.* 2009), O (Cardenas *et al. in press*), P (Engel *et al.* 2009), Q (Letica *et al.* 2009), R (Hoogendoorn *et al.* 2008), S (Jarecki *et al.* 2009), T (Rochette *et al.* 2000), U (Rochette *et al.* 2004), V (Breitenbeck and Bremner, 1986), and W (Mosier *et al.* 1982).

Another interesting observation of this meta-analysis is that  $\Delta EF/\Delta N$  input exhibited a negative correlation with soil pH (r=-0.793, P < 0.001; Table 1). It is well established that N<sub>2</sub>O reductase activity is inhibited at low pH (e.g., 4.5 to 6.5) (Knowles 1982), and consequently, N<sub>2</sub>O:N<sub>2</sub> production ratio typically increases with decreasing pH. This pH effect can also partly account for variations in  $\Delta EF/\Delta N$  input across studies.

Hypothetical mechanisms for explaining observed patterns of EF and  $\Delta$ EF/ $\Delta$ N input
Several hypotheses can be postulated to account for the observed EF shifts depending on N input rates. As discussed above, this response appears to be primarily associated with excessive N supply (e.g., > 100 kg N ha<sup>-1</sup>; Bouwman *et al.* 2002) and soil microbial mediation. This soil N surplus would concomitantly lead to lower plant N uptake efficiency, and therefore, the resulting soil residual N would likely served as substrate for additional N<sub>2</sub>O production (Zebarth *et al.* 2008). Additionally, excess soil N under these conditions could also indirectly promote soil N<sub>2</sub>O production as it is known increased NO<sub>3</sub><sup>-</sup> can inhibit N<sub>2</sub>O reduction to N<sub>2</sub> producing wider N<sub>2</sub>O:N<sub>2</sub> ratios (Firestone *et al.* 1979). Alternatively, exogenous N additions to soils can

cause priming effects by stimulating microbial mobilization of native N boned within pre-existing soil organic matter (Kuzyakov *et al.* 2000). This enhanced soil native N mobilization and accessibility can result in increased  $N_2O$  emissions derived from the soil N pool (Di and Cameron 2008). Finally, based on this meta-analysis (Table 1) and as discussed above, changes in soil pH can also determine the outcome of  $N_2O$  production by interfering with  $N_2O$  reductase activity. Therefore, it can also be hypothesized that soil pH decreases can drive abnormally greater soil  $N_2O$  emission as a result of increasing N additions in intensively managed agricultural systems using certain acidifying N sources [e.g., ammonium sulphate:  $(NH_4)_2SO_4$ ].

Table 1. Estimated  $\Delta EF/\Delta N$  input parameter and soil properties for 18 selected assessed site-years.

Reference	ID (as shown in Figure 1)	$\Delta$ EF/ $\Delta$ N input (kg <sup>-1</sup> N ha)	рН	Sand (%)	Clay (%)	C (%)	N (%)	C/N
Hyde et al. 2006	A (2002)	0.0063	5.8	22	18	0.032	0.28	11.4
Zebarth et al. 2008	C (2003)	0.0147	6.6	59.2	10.6	1.54	0.1	15.4
Zebarth et al. 2008	C (2004)	0.012	6.6	36.7	13.4	2.07	0.086	24.1
Zebarth et al. 2008	C (2005)	0.016	6	38.2	13.8	1.5	0.096	15.6
Clayton et al. 1997	D (1993)	0.018	5.5	17	22	5.5		
Zhang et al. 2008	E (grassland)	0.0012	7.21			2.45	0.238	10.3
Zhang et al. 2008	E (cropland)	0.0008	7.07			1.89	0.187	10.1
Abdalla et al. 2010	F (2004)	0.003	7.4			1.94	0.19	10.2
Abdalla et al. 2010	F (2005)	0.0009	7.4			1.94	0.19	10.2
Hua et al. 1997	G (urea)	0.0006	7.99			1.85	0.116	15.9
Hua et al. 1997	$G[(NH_4)_2 SO_4]$	0.0012	7.99			1.85	0.116	15.9
Kilian et al. 1998	I (compost-N)	0.02						
Sehy et al. 2003	L (synthetic-N)	0.0197	6.1	20	29	1.4	0.15	9.3
Mosier et al. 2006	M (no tillage)	0.0041	7.7	40.2	33.4	1.28	0.152	8.4
Mosier et al. 2006	M (with tillage)	0.0016	7.7	40.2	33.4	1.19	0.147	8.1
Ma et al. 2009	N (2006)	0.0081	6.1			2.38		
Ma et al. 2009	N (2007)	0.0027	7.7			2.18		
Ma et al. 2009	N (2007)	0.0024	6.9			2.55		

#### **Conclusions**

Results from this meta-analysis using global data for  $N_2O$  emission from agricultural fields underscore the need for additional hypothesis-driven studies to enhance the current understanding on how excess N input affect  $N_2O$  emissions in N managed ecosystems. In further detail, this study clearly evidences extremely inconsistent EF values across assessed site-years as well as a linear dependency for EF changes on N input  $(\Delta EF/\Delta N \text{ input})$ . These preliminary findings could provide insights for improving  $N_2O$  EF methodology.

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## Ectomycorrhizal fungi and N<sub>2</sub>O production

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#### **Abstract**

Denitrification is an important biogeochemical soil process largely responsible for the production of the harmful greenhouse gas, nitrous oxide ( $N_2O$ ). Several soil factors control the final  $N_2O:N_2$  product ratio, and the availability and quality of labile carbon (C) are often regarded as the most important. Low  $N_2O$  emissions compared to agricultural sources are characteristic of boreal and temperate forest soils, which are generally a result of acidic conditions and low nitrate availability. However, the role of the dominant microbial community, the ectomycorrhizal (EcM) fungi, in such forest soils during denitrification, has been overlooked. As EcM fungi are key in transferring host C throughout the soil system, we hypothesise that EcM fungal C is important in stimulating denitrification. Results from soil incubation and bacterial culture experiments using  $^{15}N$ -nitrate indicate that addition of C sources, derived from EcM fungi, to the soil microbial community or a bacterial culture under controlled anaerobic conditions, leads to greater production of  $^{15}N$ -( $N_2O$  and  $N_2$ ). Therefore taking account of the presence of EcM fungi during denitrification could further our understanding of the processes involved in forest soil  $N_2O$  emissions.

#### **Key Words**

Nitrogen cycle, mycorrhizal fungi, Paxillus involutus, denitrifying bacteria, greenhouse gases.

#### Introduction

Denitrification is an important soil process responsible for significant emissions of nitrous oxide (N<sub>2</sub>O). N<sub>2</sub>O emissions are closely related to anthropogenic activities, with increasing concentrations in the atmosphere a direct consequence of enhanced nitrogen (N) fertiliser use (Houghton *et al.* 2001). Therefore, agricultural soils are the dominant sources of N<sub>2</sub>O, and the factors relevant to controlling source-sink relationships have been well-studied in these systems. In comparison to agricultural soils, N<sub>2</sub>O emissions from boreal and temperate forest soils, linked to denitrification and nitrification processes, are relatively low (Kesik *et al.* 2005). As forest systems are distinct to agricultural soils, different factors have been examined to try and improve our understanding of highly variable forest N<sub>2</sub>O emissions, such as forest type/tree species (Priha *et al.* 1999; Maljanen *et al.* 2003), distance from trees and tree roots (Butterbach-bahl *et al.* 2002; von Arnold *et al.* 2005), and management practices (Ineson *et al.* 1991; Zerva and Mencuccini 2005). However, N<sub>2</sub>O emissions from forest biomes have largely been investigated without consideration of the dominant soil microbes unique to these forest soils, the ectomycorrhizal (EcM) fungi.

EcM fungi form symbiotic mutualistic associations with the roots of trees, such as pine, birch and spruce. EcM fungi develop an extensive mycelial network, and in return for nutrient and moisture acquisition for their hosts, the fungi receive up to 30% of the host's photoassimilate, which is used for further growth and reproduction (Smith and Read 2008). These fungi play key roles in forest soil biogeochemical cycling, mainly through their mineralization of mineral and organic matter, uptake of essential nutrients, and exudation of labile carbon (C) and other organic compounds (Chalot and Brun 1998; Jones *et al.* 2004). The EcM fungi also have positive and negative effects on other soil microbes (Olsson *et al.* 1996; Nurmiaho-Lassila *et al.* 1997), therefore it is likely that denitrifying bacteria are also affected. The product ratio of N<sub>2</sub>O:N<sub>2</sub> by denitrifying bacteria is controlled by access to labile C (Burford and Bremner 1985; Firestone 1982; Henry *et al.* 2008), and there is the potential for bacteria in close proximity to EcM mycelia to utilise C derived from EcM fungi. EcM fungal-derived C could be in various forms, such as that released by actively foraging fungal mycelia, by modification of root exudation (quantity and quality) following EcM fungal colonisation of root tips, or from C released during decay of senescent fungal mycelia. Several studies have identified the main components of EcM fungal exudates, and key differences have been found between

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mycorrhizal and non-mycorrhizal roots, especially with regards to organic acids (e.g. Ahonen-Jonnarth  $\it et al.$  2001; van Hees  $\it et al.$  2003, 2005; Fransson  $\it et al.$  2007). Therefore, there is the potential that C from EcM fungi affects denitrification and subsequent  $N_2O:N_2$  ratios. Here we report on two experiments that tested the hypothesis that EcM fungal C (from synthetic sources and natural exudates) would stimulate denitrification.

#### Methods

N<sub>2</sub>O production from soil incubations with EcM fungal sources

Soil incubations were established containing sieved (< 2 mm) forest soil collected from the organic layer (0 – 10 cm depth; pH 3.5) and the underlying mineral layer (pH 3.7) of a semi-natural pine forest (northeast Scotland, UK). Mannitol and oxalic acid (known components of EcM fungal exudates) and glucose (an easily assimilated C source) were added to the soils as single doses at 3.6 g C/L. Nitrate was added as  $\rm K^{15}NO_3$  (10 at% excess  $\rm ^{15}N$ ) at 5 g N m $^{-2}$ . The control treatment received nitrate addition only. Carbon and N additions were in solution, thus increasing the water-filled pore space of each soil type to 70%; this ensured denitrification was the dominant N<sub>2</sub>O-producing process (Bateman and Baggs 2005). Each treatment was replicated three times. N<sub>2</sub>O production was measured periodically over 14 days from sealed incubations and soil was sampled from additional replicate incubations.

N<sub>2</sub>O production by a denitrifying bacterial culture with EcM fungal exudates

EcM fungal C was collected from two mycorrhizal sources: mycorrhizal exudate was collected from mycorrhizal birch seedlings (with the EcM fungus Paxillus involutus) growing in a sterile liquid nutrient medium, and C representing water-soluble C that would be released from decomposing fungal mycelia was collected from dried fungal cultures of P. involutus. Non-mycorrhizal root exudate was collected from birch seedlings (without P. involutus) growing in a sterile medium. These three C sources were provided as the

seedlings (without *P. involutus*) growing in a sterile medium. These three C sources were provided as the sole C supply (10 µg C/L) to an anaerobic culture (with 25 mM K<sup>15</sup>NO<sub>3</sub>, 10 at% excess <sup>15</sup>N) of the denitrifying bacterium *Paraccocus denitrificans* 1222. Nutrient media (with and without glucose) were also provided as control treatments. Each treatment (C source) was replicated five times. N<sub>2</sub>O production was measured every 4 hr over a 12 hr growth period.

### Results and discussion

 $N_2O$  production from soil incubations with EcM fungal sources

Total  $N_2O$  production over 14 days was significantly higher (P < 0.001) in the organic soil than in the mineral soil (Figure 1). In the organic soil, addition of mannitol and oxalic acid (known components of EcM fungal exudate) had significant effects on  $N_2O$  production over 14 days compared to glucose and control treatments, whereas in the mineral soil, addition of different C sources had no effect on  $N_2O$  production (Figure 1). In the organic soil, mannitol as a C source increased  $N_2O$  production, while addition of oxalic acid reduced  $N_2O$  production. <sup>15</sup>N analyses of gas samples indicated higher enrichment of <sup>15</sup>N- $N_2$  from the organic soil oxalic acid treatment, suggesting that this C source stimulated greater nitrate reduction to  $N_2$  compared to other C sources. The results suggest that when added as single C sources, mannitol and oxalic acid alter forest soil  $N_2O$  production, and that the use of oxalic acid in denitrification can lower the  $N_2O:N_2$  product ratio. Thus oxalic acid is a higher quality C source for denitrifying bacteria compared to glucose or mannitol. EcM fungal biomass is lower in the mineral layer compared to the organic layer (Genney *et al.* 2006), and as  $N_2O$  production was not affected, this suggests that the microbial biomass is smaller and not 'conditioned' to assimilate EcM fungal C to the same degree as the microbes in the organic layer.

 $N_2O$  production from direct EcM fungal C sources by a denitrifying bacterial culture. In this culture experiment, different C sources (mycorrhizal root exudate, non-mycorrhizal root exudate, mycorrhizal fungal extract, and nutrient media controls) were provided at the same C concentration to anaerobic bacterial cells. The maximum growth rates and final biomass from all treatments were similar after 12 hr growth period, however,  $N_2O$  and  $N_2$  production was significantly different. Peak  $N_2O$  production occurred at different times for each treatment (P < 0.001), and bacterial cells growing in the mycorrhizal fungal extract had the highest  $N_2O$  production at 12 hr (Figure 2). There was a clear preference shown by *P. denitrificans* for the two mycorrhizal C sources, as  $^{15}N-N_2O$  and  $^{15}N-N_2$  production were significantly greater in these treatments compared to the non-mycorrhizal root exudate and control treatments (P < 0.05). Qualitative analyses (dissolved organic carbon and specific UV absorbance) of the different C sources indicated that the mycorrhizal exudate and extract C sources contained a higher proportion of aromatic compounds, compared to the non-mycorrhizal root exudate, which are known to be produced by *P. involutus* 

and other EcM fungi (Dickinson and Hutchison 1997). These novel results show the direct use and preference for mycorrhizal C sources by denitrifying bacterial cells.

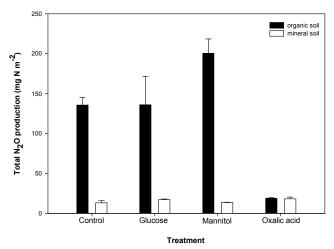


Figure 1. Total N<sub>2</sub>O production over 14 days from forest organic and mineral soil layers after addition of glucose, mannitol and oxalic acid as single doses (3.6 g C/L).

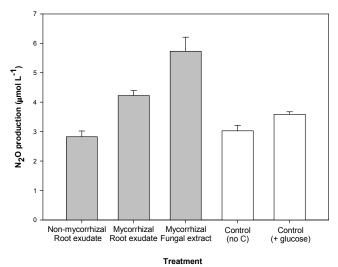


Figure 2. Final  $N_2O$  production after 12 hr growth by *P. denitrificans* 1222, under anaerobic conditions, with different C sources added at 10  $\mu$ g C/L: non-mycorrhizal root exudate; mycorrhizal root exudate; mycorrhizal fungal extract; and controls (media without added C, and media with added glucose).

#### Conclusion

EcM fungi are the dominant microbes in acidic soils of boreal and temperate forests, and despite their important roles in biogeochemical cycling, this group of microbes has been largely ignored as a potential factor controlling  $N_2O$  production via denitrification. The key results indicate (1) that EcM fungi may have a role to play in denitrification, via provision of high quality C to denitrifying bacteria; and (2) that bacterial denitrifiers in the forest organic soil layer may be 'conditioned' to utilising mycorrhizal C compounds. Therefore, in order to understand the mechanisms and factors controlling  $N_2O$  emissions from boreal and temperate forest soils, the presence of EcM fungi and their potential contribution to denitrification and  $N_2O$  production rates, should be taken into account and investigated further.

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## Effect of marsh reclamation on heterotrophic soil respiration in Sanjiang Plain, Northeast China

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#### **Abstract**

The Sanjiang Plain is the largest low-altitudinal swampy plain in China where has been strongly affected by human activities particularly the conversion of marsh to cropland. Four plots of *Carex lasiocarpa* marsh, *Deyeuxia angustifolia* marsh, rice field and dryland were selected in this study to evaluate the effect of marsh reclamation on heterotrophic soil respiration. Results showed that the seasonal changes of heterotrophic soil respiration from *C. lasiocarpa* marsh and *D. angustifolia* marsh were identical with a single-peak. The largest values appeared in summer and the lowest ones appeared in winter. The seasonal variation of heterotrophic soil respiration from dryland was the same as the marshlands, but the seasonal course of heterotrophic soil respiration from rice field changed and the peak values were postponed in autumn. The carbon effluxes by heterotrophic soil respiration from *C. lasiocarpa* marsh, *D. angustifolia* marsh, dryland and rice field were 3.14±0.45, 4.81±0.68, 2.85±0.38 and 2.18±0.31 t C/ha/a, respectively. Significant relationships were found between temperature and heterotrophic soil respiration from *C. lasiocarpa* marsh, *D. angustifolia* marsh and dryland, and Q<sub>10</sub> values were 2.1, 2.5 and 1.8, respectively. The relationships between heterotrophic soil respiration and soil moisture/water table were best described by quadratic equations.

#### **Key Words**

Marsh, reclamation, farmland, heterotrophic soil respiration.

#### Introduction

Wetlands now contain a considerable share of the terrestrial carbon pool with their estimated reservoir of 225 Gt C and serve as a significant sink for atmospheric carbon (IPCC 2000). CO<sub>2</sub> evolution from soil is one of the major components of the global C cycle and the minor change of soil respiration maybe result in a significant influence on atmospheric CO<sub>2</sub> concentration which would further enhance climate change (Schlesinger and Andrews 2000). Land use change has the potential to enhance or reduce soil respiration. The Sanjiang Plain is the largest low-altitudinal marshy plain in Northeast China. Large areas of marsh have been converted into agricultural lands since late 1940s and now the Sanjiang Plain has become one of the areas with the most intensive land use/cover changes in China (Liu and Ma 2002). To date, however, no soil CO<sub>2</sub> efflux data on marsh have been published that conclusively indicate whether reclamation could actually decrease rather than increase the decomposition rate in China. The present study was undertaken to investigate the soil CO<sub>2</sub> efflux in relation to land-use change of freshwater marsh in the Sanjiang Plain, China.

#### Methods

*Site description* 

This study was carried out at the Sanjiang Mire Wetland Experimental Station (47°35′N, 133°31′E), China. The average altitude is between 55.4 and 57.9 m. The study site is in a seasonal frozen zone and the non-frost period is 125 days. In 2004, annual precipitation was 431.6 mm, with nearly 55% of which fell in May and July. Daily mean air temperature was 2.3°C. Before the intensive reclamation, *Carex lasiocapa* and *Deyeuxia angustifolia* were the dominant vegetations in the Sanjiang Plain (Liu and Ma, 2002). Agricultural conversion of marsh to irrigated rice and dryland soybean is the prevalent practices in this region. Therefore, four sites of *C. lasiocapa* marsh, *D. angustifo*lia marsh, rice field and dryland to investigate the effect of land-use change on soil CO<sub>2</sub> emissions from freshwater marsh in the Sanjiang Plain. *C. lasiocapa* marsh is continuously flooded and *D. angustifolia* marsh is seasonal flooded. Marsh plants burgeon in late May and defoliate in mid-October, respectively. The dryland and rice field were both converted from marsh in 1993 and 1997 where crops were planted with one harvest per year. Characteristics of the soils in the experimental plots are listed in Table 1.

Table 1. Characteristics of soil in the experimental plots.

Land types	SOC (g/kg)	DOC (g/kg)	TN (g/kg)	C/N	pН
C. lasiocapa marsh D. angustifolia marsh	268.89±41.27	6.31±0.53	16.11±3.12	18.59	5.84
	105.63±24.2	3.0±0.27	9.37±2.14	13.03	5.68
Dryland	21.92±5.99	0.68±0.37	2.40±0.57	12.46	6.34
Rice field	24.94±6.13	0.91±0.54	3.33±1.04	11.43	5.85

#### CO2 efflux measurements

In C. lasiocarpa marsh and D. angustifolia marsh, three neighboring plots at each site were established for soil CO<sub>2</sub> efflux (i.e., heterotrophic respiration from soil organic carbon decomposition) measurements. In the summer of 2003, the plots were trenched to a depth of 60cm according to different soil layers from top to bottom, and then the soil was backfilled based on the normal sequence of the soil layers from bottom to top with the intention of excluding root respiration and the further growth of new roots. We started the measurement of soil CO<sub>2</sub> efflux at the beginning of 2004. Newly deposited litter was removed, and litter nets served to prevent the further accumulation of litter. Aboveground parts of the ground vegetation were removed from all sample plots, and the plots were kept free of vegetation by regular cuttings. Three bare plots (2m×2m) were established to measure soil CO<sub>2</sub> efflux in dryland and rice field, respectively. We digged a trench of 30cm deep around every plot in dryland and installed PVC panel to a depth of 30cm in the soil around each plot in rice field with the intention of preventing roots near the plots from influencing the measurements of heterotrophic soil respiration. The local agricultural practices including water and fertilizer managements were followed in the croplands and in the experimental bare plots. All fields were ploughed to about 15-20 cm deep by machine. The dryland was fertilized with 40 kg N/ha, 90 kg P<sub>2</sub>O<sub>5</sub>/ha and 15 kg K<sub>2</sub>O/ha surface-applied before sowing. There was no factitious irrigation practice during the soybean growing season. The rice field was fertilized three times. The first fertilization (23 kg N/ha, 50 kg P<sub>2</sub>O<sub>5</sub>/ha and 45 kg K<sub>2</sub>O/ha) was surface-applied before transplanting. The second (26 kg N/ha) and the third (23 kg N/ha and 15 kg K<sub>2</sub>O/ha) fertilization were provided by top dressing on 27 May and 26 July, respectively. The rice was continuously flooded with 4-8 cm of water until late September. Soil heterotrophic respiration was measured using a static opaque chamber-based technique. The detailed information please see the reference (Hao et al. 2006). Concentrations of CO<sub>2</sub> were analyzed in the laboratory using a gas chromatograph equipped with a flame ionization detector (Wang and Wang 2003).

## Statistics

Statistical analysis was done with SPSS. A paired t-test was applied to test the effect of land use change on soil heterotrophic respiration rates on the time series. The Pearson Correlation was performed to analyse correlations between temperatures and soil respiration rates, and Partial Correlation was performed to analyse correlations between water tables/soil water contents and soil respiration rates. In all analysis where p<0.05, the compare and correlate tests were considered statistically significant.

We adopt the following exponential model to analyse the relationship between temperature and soil heterotrophic respiration rate (Raich and Potter 1995):  $y = ae^{bt}$ , where y is soil heterotrophic respiration rate, t is soil temperature, a is soil heterotrophic respiration rate when t is zero, b is temperature coefficient.  $Q_{10}$  was calculated by the following equation (Luo *et al.* 2001):  $Q_{10} = e^{10b}$ .

#### Results

The seasonal variations of heterotrophic soil respiration

The seasonal curves of heterotrophic soil respiration from *C. lasiocarpa* marsh, *D. angustifolia* marsh and dryland were similar, and presented as a single peak. Maximum rates occurred in summer and the highest values were 714.27 $\pm$ 51.17, 423.73 $\pm$ 18.31 and 407.92 $\pm$ 54.62 mg CO<sub>2</sub>/m²/h, respectively. The temporal changes of heterotrophic respiration from rice field also exhibited as a single peak, but the maximum value delayed to September, 466.92 $\pm$ 54.47 mg CO<sub>2</sub>/m²/h. The minimal rates of heterotrophic respiration appeared in winter.

The C losses with heterotrophic soil respiration in *C. lasiocarpa* marsh, *D. angustifolia* marsh, dryland and rice field were 3.14±0.45, 4.81±0.68, 2.85±0.38 and 2.18±0.31 t C/ha/a in 2004, respectively. Marshland conversion to farmland resulted in the decrease of soil organic carbon decomposition. The reason for this may be related with the changes of some factors owing to marshland reclamation, such as the changes of micro-climate and soil underground process (the proportional rate of biomass between aboveground and underground, and the change of microbial flora, etc.), the removal of residues, the decrease of soil organic

content and the reduction of soil carbon input (Larionova *et al.* 1998). Meanwhile, the variations of soil physical properties (soil porosity and aggregate structure, etc.) caused by tillage would also affect soil CO<sub>2</sub> efflux (Trumbmore *et al.* 1995).

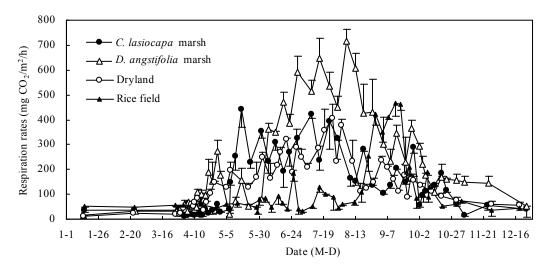


Figure 1. The seasonal changes of heterotrophic soil respiration from *C. lasiocarpa* marsh, *D. angustifolia* marsh, dryland and rice field.

Effects of soil temperature on heterotrophic soil respiration derived from soil decomposition Heterotrophic soil respiration rates of *C. lasiocarpa* marsh, *D. angustifolia* marsh and dryland were remarkably correlated with soil surface temperatures (p<0.001), but the correlation between them in rice field was not significant. Heterotrophic respiration increased with the increase of temperature, showing an exponential correlation (Figure 2).

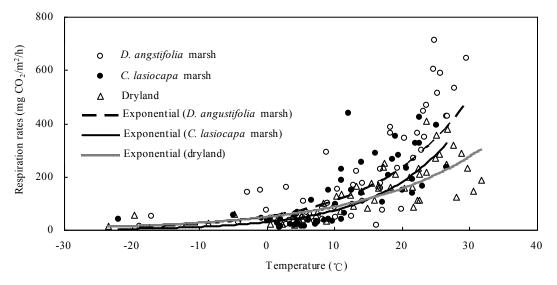


Figure 2. The relationships between heterotrophic soil respiration and soil temperature.

The  $Q_{10}$  values were 2.1, 2.5 and 1.8 in *D. angustifolia* marsh, *C. lasiocarpa* marsh and dryland, respectively.  $Q_{10}$  in *D. angustifolia* marsh was lower than that in *C. lasiocarpa* marsh, which is consistent with the result of Sommerkorn *et al.* (2008), they found  $Q_{10}$  values at wet sites were higher than any  $Q_{10}$  values at drier sites.  $Q_{10}$  in dryland was lower than that in marshlands, which was related to the low nutrition in the dryland soil because the response of heterotrophic soil respiration to temperature was mainly regulated by the quantity and quality of soil substrate (Huang *et al.* 2002).

Effects of soil moisture on heterotrophic soil respiration derived from soil decomposition

Based on the fact that there was a close correlation between soil moisture and soil temperature, Partial

Correlations was adopted to analyse the correlativity between soil moisture and heterotrophic respiration in order to eliminate the effect of soil temperature. Results showed that water levels above the soil surface was

significantly negative with heterotrophic respiration in *D. angustifolia* marsh, *C. lasiocarpa* marsh and rice field, while soil volumetric water content was remarkably positive with heterotrophic respiration in the dryland. The relationships between heterotrophic respiration and soil moisture were expressed by quadratic equations in these four land uses (Table 2), which is consistent with the results from subtropical planted forest (Wang *et al.* 2008).

Table 2. The relationships between heterotrophic soil respiration and soil moisture.

Land types	Fitting equation	$R^2$
C. lasiocarpa marsh	$y = 0.83  w^2 - 23.80w + 255.03$	0.34**
D. angustifolia marsh	$y = 41.03w^2 - 457.37w + 1292.3$	0.29**
Rice field	$y = 3.96w^2 - 40.29w + 145.28$	0.28**
Dryland	y = 0.16m <sup>2</sup> - 3.54m+ 202.5	0.23**

Where the w is the water level above the soil surface in marshlands and rice field (cm), m is the soil volume water content (%).

#### Conclusion

The seasonal variations of heterotrophic soil respiration from C. lasiocarpa marsh and D. angustifolia marsh presented as a single peak. Maximum rates occurred in summer and minimum values occurred in winter. The seasonal curve of heterotrophic soil respiration from dryland was similar with which from marshlands, while the peak value delayed to autumn in rice field. Heterotrophic respiration was much higher from D. angustifolia marsh than from C. lasiocarpa marsh, and the position of water table was the primary factor controlling heterotrophic respiration at the microsites in wetland. Heterotrophic respiration decreased owing to the conversion from marshland to farmland, and the decrease of soil organic carbon was the main reason. Heterotrophic respiration was exponentail correlated with soil temperature in D. angustifolia marsh, C. lasiocarpa marsh and the dryland, and  $Q_{10}$  value was higher in dryland than that in marshland. Water levels above the soil surface was significantly negative with heterotrophic respiration in D. angustifolia marsh, C. lasiocarpa marsh and rice field, while soil volumetric water content was remarkably positive with heterotrophic respiration in the dryland. The relationship between heterotrophic respiration and soil moisture was expressed by quadratic equations in these four land uses.

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# Effect of climate change on field crop production and greenhouse gas emissions in California's Central Valley

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#### **Abstract**

Predictions of climate change under various emission scenarios is highly uncertain but is expected to affect agricultural crop production in the 21st century. However, we know very little about future changes in specific cropping systems under climate change in California's Central Valley. Here, we used DAYCENT to simulate changes in yield and fluxes of greenhouse gases under A2 (medium-high) and B1 (low) emission scenarios. In total, 18 climate change predictions for the two scenarios were considered by applying different climate models and downscaling methods. The following crops were selected: alfalfa (hay), cotton, maize, winter wheat, tomato, rice, and sunflower. The simulations suggest that future climate change under the different emission scenarios will lead to a broad range of impacts on crop yields. By 2097, yields under A2 decreased in comparison to the 2009 baseline in the following order: cotton (29%) > sunflower (27%) > wheat (17%) > rice (12%) > tomato (9%) > maize (8%). Yields were between 5% (alfalfa) and 21% (cotton) lower under A2 compared to B1. Under A2, soil carbon (C) storage tended to decrease under climate change due to a decrease in C inputs to the soil and an increase in soil C decomposition. However, differences in nitrous oxide ( $N_2$ O) flux between A2 and B1 were not clear.

#### **Key Words**

Ecosystem modeling, Mediterranean climate, global warming potential, soil organic carbon.

#### Introduction

Agricultural crop production is fully expected to be impacted by climate change, but our understanding of climate change and its impacts on California cropping systems in the 21st century is limited. Lobell *et al.* (2006) investigated the impact of climate change on perennial crops (e.g., wine grapes), which are high-value commodities in California. However, long-term climate change effects have not been fully tested for major California annual crops and alfalfa (hay). Therefore, it is pertinent to further evaluate potential changes in the production of these systems in California's Central Valley under a changing climate. A detailed analysis of baseline climate change impacts on cropping systems should precede the development of adaptation scenarios based on alternative management practices under various climate change predictions.

Complex ecosystem models, such as DAYCENT, represents an excellent tool for predicting yields as it accounts for a range of interacting conditions in climate, soil, and management. These process-based models can effectively integrate crop growth, nutrient dynamics, hydrology, management, and climate for diverse cropping systems and therefore provide a best-estimate of climate change effects on crop yields and greenhouse gas emissions from these systems. Future climate change under A2 and B1 emission scenarios from the IPCC Fourth Assessment Report were evaluated extensively (Cayan *et al.* 2008). Temperatures are predicted to increase from 1.5°C under B1 to 6°C under A2 by the end of the century relative to 1960–1990. Specifically for California, more warming is expected in summer than winter with increasing frequency of heat waves. Annual precipitation shows relatively small changes (less than 10%) in the same period.

The objective of this study was (1) to project long-term field crop yields and greenhouse gas emissions in California's Central Valley under the A2 and B1 emission scenarios using the DAYCENT model, and (2) to quantify uncertainties in simulations derived from uncertainties around predicted changes in climate.

## Methods

Data acquisition

Climate data under the A2 and B1 emission scenarios were obtained from the Climate Research Division of Scripps Institution of Oceanography, at the University of California, San Diego. Six GCMs were applied for the two emissions scenarios: (1) CNRM-CM3, (2) GFDL-CM2.1, (3) CCSR-MIROC3.2 (medium resolution), (4) ECHAM5/MPI-OM, (5) NCAR-CCSM3.0, and (6) NCAR-PCM1 (Randall *et al.* 2007). Each climate change scenario was simulated over the time span 1950–2099. The climate data were downscaled

using a constructed analogues (analog) method and a bias correction and spatial downscaling (bcsd) method. We obtained soil data for all climate grids in California from the Soil Survey Geographic Database of the Natural Resources Conservation Service. The land use survey data for agriculture were obtained from the California Department of Water Resources. The statewide historical data were obtained from the United States Department of Agriculture - National Agricultural Statistics Service (NASS). Crop phenology and growing patterns were calibrated using historical crop yield data from NASS. Biomass C and N data, C allocation to shoots and roots, and N dynamics data were also calibrated from various literature sources. Details on conventional management practices in the region (e.g., planting, fertilization, irrigation, weed control, and harvesting) were obtained from the Agronomy Research and Information Center and Cost and Return Studies (2000–2005) available through the University of California Cooperative Extension.

#### Modeling

We modeled approximately 50% of California's Central Valley, currently covering  $1.4 \times 10^6$  ha. After initializing the size of soil organic matter pools in the model (years 0-1949), crop rotations for years 1950–2099 were randomly selected based on the acreages of the selected crops. We simulated the increasing use of fertilizer as indicated in the USDA historical records, and also considered different varieties for each period (e.g., low yielding vs. high yielding maize varieties). We did not consider any future adaptations for management practices (e.g., adjustment of crop variety and planting dates, alternative cultivation methods, timing and amount of fertilizer and irrigation use, etc.) in response to changes in climate for years 2007–2099.

#### Data analysis

For a combination of crops, climate models, and downscaling methods, annual average yields and greenhouse gas fluxes were calculated from 1950 to 2099, weighted by the acreage of the crop planted in each grid. A five-year moving average was then computed to consider trends in yield and greenhouse gas variance.

#### Results and discussion

The model simulated the observed yields relatively well for all crops in the period 1953 to 2004, although yield variance for some crops (i.e., cotton and sunflower) were not very well reproduced. In general, the effects of climate change on changes in yield (relative to the 2009 average yields) were not obvious in the period 2010 to 2050. However, in the next period (2051–2097), the crop yields were negatively affected by the increase in temperature with greater precipitation variation, particularly for cotton and sunflower. The exception was alfalfa because its yields did not consistently respond to climate change across the counties. Our results suggest that climate change will decrease crop yields in the long-term, particularly for cotton, unless greenhouse gas emissions and resulting climate change is curbed and/or adaptation of new management practices and improved cultivars occurs.

Annual soil C change was highly variable over time. Soil C storage did not differ between the climate change scenarios for the years 2010 to 2050 but tended to decrease more under A2 then B1 for years 2051-2097. Thus, soil  $CO_2$  emissions were expected to increase in the same period under both climate change scenarios but soil C decomposition potentials would be higher under A2 compared with B1. Differences in  $N_2O$  flux between A2 and B1 did not show any apparent trend. This suggests that the effect of climate change on  $N_2O$  emissions was highly uncertain. Overall, global warming potential generally followed the changes in  $N_2O$  flux. However, the decrease in soil C was responsible for increasing global warming potential particularly for years 2050–2097.

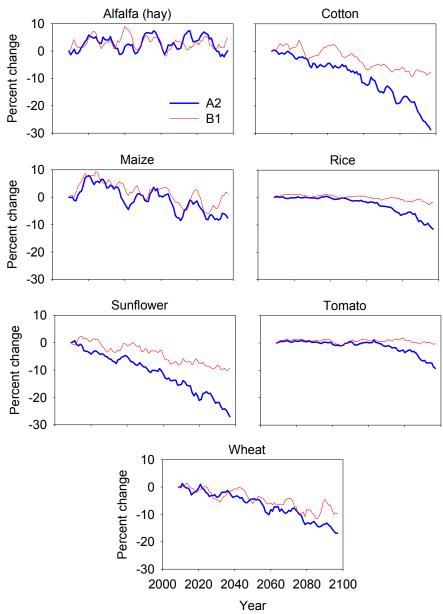


Figure 1. Changes in yield under A2 (medium-high) and B1 (low) emission scenarios. Five-year moving averages are calculated for the period from 2009 to 2097. Changes in yield are then expressed as percent deviation from the five-year moving averages in 2009.

#### Conclusion

The simulations suggest that future climate change under the different emission scenarios will lead to a broad range of impacts on yields of major crops grown in California. By 2097, yields under A2 decreased in comparison to the 2009 baseline in the following order: cotton (29%) > sunflower (27%) > wheat (17%) > rice (12%) > tomato (9%) > maize (8%). Yields were between 5% (alfalfa) and 21% (cotton) lower under A2 compared to B1. Greenhouse gas emissions are expected to be highly uncertain under climate change. In general,  $CO_2$  flux did not differ between the climate change scenarios for the years 2000 to 2050 but tended to be higher under A2 then B1 for years 2051-2097. In the same period,  $N_2O$  flux did not differ between A2 and B1. Overall, global warming potential followed the trend of  $N_2O$  flux over time. However, the decrease in soil C was responsible for increasing global warming potential particularly for the years 2050–2097. In conclusion, climate change will decrease crop yields in the long-term, unless there are statewide adaptation scenarios and management strategies to climate change that maintain or increase yields while mitigating emissions of greenhouse gases.

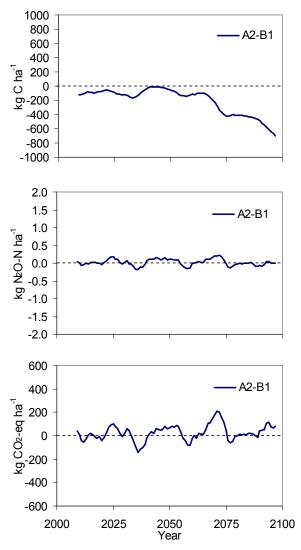


Figure 2. Modeled differences in soil C (top) and N<sub>2</sub>O flux (middle), and global warming potential (bottom) between A2 and B1. 2009 average fluxes were used as baseline.

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# Effect of DOM (dissolved organic matter) derived from litter of *Acacia mangium* and *Eucalyptus pellita* on soil $N_2O$ emissions

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#### **Abstract**

To investigate the effects of dissolved organic matters (DOM) and particulate organic matters (POM) on soil N<sub>2</sub>O emissions, soils with added DOM or POM obtained from the leaf litters at different decomposition degrees of two species (*Acacia mangium* and *Eucalyptus pellita*) were incubated under a wet condition for 7 days. Soil with added DOM showed greater N<sub>2</sub>O emission than control, while POM addition seemed to have no effects on N<sub>2</sub>O emission at least in a 1-week incubation. *A. mangium* DOM caused greater N<sub>2</sub>O emission than *E. pellita* DOM probably because *A. mangium* DOM with low CN ratio provided larger amount of readily mineralizable N substrate for microbial N<sub>2</sub>O production. Among two different decomposition degrees of litter, DOM from more decomposed litter had less N<sub>2</sub>O emission than that from fresh litter. These results suggest that the function of DOM and POM of leaf litter as N<sub>2</sub>O production substrate is quite different from each other, and the former is also different among species and decomposition stages, implying the importance of DOM quality (CN ratio and bioavailability of dissolved organic C) to control N<sub>2</sub>O emission.

#### **Key Words**

Soil incubation, legume, tropic, forest litter, plantation.

#### Introduction

Fast growing tree species such as Acacia and Eucalyptus are important for industrial plantation expanding in Southeast Asia. Soil of Acacia plantation rich in nitrogen, however, emits nonnegligible amounts of  $N_2O$  (Arai *et al.* 2008), which is the third important GHGs following to  $CO_2$  and  $CH_4$  (IPCC 2007). Soil  $N_2O$  is mainly produced through microbial nitrification and denitrification processes which need substrates such as inorganic N and organic C in addition to the suitable condition of  $O_2$  and temperature (Firestone and Davidson 1989). Large parts of these substrates are provided from litter likely in the forms of dissolved organic matter (DOM,  $< 0.45~\mu$  m) and fine particulate organic matter (POM,  $> 0.45~\mu$  m) leaching from litter layer with rainwater. Because of high precipitation, which is reported to accelerate production of DOM (Cleveland *et al.* 2006), the substrate for  $N_2O$  emission in the humid tropics might be largely supplied in the forms of DOM and POM in addition to incorporation of organic matter by soil fauna. But there are few reports explaining the effect of litter species and decomposition degrees of these organic matters on  $N_2O$  emission in tropical area. In this study, we demonstrated the effect of DOM and POM from leaf litter of different tree species and decomposition degrees on  $N_2O$  emission under a wet soil condition to clarify the mechanism of  $N_2O$  emission from soil in tropical plantation area.

#### Materials and methods

#### Sampling

Leaf litters were collected from 6-year-old *A. mangium* and 4-year-old *E. pellita* stands in South Sumatra Province, Indonesia (3° 48'S, 103° 55"E) in September 2008. Air-dried leaves of 2 species were devided into two decomposition degrees; relatively fresh leaves (L1) and relatively decomposed leaves (L2). A part of the litter samples were milled for CN analysis. For incubation experiment, soil was collected from 0-5 cm depth of 0-year-old *A. mangium* plantation in September 2007 (3° 47'S, 103° 55'E). It was air-dried and passed through 2mm stainless steel sieve. The soils are Acrisols (International Society of Soil Science (ISSS) Working Group RB, 1998) with a parent material of Tertiary sedimentary rocks. Total C and N of incubation soil were 37.3 mgC/g and 3.0 mg N/g and pH was 4.74.

#### DOM and POM extraction from litters

Each air-dried litter sample was pre-sprayed with distilled water to make the water contact close to field condition. Ten times distilled water (w/w) was added to the leaves and the suspension was kept at 5 °C in the

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dark for 24 hrs with occasional shaking. The suspension was passed through 53  $\mu$  m sieve and subsequently filtered through 0.45  $\mu$  m membrane filters (cellulose acetate, Toyo) to obtain DOM (< 0.45  $\mu$  m) and POM (0.45 - 53  $\mu$  m). These fractions were immediately freeze-dried.

### Incubation and gas sampling

For each treatment, air-dried soil corresponding to 20 g on an oven dry basis was placed in a 250ml glass bottle and the soil was pre-incubated at 60% WHC (water holding capacity) for 2 days to stabilize the microbial activity. Pre-incubation and the next incubation were carried out at 25 °C in the dark in four replications. DOM and POM equivalent to 2 mgC/g soil were added with distilled water to adjust the water content to 100% WHC. Bottles without organic matter addition were also set up as control. The bottles were incubated for 7-day and the soil water content was adjusted occasionally to 100% WHC. Gas was sampled from the headspace of each incubation bottle at 0 and 30 min after sealing the bottle with a rubber topper equipped with a septum. Gas sampling was conducted at 0, 0.5, 1, 2, 3, 5 and 7days. We measured N<sub>2</sub>O and CO<sub>2</sub> concentration by using gas chromatographs (GC-14B, Shimazu, Kyoto, Japan) equipped with an electron capture detector and with a thermal conductivity detector, respectively. Gas fluxes were calculated from the linear increase of gas concentration in the bottle headspace during 30 min.

#### Statistics analysis

All statistical analyses were performed using SPSS 10.0 (SPSS Inc., Chicago, USA). Kruskal-Wallis test and thereafter Mann-Whitney test were used to determine significant differences of among the treatments. Statistical significant differences were set at *P* values < 0.05.

Table 1. The amount, and C and N concentrations in DOM and POM added soil.

Species	Decomposition		DOM			POM			
	degree	Total (mg)	C (mg)	N (mg)	C/N	Total (mg)	C (mg)	N (mg)	C/N
A. mangium	L1	108	40	2.5	15.8	89	40	3.5	11.3
	L2	100	40	3.1	12.7	109	40	3.1	12.9
E. pellita	L1	93	40	0.6	63.9	127	40	2.5	16.0
-	L2	97	40	1.2	34.1	151	40	2.6	15.2

#### **Results**

Addition of DOM to soil significantly increased  $N_2O$  emissions though POM did not compare with control (Figure 1 left). DOM from A. mangium L1 recorded the greatest cumulative  $N_2O$  emission (1.74  $\mu$  gN/gsoil), twice as high as the control (0.702  $\mu$  gN/gsoil). Comparing to DOMs from L1 of A. mangium and E. pellita, there were no significant differences in  $N_2O$  emission though their emissions were significantly greater than control (P < 0.05). DOM from A. mangium L2 showed significantly larger cumulative  $N_2O$  emission than control (P < 0.05) but that from E. pellita L2 did not. Comparing the decomposition degrees of litter, DOM from fresher litter had significantly greater effect on  $N_2O$  emission than that from decomposed litter (A. mangium L1 > A. mangium L2 > control, E. pellita L1 > control, E0.05). Cumulative E0.05 mission increased with the addition of DOM significantly (Figure 1 right, E0.05). DOM from E1 mangium L1 was the highest in E3 mangium (0.69 mgC/gsoil) among the all of DOM treated soils, and was more than twice as high as control (0.31 mgC/gsoil). Among the decomposition degrees, DOM from L1 caused significantly higher E1 mangium L2 in E2 mangium but not in E3. Pellita (E4. mangium L1 in E5. Pellita L1, E6. Pellita L2 in E8. Though there were no significant differences in E9. Pomission between soil treated POM and control, POM from E8. mangium L1

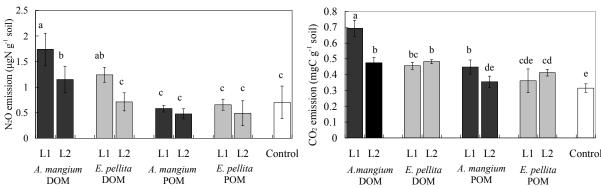


Figure 1. Cumulative emissions of N<sub>2</sub>O (left) and CO<sub>2</sub> (right) during 7-day incubation from soil added with

## DOM, POM and control. The vertical bars represent standard deviation (SD). Significant differences are indicated by different letters (Man-Whitney, p < 0.05).

and E. pellita L2 were significantly higher in cumulative  $CO_2$  emission than control (P < 0.05). As a whole,  $N_2O$  emission tended to be higher in soils with added DOM from A. mangium rather than E. pellita and fresher litter than decomposed litter, and POM did not change  $N_2O$  emission significantly though some POMs accelerated  $CO_2$  emission.

#### **Discussion**

DOM and POM showed completely different effects on N<sub>2</sub>O production. Little N<sub>2</sub>O emission and low C mineralization in POM added soil suggests that POM contains much recalcitrant organic matter which is more resistant against microbial utilization at least in 1 week of incubation. Higher N<sub>2</sub>O emission from soils with added *A. mangium* DOM might be associated with the lower CN ratio of *A. mangium* DOM. This fact agrees with the results by Huang *et al.* (2004) suggesting the addition of lower CN ratio litter species increased N<sub>2</sub>O emission. Coincidentally, the biodegradability of dissolved organic C often declines with decomposition of litter (Don and Kalbitz 2005). These facts can explain the reason why N<sub>2</sub>O production from fresh litter DOM was higher than that from decomposed litter DOM though the CN ratio was higher in fresh litter DOM.

#### Conclusion

In the short term incubation under wet soil condition, the species and decomposition degrees of litter DOM affected  $N_2O$  emission while those of POM did not. These results suggest the importance of litter DOM supplied as substrates for  $N_2O$  production in the humid tropics.

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## Effect of nitrification inhibitor on nitrous oxide emissions in pasture soils

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#### **Abstract**

In this paper we present findings from lysimeter studies that determined the effectiveness of the nitrification inhibitor dicyandiamide (DCD) on decreasing nitrous oxide ( $N_2O$ ) emissions from dairy cow urine (loading 1000 kg N/ha) applied to three different soils in New Zealand under two rainfall regimes (annual average rainfall for the lysimeter site, 1100 mm, and twice the average, 2200 mm). Total  $N_2O$  emissions from the urine over the measurement period of 5 months varied significantly between the three soils, from 2.94 to 35.9 kg  $N_2O$ -N/ha. The DCD treatment reduced these  $N_2O$  emissions to between 2.45 and 19.5 kg  $N_2O$ -N/ha. The average  $N_2O$  emission factors of the urine-N (EF3) were 2.0% and 1.6% under the 1100 mm and 2200 mm rainfall regimes, respectively. These were decreased to 1.3% by the application of DCD under both rainfall regimes. The results indicate that under heavy rainfall DCD effectiveness may be reduced. The very wet (anaerobic) soil conditions may have resulted in the production of di-nitrogen gas ( $N_2$ ), rather than  $N_2O$  gas. This could have influenced the effectiveness of DCD on reducing  $N_2O$  emissions.

#### **Key Words**

Nitrous oxide, grazed pasture, nitrification inhibitor, dicyandiamide, DCD.

#### Introduction

Nitrous oxide is produced in soils during the microbiological processes of nitrification and denitrification.  $N_2O$  production by nitrifying bacteria may arise either during  $NH_4^+$  oxidation to nitrate ( $NO_2^-$ ) or during dissimilatory NO<sub>2</sub> reduction when oxygen supply is limited. During denitrification, N<sub>2</sub>O is an intermediate in the dissimilatory reduction of nitrate (NO<sub>3</sub>) and/or NO<sub>2</sub> to N<sub>2</sub> under anaerobic conditions and is, therefore, both produced and consumed by denitrifying bacteria in soil (Bolan et al. 2004). Research in New Zealand (NZ) and overseas has shown that nitrogen (N) from urine patches is the major source of N<sub>2</sub>O loss from grazed pastures (e.g. de Klein and Eckard 2008). One of the proposed options for reducing N<sub>2</sub>O emissions is the use of nitrification inhibitor dicyandiamide (DCD; e.g. de Klein and Eckard 2008; Luo et al. 2010). DCD delays the bacterial oxidation of NH<sub>4</sub><sup>+</sup> to NO<sub>3</sub> in the soil for a certain period by depressing the activity of *Nitrosomas* bacteria, therefore slowing nitrification and N<sub>2</sub>O production. Research conducted largely in the South Island of NZ has shown that DCD can substantially reduce N<sub>2</sub>O emissions from urine patches and grazed pastures with reduction potentials ranging from 60 to 80% (e.g. Di et al. 2007; Smith et al. 2008). Rainfall or irrigation is one of the key environmental drivers for N<sub>2</sub>O emissions. In addition, rainfall/irrigation can displace DCD down the soil profile, away from the soil ammonium source, but very little is known about the impact of DCD displacement on its effectiveness for inhibiting nitrification. Therefore, there is need to examine the effectiveness of DCD on decreasing N<sub>2</sub>O emissions from contrasting soils and under contrasting climatic conditions. In this paper we report results from a field lysimeter study which investigated the effect of DCD on N<sub>2</sub>O emission on three pasture soils in the North Island of NZ under two rainfall regimes. A parallel study was also conducted on three soils in the South Island of NZ at the Lincoln university site (Di et al. 2010).

#### Material and methods

Lysimeter collection and installation

Intact soil monolith lysimeters (50 cm diameter by 70 cm deep) were collected from the Waikato, Rotorua and Northland regions in the North Island of NZ: free draining Horotiu silt loam (Typic Orthic Allophanic Soil), free draining Oropi sand (Buried Allophanic Orthic Pumice Soil) and slowly draining Waikare clay soil (Gleyed clay alluvial fulvi-appodic Soil) (Hewitt 1993). Measured soil properties are presented in Table 1. The pastures were a permanent mixed pasture of perennial ryegrass (*Lolium perenne* L.) and white clover (*Trifolium repens* L.) and had been under a cutting regime for 4 months prior to collection of the lysimeters to avoid the presence of fresh urine patches. The lysimeters were extracted by placing a metal cylinder casing with an internal cutting ring onto the soil surface, and carving around the cylinder edge while gradually pushing the cylinder down until the desired depth was reached. The soil monolith was then cut

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from the subsoil and removed from the collection site. The internal cutting ring created a small gap between the soil monolith and the cylinder wall, which was sealed using petroleum jelly to prevent edge-flow effects (Cameron *et al.* 1992). The lysimeters were transported and installed at ground level at the AgResearch Ruakura Research Centre lysimeter facility in Hamilton, NZ. In addition, 12 "mini-lysimeters" (25 cm deep and 4 for each soil type) were installed by the same method.

Table 1. Soil chemical (0-7.5 cm) and physical (0-70 cm) properties of the three soils.

Soil type	Waikato	Rotorua	Northland
	Horotiu silt loam	Oropi sand soil	Waikare clay
$pH(H_2O)$	5.9	5.7	5.9
Organic C (%)	6.5	10.7	9.6
Total N (%)	0.56	0.65	0.86
Olsen P (mg/kg)	16.0	53.0	56.0
CEC (cmol <sub>c</sub> /kg) <sup>A</sup>	22.0	15.0	31.0
Base saturation (%)	53.0	41.0	78.0
Particle size (%)			
Sand	34.5	63.3	2.3
Silt	50.8	27.5	20.5
Clay	14.8	9.3	77.3

<sup>&</sup>lt;sup>A</sup>cation exchange capacity

#### **Treatments**

Treatments included: Control (no urine and no DCD); Urine alone, applied on 15 May 2008 and Urine plus a nitrification inhibitor (DCD solution @10 kg DCD/ha), applied in May 2008, with a second application of DCD in July 2008. The urine was applied as fresh cow urine, adjusted for N concentration to achieve a loading of 1000 kg N/ha applied in a single application. The DCD was applied in solution sprayed onto the soil surface after urine addition (1 mm). Two nominal annual rainfall regimes (1,100 and 2,200 mm) were employed by using simulated rainfall/irrigation as required. Simulated rainfall was applied weekly to the appropriate lysimeters as spray irrigation to meet the targeted annual rainfall regimes. Total water input amounts (including natural rainfall and added water) were 756 and 1,374 mm over the period of the trial (5 months from May to Sept 2008) for the nominal annual rainfall regimes of 1,100 mm and 2,200 mm, respectively. There were 4 replicates of each treatment, except for the control, for which measurements of N<sub>2</sub>O emissions were made from two mini lysimeters (25 cm diameter) for each soil type at each rainfall rate.

#### N<sub>2</sub>O sampling and analysis

 $N_2O$  emission measurements were made using a soil cover techniques by fitting headspace chambers to the top of the lysimeters. The rim of each lysimeter was fitted with a channel filled with water to form a gas-tight seal when the headspace chambers were in place during measurement. The sampling procedure and  $N_2O$  emission calculation have previously been reported (Luo *et al.* 2008). Emission factors (EF3,  $N_2O$ -N emitted as % of N applied) were also calculated. Statistical analysis of the log-transformed data was performed using GenStat and least significant ratios (LSR) were calculated to compare the differences.

### Results and discussion

#### Daily N<sub>2</sub>O emissions

The  $N_2O$  fluxes from the control treatments (no urine and no DCD) remained low over the sampling period, confirming that most of the  $N_2O$  from grazed pastures is derived from animal urine. Dairy cow urine application sharply increased the initial  $N_2O$  fluxes on all three soils. The initial peaks occurred within a couple of days after urine application. The magnitude of the  $N_2O$  fluxes varied between soils. The  $N_2O$  fluxes from application of urine were lower from the Waikato Horotiu silt loam soil than from the Northland Waikare clay and Rotorua Oropi sand soils at most sampling times. At the 1,100 mm water regime, the DCD application significantly (p<0.05) reduced  $N_2O$  emissions on the Waikato soil and Rotorua soil, with lower  $N_2O$  fluxes from the soils treated with DCD than from the soils without DCD on most sampling days within a month after urine application. However, the DCD application had little effect on  $N_2O$  emissions on the Northland soil. At 2,200 mm water regime, the DCD application reduced  $N_2O$  emissions on the Rotorua soil, but had little effect on  $N_2O$  emissions on the Waikato and Northland soils.

#### Total N<sub>2</sub>O emissions

At 1,100 mm water regime, total  $N_2O$  emissions from the urine treatments over the measurement period of 5 months were 3.39, 23.4 and 35.9 kg  $N_2O$ -N/ha on the Waikato, Northland and Rotorua soils, respectively (Table 2). DCD application significantly (p<0.05) reduced the  $N_2O$  emissions from the Waikato and Rotorua soils. The EF3 values ranged from 0.3% to 3.5% for the urine treatment and 0.2 to 1.9% for the Urine + DCD treatment. The average reduction in the EF3 value due to DCD use was 35%.

Table 2. Total N<sub>2</sub>O emissions and EF3 as affected by soil, water input, and urine-N and DCD. Bracketed values are standard errors of the mean (SEM)

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Soil	Water input	Treatment	N <sub>2</sub> O emissions	EF3	Reduction of EF3
	(mm/y)		(kg N/ha)	(%)	by DCD (%)
Waikato, Horotiu	1,100	Control	0.550		
		Urine	3.39 (0.29)	0.3	
		Urine + DCD	2.45 (0.14)	0.2	33.3
Northland, Waikara	1,100	Control	0.299		
		Urine	23.4 (1.49)	2.3	
		Urine + DCD	19.1 (3.80)	1.9	17.4
Rotorua, Oropi	1,100	Control	0.582		
		Urine	35.9 (6.26)	3.5	
		Urine + DCD	19.5 (2.94)	1.9	45.7
Average under 1,100 mm rainfall regime					35.0
Waikato, Horotiu	2,200	Control	0.318		
		Urine	2.94 (0.33)	0.3	
		Urine + DCD	2.94 (0.30)	0.3	0
Northland, Waikara	2,200	Control	0.368		
		Urine	18.6 (1.12)	1.8	
		Urine + DCD	18.5 (1.76)	1.8	0
Rotorua, Oropi	2,200	Control	0.304		
		Urine	27.4 (1.71)	2.7	
		Urine + DCD	17.4 (4.54)	1.7	37.0
Average under 2,200 mm rainfall regime					18.8
Least significant ratios (LSR) for treatments (exclusive of control) 1.31 1.33					
Average under both rainfall regimes					27.8

At 2,200 mm water regime, total  $N_2O$  emissions from the urine treatments were 2.94, 18.6 and 27.4 kg  $N_2O$ -N/ha on the Waikato, Northland and the Rotorua soils, respectively (Table 2). Under the higher water regime, DCD significantly (p<0.05) reduced  $N_2O$  emissions only on the Rotorua soil. The EF3 values for the urine treatment ranged from 0.3% to 2.7%. DCD application reduced the EF3 value from the Rotorua soil by 37%. Under both rainfall regimes the average EF3 was 1.8% for the three soils and this was decreased to 1.3%, representing a 28% reduction.

The lower  $N_2O$  emissions observed from the Waikato soil are not unexpected as low emissions from this free-draining soil have been reported before (de Klein *et al.* 2003). Results from a concurrent study showed that N leaching losses of this soil were 40% higher than from the other soils (data not shown). The Rotorua soil is also classified as a free-draining soil but has a relatively high organic C content (Table 1), which could explain the high emissions observed from this soil. The high emissions from the Northland soil are likely to be due to prolonged wet soil conditions in this slow draining clay soil.

The effectiveness of DCD in reducing EF3 on the three North Island soils under both water input conditions was lower than that for the three South Island soils in a parallel study at the Lincoln site (Di *et al.* 2010). The average EF3 was 2.3% on the three South Island soils and this was decreased to 0.9%, representing a 61% reduction. The smaller DCD effectiveness on the three North Island soils may have been due to the above average rainfall during the measurement period, and possibly due to the milder North Island temperatures (data not shown), as both rainfall and temperature influence DCD movement and longevity. The results from this study indicate that under heavy winter rainfall DCD effectiveness may be reduced. This could either be due to DCD displacement done the profile or due to the very wet (anaerobic) soil conditions that may have resulted in the production of  $N_2$ , rather than  $N_2$ O gas from denitrification. Both these factor could have influenced the effectiveness of the DCD on reducing  $N_2$ O emissions.

A heavy and intensive rainfall event (total rainfall for 24 hours was 48 mm, of which 21 mm occurred over a 4 hour period) about a month after treatments were applied on the three soils caused large amounts of NO<sub>3</sub><sup>-</sup> to be leached out of the soils (up to 29 kg leached N as a result of this rainfall; Shepherd *et al.* 2009). Consequently, N<sub>2</sub>O fluxes rapidly declined after the rainfall. These results from North Island soils suggest that rainfall patterns (not just total annual rainfall) can be an important driver that determines DCD effectiveness for reducing N<sub>2</sub>O emissions.

#### Conclusion

There were variations in the effectiveness of DCD to reduce  $N_2O$  emissions from animal urine. DCD was most effective in the Rotorua sand that exhibited the highest  $N_2O$  emission during the measurement period. Rainfall also altered DCD effectiveness with a lower reduction being found under the higher rainfall regime. The results also suggest that rainfall patterns (not just total amount of rainfall) can be an important driver that determines DCD effectiveness for reducing  $N_2O$  emissions. Overall, the DCD was not as effective in reducing  $N_2O$  emissions from the three soils at the Ruakura site as it was found to be in the soils at the South Island site (Di *et al.* 2010).

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# Effects of phosphorus addition on $N_2O$ emission in an *Acacia mangium* plantation with and without root exclusion

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#### **Abstract**

Effects of phosphorus (P) fertilization on  $N_2O$  emissions in an *Acacia mangium* plantation were compared among C-plot (control), T-plot (trenched), P-plot (P added), and TP-plot (both trenched and P added) for 106 days in the wet season.  $N_2O$  emissions from P-plot were significantly smaller than that of C-plot, and are attributed to accelerated root absorption of N. In contrast,  $N_2O$  emissions from TP-plot were not significantly smaller and rather seemed to be larger than that of T-plot. We concluded that P application suppress  $N_2O$  emissions from *Acacia mangium* plantations, possibly because P addition accelerates root absorption of N.

## **Key Words**

Nitrous oxide, humid Tropics, P limitation, fast-growing wood plantation.

#### Introduction

It is well known that nitrous oxide (N<sub>2</sub>O) is an important greenhouse gas following CO<sub>2</sub> and CH<sub>4</sub> (IPCC, 2007). Soils are major sources for N<sub>2</sub>O, which is a byproduct or intermediate product of microbial nitrification and denitrification (Bremer *et al.* 1997; Davidson *et al.* 2000; Wrage *et al.* 2001). Tropical forests are important sources of N<sub>2</sub>O (Matson and Vitousek 1990). Several studies have demonstrated that *Acacia mangium* was a non-negligible emission source of N<sub>2</sub>O (Dick *et al.* 2006; Arai *et al.* 2008; Konda *et al.* 2008) because of Acacia's high N-fixing ability as a leguminous tree. Hall and Matson (1999) suggested that poor soil P availability, which is common in tropics (Vitousek *et al.* 1993, Cleveland *et al.* 2002), causes higher emissions of N<sub>2</sub>O by demonstrating that nitrogen (N) fertilizer inputs to the P-limited ecosystems generated 10-100 times greater N<sub>2</sub>O fluxes than the same treatment to the N-limited ecosystems. Their report suggests that the removal of P limitation may lead to suppression of N<sub>2</sub>O and NO<sub>2</sub> loss. Here we tested the hypothesis that the removal of P limitation suppresses N<sub>2</sub>O emission from *Acacia mangium* plantations. We used trench method to investigate the effects of P fertilization on N<sub>2</sub>O emission both in vegetation-existing condition and non-vegetation-existing condition in an *Acacia mangium* plantation.

#### Materials and methods

Plot setting

The experiment site is located at an *Acacia mangium* plantation in South Sumatra Province, Indonesia (3°47.394' E, 103°55.236' S). This region is humid tropical rain forest with an annual precipitation of 2000~3000 mm and a mean annual temperature of 27.3°C (Hardjono *et al.* 2005). The period from April to September is a relatively dry season and from October to May is wetter season, although there is no clear distinction. The soils in the area are Acrisols with Tertiary sedimentary rock as the parent material. A 6-year-old *Acacia mangium* stand, where trees were planted 3 m interval, was selected for the experiment. The experimental design included four treatments, C-plot (control), T-plot (trenched), P-plot (P added), and TP-plot (both trenched and P added). Plots of 9 m×9 m were established randomly in 6 replications for every treatment. In T-plots and TP-plots, we established 1 m×1 m subplots and made vertical cuts along the boundaries down to 0.5 m below the ground surface (approximately the bottom of the root zone) at the beginning of September 2008. Pieces of polyethylene board were inserted into the vertical cuts to inhibit root re-growth. Soils were refilled into the trench to minimize disturbance as little as possible. Seedlings and herbaceous vegetation in T-plots and TP-plots were removed by hand when necessary. At the beginning of November, TSP (Triple Super Phosphate) was applied to each P-plot and TP-plot by hand at the rate of 200 kg/P/ha/yr.

#### Gas flux measurement

From the end of November to the beginning of March, N<sub>2</sub>O emissions were measured 6 times (3-day before and 4-, 7-, 15-, 29-, and 106-days after P addition) with a static chamber method (Ishizuka *et al.* 2002), using PVC chambers (20 cm diameter, 15 cm height). We chose this period because N<sub>2</sub>O emissions were reported to be larger in the wetter season (Arai *et al.* 2008). Forty-ml gas samples at 0, 15, and 30 min were taken into 30-ml glass vacuum vials with butyl rubber lids. N<sub>2</sub>O concentration was analyzed using a gas chromatograph (GC-14B, SHIMADZU, Kyoto, Japan) equipped with an electron capture detector. We calculated N<sub>2</sub>O emission rates using a linear regression slope, using data at 0, 15, and 30 min, because the increase in gas concentration appeared linear. The cumulative gas emissions were estimated using the linear trapezoidal method.

## Soil sampling and analysis

At each gas sampling day, soils were also sampled from 0-5 cm depth. We collected a single soil core within 1 m radius of each chamber using 100 mL cylinder. Soil water content was immediately measured using a portion of the sample. WFPS was calculated as follows:

WFPS = (Gravimetric water content) 
$$\times$$
 (Bulk density/Porosity)  $\times$  100, (1)

where Porosity = 1 - (Bulk density/Particle density). Soil pH (H<sub>2</sub>O) was measured using moist soils. Ten g soil and distilled water were mixed to 1 : 2.5 ratio, and pH was measured after shaking 30 min.

#### Data analysis

The level of significance was examined by ANOVA followed by Tukey's multiple comparison tests after confirming the normality of data by the Kolmogorov-Smirnov test. Each statistical analysis was performed using SPSS version 10.0 (SPSS Inc., Chicago, USA).

#### Results and discussion

The values of pH did not change during experiment period. N<sub>2</sub>O emissions from P-plot were significantly smaller than that of C-plot (Figure 1). In contrast, N<sub>2</sub>O emissions from TP-plot were not significantly smaller and rather seemed to be larger than that of T-plot (Figure 1), showing that P application suppressed N<sub>2</sub>O emissions only if vegetation existed. Figure 2 shows the relationship between N<sub>2</sub>O emission rate and WFPS at 4-, 7-, 15-, 29-, and 106-days after the start of experiment. N<sub>2</sub>O emissions seemed to be smaller in P-plot than C-plot in a similar WFPS condition, while there were no such trends for TP-plot and T-plot. Earlier studies suggest that P addition to P-limited soils reduces N<sub>2</sub>O emissions by removing the P limitation on microbial N immobilization and decreasing N for nitrification and denitrification processes. Sundareshwar *et al.* (2003) showed that P addition to swampy ecosystem reduced the denitrification rate and N<sub>2</sub>O emissions. In our study, however, such a mechanism did not operate, for P addition to T-plot did not suppress N<sub>2</sub>O emissions significantly.

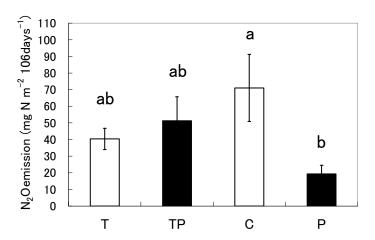


Figure 1. The cumulative  $N_2O$  emissions from each subplot. The same letters are not significantly different using ANOVA followed by Tukey's multiple comparison tests (P < 0.05).

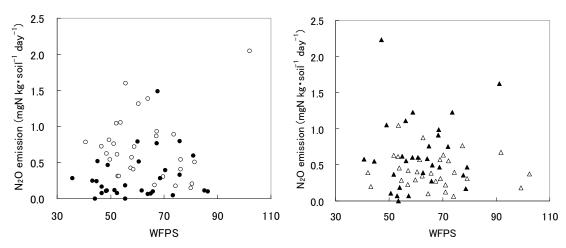


Figure 2. Relationship between  $N_2O$  flux and WFPS at 4, 7, 15, 29, and 106 days after the start of experiment. Open and closed circles represent C-plots and P-plots, respectively, and open and closed triangles represent T-plots and TP-plots, respectively.

Meanwhile, P addition significantly decreased N<sub>2</sub>O emissions from the plot without trenching, probably because P addition accelerated root absorption of N. Vegetation is presumably the main competitor of nitrifying and denitrifying microbes because plant growth is dependent on N availability as well as N<sub>2</sub>O emission (Aerts *et al.* 1995). Although it has been recognized in various forest ecosystems that microorganisms are stronger competitors for inorganic N than plants, (Johanson, 1992; Kaye and Hart, 1997), some studies have that particular plant species to be the stronger competitor (Silvan *et al.* 2005). Probably *Acacia mangium* is also stronger competitor for inorganic N than nitrifying and denitrifying microbes, thereby the P addition released P limitation of *Acacia mangium* and increased N uptake and suppressed N<sub>2</sub>O emissions.

#### Conclusion

This study showed that P application should suppress N<sub>2</sub>O emissions from the *Acacia mangium* plantation, possibly because P addition accelerates root absorption of N. P application to the *Acacia mangium* plantation might be an effective global warming mitigation option by suppressing N<sub>2</sub>O emissions

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## Emission of N<sub>2</sub>O from nitrogen-saturated, sub-tropical forest ecosystems in south China

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#### **Abstract**

Surplus reactive nitrogen (Nr) is one of China's most pressing environmental problems, and may cause a positive feedback to climate change through increased emission of  $N_2O$ , an important greenhouse gas. Forests in sub-tropical south China receive high atmogenic N loads (4g N/m²/yr), primarily as ammonium (NH<sub>4</sub><sup>+</sup>). Having limited ability to retain Nr, these forests may become N-saturated. Here we present mass balance data for the TieShanPing (TSP) forested catchment, near Chongqing, P.R. China; a site with acidic alisols and monsoonal climate (wet, hot summers). Data confirm N-saturation and show that much of the atmogenic N load is nitrified and leached as nitrate (NO<sub>3</sub><sup>-</sup>) from the root zone. Yet, only a fraction of the NO<sub>3</sub><sup>-</sup> flux leached from the soil is detected in catchment runoff, suggesting that denitrification may be a major sink of excess N. Initial data are presented showing elevated N<sub>2</sub>O emission rates during the monsoon with rates varying between about 100  $\mu$ g N<sub>2</sub>O-N/m²/hr in soils with permanently high groundwater table to > 500  $\mu$ g N<sub>2</sub>O-N/m²/hr in soils with variable groundwater table at the foot of hill slopes.

#### **Key Words**

N<sub>2</sub>O, nitrogen deposition, denitrification, *Pinus massoniana*, haplic alisol, monsoon.

#### Introduction

Population growth, intensification in agriculture and burning of fossil fuels lead to ever increasing emissions of reactive nitrogen (Nr) in the biosphere (Galloway et al. 2008). In China, fertiliser N input alone has increased from 0.54 Tg in 1961 to 28 Tg in 2005 (Xiong et al. 2008), giving rise to substantial emissions of ammonia-nitrogen (NHy). Together with NOx from combustion of fossil fuel this leads to a high atmospheric N load resulting in increasing N-deposition rates, particularly in forest, one of the dominant land-cover types in sub-tropical south China. Surplus of reactive nitrogen (Nr) is one of China's most pressing environmental problems, and may cause a positive feedback to climate change through increased emission of N<sub>2</sub>O<sub>2</sub>, an important greenhouse gas (Schlesinger, 2009). Recently, we found that forests in subtropical China receiving high atmogenic N loads (> 4g N/m<sup>2</sup>/yr) have a limited ability to retain Nr and that forests may become N-saturated. Earlier mass balance studies suggest that denitrification may be a major sink for excess N (Chen & Mulder, 2007). Rapid N-cycling, in systems with acidic alisols and monsoonal climate (wet, hot summers) imply potentially high N<sub>2</sub>O emissions from multiple sources, N<sub>2</sub>O is produced both during the microbial processes of nitrification and denitrification and is a potent greenhouse gas (Firestone and Davidson, 1989). To date, no systematic assessment of N<sub>2</sub>O emissions on a watershed level has been conducted. Here, we present annual mass balances of nitrogen TieShanPing forest (Chongqing, China; Larssen et al. 2006) from 2001 to 2004. Nitrogen mass balances were assessed both at the plot scale and integrated at the catchment level. In addition, initial data will be presented on N<sub>2</sub>O emission rates in different landscape positions in relation to the availability of Nr and hydrological conditions. The overall goal is to estimate N<sub>2</sub>O emission rates in humid sub-tropical south China and to understand the environmental controls at a watershed level. Ultimately, these data are needed to facilitate upscaling approaches for N<sub>2</sub>O emissions and to predict the effect of changing hydrological conditions on N<sub>2</sub>O emissions at a regional scale.

#### Methods

The study site

TieShanPing (TSP), 25 km northeast of Chongqing, is a 16.3 ha protected forest catchment, typical for southwest Chinese subtropical forest. The climate is monsoonal, with relatively dry winters and wet summers. Situated at 450 – 500 m asl, soil temperatures reach about 24°C in early summer, whereas in winter values decrease to about 9°C. Annual precipitation is about 1200 mm, and most precipitation occurs in the wet season between April and September. Only in the last part of the summer, when precipitation decreases, soil water potentials reach strongly negative values, indicating dry soils. By contrast, spring, early

summer and winter are characterised by moist to wet soils, as indicated by soil water potentials close to zero (Chen 2006). The vegetation is dominated by Masson pine mixed with broad-leave sub-tropical forest and a well developed understory of evergreens. Typical for the region, the forest soils on the hill slopes are well-drained acidic Haplic Alisols (pH<sub>H2O</sub> 3.5-3.8 in the O/A horizon; values increasing to about 4.5 in the B horizon) with a large nitrification potential; however, at the foot of the slopes in the groundwater discharge zone, the soils have developed aquic properties, so that they may act as important zones for denitrification. Soils have high clay contents; Low hydraulic conductivities may increase the residence time of NO<sub>3</sub><sup>-</sup> on its way to the streams, possibly exposing it to denitrification conditions in hypoxic sub-soils. During intensive precipitation events, runoff from surface soil horizons may give rise to direct input of surface soil water and NO<sub>3</sub><sup>-</sup> (but not NH<sub>4</sub><sup>+</sup>) into the stream. Soils on the hill slopes have very thin litter layers and A horizons with low organic matter contents (Chen 2006).

## Field and laboratory investigations

Atmogenic input of Nr is calculated as wet-only deposition and throughfall deposition. Ammonium ( $NH_4^+$ ) and nitrate ( $NO_3^-$ ) are analysed as described in ISO14911 and ISO10304-1, using ion chromatography. Occasional ring-tests indicate that the internal quality of the analyses is satisfactory.

Wet-only deposition, collected using a standardized wet-only collector (Dept. of Meteorology, Stockholm University, Sweden), is measured and sampled for chemical analysis at weekly intervals. Throughfall deposition is collected below the canopy of the ground vegetation at four plots in the catchment, using four collectors per plot. Throughfall collectors, made of plastic funnels, are located at permanent positions in the plots. At weekly intervals, the collected throughfall in all four collectors is pooled and weighed. Chemical analysis is done at monthly intervals in pooled samples. Pooled samples are stored in the refrigerator and filtered (0.45 µm membrane filter) prior to analysis.

Leaching of Nr is calculated at the plot-scale, based on concentrations in soil water and at the catchment-scale using concentrations in streamwater. Soil water is collected at monthly intervals below the root zone (at about 50 cm soil depth) using ceramic suction cups (P80). The suction applied is approximately 50 kPa. Streamwater discharge is recorded continuously using a V-notch weir, stage sensor and data-logger and streamwater samples are collected weekly for chemical analysis. Weekly and monthly fluxes of Nr in streamwater and soil water, respectively, are calculated using recorded water fluxes in the stream, thus assuming that soil water flux at 50 depth equals the flux measured as catchment runoff.

Emission of  $N_2O$  at a large number of landscape positions in the catchment is assessed using the closed chamber method. Concentrations of  $N_2O$  are determined in gas samples taken at fixed time intervals during a 30-minute period. Hot spots (selected for further  $N_2O$  monitoring) are characterised with respect to landscape position (hydrological setting, vegetation). Measured  $N_2O$  emissions at the plot-scale are combined with measuring soil physical conditions, biological process rates and  $N_2O$  product stoichiometries. For the period 2010 - 2012, we plan to study  $N_2O$  emission rates in response to the addition of  $^{15}N$  labelled  $NH_4^-$  and  $NO_3^-$ . Supplementary studies will include determination of natural abundance (15N, 18O) and laboratory incubation experiments.

#### Results

The mass balance for inorganic nitrogen at TSP is shown in Figure 1. Median values of the annual flux of Nr in wet-only and throughfall deposition are about 1.2 keq/ha/yr (1.7 g/m²/yr) and 2.5 keq/ha/yr (3.5 gm²/yr), respectively. In both cases  $NH_4^+$ -N deposition contributes about 70% to total N. This illustrates the importance of agricultural sources for atmogenic N in this part of China. The doubling of the Nr flux in throughfall compared with the flux in wet-only deposition suggests that dry deposition is equally important as wet-only deposition. Possibly, the Nr flux in throughfall is underestimated, due to direct N uptake in the canopy of the trees and ground vegetation, but we have no data to quantify this.

The median annual flux of  $NH_4^+$ -N in soil water and streamwater is close to zero. All  $NH_4^+$  is effectively converted, mostly to  $NO_3^-$ , in the upper few centimetres of the mineral soil. The median flux of  $NO_3^-$ -N in soil water at 50 cm depth is about 2.9 keq/ha/yr (4 g/m²/yr), which indicates that virtually all atmogenic N is leached from the root zone and little net retention occurs at TSP. This is in line with the small rates of growth of Masson pine at TSP (Wang YH, pers. comm.). The annual flux of  $NO_3^-$ -N in streamwater is about 0.5 keq/ha/yr (0.7 g/m²/yr). Thus, only 20% of the annual atmogenic input of Nr leaves the catchment with streamwater. Since the trees and ground vegetation on the well-drained soils on the hillslopes do not seem to be a major sink of reactive N at TSP, it is likely that the groundwater discharge zones in the catchment, converting groundwater to stream, constitute an important sink, probably through denitrification.

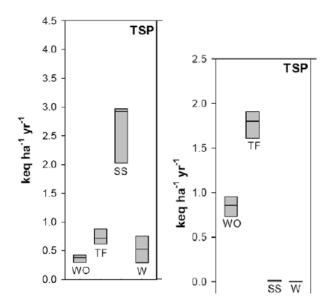


Figure 1. Medians, 10-percentiles and 90-percentiles of annual fluxes of inorganic nitrogen at TSP (2001-2004). Left panel is NO<sub>3</sub>, right panel NH<sub>4</sub><sup>+</sup>. Values are in keq/ha/yr. Abbreviations indicate NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> fluxes in wet-only deposition (WO), throughfall (TF), soil water below the root zone (SS) and streamwater (W). The nitrogen flux in soil water refers to values at 50 cm soil depth, which were estimated, multiplying the monthly water flux, measured as streamwater discharge, with the nitrogen concentration in soil water.

The data in Figure 1 suggests that both nitrification and denitrification are important processes in the TSP catchment.  $N_2O$  emission may result from both processes and its importance is confirmed by initial measurements for July and August 2009, which indicate elevated  $N_2O$  emission rates throughout the catchment. Values, although variable in space and time, are particularly high (> 500  $\mu$ g  $N_2O$ -N/m²/hr) at the foot of the hill slopes, where the groundwater table is most variable. Thus, these positions may constitute important hot spots for  $N_2O$  emission in the TSP catchment. In the groundwater discharge zone, where the soils are permanently close to saturation, the  $N_2O$  emission rates are about 100  $\mu$ g  $N_2O$ -N/m²/hr. Similar values are found at the well drained soils on the hill slope. Currently, additional data on  $N_2O$  emissons, and  $N_2O$  concentrations in the soil atmosphere are collected also during the drier and cooler part of the year.  $N_2O$  emission data will be related to measurements of groundwater table (piezometers) and soil water contents (TDR).

### Conclusion

As many other forest ecosystems in south China, the TieShanPing catchment, near Chongqing receives large amounts of atmogenic reactive nitrogen (3.5 g/m $^2$ /yr), in particular as NH<sub>4</sub><sup>+</sup>. Complete nitrification and little retention in the forest results in large nitrate fluxes from the root zone. Denitrification is the major sink of reactive N in the TieShanPing catchment, responsible for the removal of about 80% of the annual input. The TieShanPing catchment shows elevated emission rates of N<sub>2</sub>O during the monsoon, most notably at the interface of the foot of the hill slopes. and the groundwater discharge zone. The project will continue until the end of 2012.

#### Acknowledgment

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## Enhanced greenhouse-gases emissions in an irrigated rice paddy fertilized with biofiltration leachate

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#### **Abstract**

To investigate how biofiltration leachate (BL) affects carbon dioxide ( $CO_2$ ), methane, nitrous oxide ( $N_2O$ ) emissions in rice paddies, we periodically collected air samples and soil-entrapped gas samples. Compared with the control plot where mineral fertilizers were applied, the BL plot showed significantly higher emissions of  $CO_2$  and methane for both gas emissions through rice plants and the soil surface. We also found that the amounts of soil-entrapped  $CO_2$  and methane were higher in the BL-treated plot. On the other hand,  $N_2O$  emission was not significantly different between the treatments. The results suggest that biofiltration leachate, which had been subjected to various nitrogen processes in the biofile and thus is usually of low N content, mainly influences belowground carbon flux under anaerobic conditions, rather than nitrogen turnovers in the soil.

### **Key Words**

Methane production, microbial decomposition, entrapped gas, water management, soil temperature, flux.

#### Introduction

Although rice paddies share many common biogeochemical traits, it has been well documented that the individual emission strengths of  $CO_2$ , methane, and  $N_2O$  depend largely on various factors that control decompositions of organic matter, production or consumption of the gas in the soil, and transport of belowground gases into the atmosphere. On the other hand, biofiltration is an odour removal technology in which an odorous fluid (or slurry) is passed through a moist, porous medium prior to emission into the atmosphere. Recently, biofiltration coupled with concurrent composting is getting widely adopted in Korea, with the aim to control the environmental harmfulness of livestock wastes, especially of swine slurry. The anaerobic storage conditions and the excessive use of slurry itself for agricultural fertilization contribute to emission of greenhouse gases and to aquatic pollution. One practical limitation of biofiltration is that it produces large amounts of liquid waste (leachate). Ideally, the biofiltration leachate has quite less carbon and nutrient (N and P) contents compared with that of swine slurry, thus mitigating its adverse effects on the environment. In the present study, we conducted a field experiment in a rice paddy to investigate how  $CO_2$ , methane,  $N_2O$  emissions are affected by treatment of biofiltration leachate as the sole external nutrient source.

### Materials and methods

Study site

The study was done in an irrigated rice filed (100 x 30 m) in Yoju, central Korea (36°47′N, 127°98′E; 30 m above sea level) from 24 May to 5 October, 2009. The field was planted with rice seedlings on 23 May in rows 25 cm apart. The soil was flooded 2 weeks and fertilized with biofiltration leachate twice at a rate of 43 Kg N/ha, and puddled before the transplanting. A control plot of the same area was managed similarly, but with compound mineral fertilizers of N, P, and K. Soil moisture content and soil temperature were monitored with reflectometry sensor (CS616, Campbell Scientific, Utah, US) and T-type thermocouples, respectively.

### Flux measurements and soil gas sampling

To determine fluxes of CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O, the closed chamber technique was used. To take gas emissions from both rice plants and soil surface into account, triplicate phytochambers (60 x 60 cm, covering 4 rice hills) and soil chambers (27 x 60 cm; between plant rows) were installed right after the transplanting. During a sampling period of 25 min, air samples were drawn into 100-ml sample gas containers every 5 min using 3-way solenoid valves and a datalogger (CR1000, Campbell Scientific, Utah, US). The air pressure, air temperature and relative humidity inside the chamber were monitored during the sampling period with appropriate sensors and the datalogger. Soil-entrapped gas samples at the depths of 3, 8, and 15 cm were collected biweekly using a capillary rhizosampler (Eijkelkamp, Giesbeek, Netherlands) and 20-ml amber

vials that had been fully evacuated and then half-filled with pure He. *Laboratory analyses* 

The gas concentrations for CO<sub>2</sub> and methane in the collected air samples or in the headspace gas samples were measured with a GC (YL-6100, Younglin, Anyang, Korea) equipped with TCD and FID. CO<sub>2</sub> in the sample gas was quantitative converted into methane right after passing TCD using a methanizer at 350 °C prior to entering into FID. N<sub>2</sub>O concentrations were determined with a μECD-equipped GC (Agilent 6890).

#### **Results and discussion**

Throughout the growing season, we observed that methane emission was consistently higher in the BLtreated plot than in the control plot (Figure 1a). Many previous studies demonstrated that, in flooded rice paddies, belowground methane is mainly transported into the atmosphere via rice plants. Therefore, methane emission depends largely on rice growth. We found little difference in plant growth or in crop yield between the BL and control plots. In addition, we observed enhance methane emission through the soil surface (Figure 1b). Although distinguishing the relative proportions of each transport pathway is not feasible in this study, our results indicate that BL amendment increased methane emissions via both rice plants and the soil surface. We have observed a similar increase in CO<sub>2</sub> emission through the soil surface when fertilized with BL. These increases in methane and CO<sub>2</sub> emission were further confirmed by the amounts of methane and CO<sub>2</sub> entrapped in the soil. However, N<sub>2</sub>O emission was not significantly different between the treatments, which may be attributed to the generally low nitrogen content of biofiltration leachate. As reported in the previous studies, we also found a strong correlation between soil temperature and methane emission flux. In addition, similar relationship was observed between CO<sub>2</sub> flux from the soil surface and soil temperature. By utilizing those relationships between flux and soil temperature, we could evaluate every 30-min fluxes of methane and CO<sub>2</sub> throughout the growing season. The cumulative methane and CO<sub>2</sub> fluxes over the growing season were estimated to be around 1.3 and 10 times, respectively, greater in the BL-amended rice paddy.

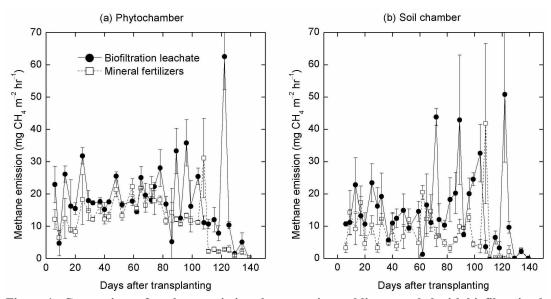


Figure 1. Comparison of methane emissions between rice paddies amended with biofiltration leachate and mineral fertilizers. (a) Methane emission from plant + soil. (b) Methane emission through the soil surface. Error bars are standard errors (n=3).

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# Estimating the carbon benefits of sustainable land management projects: the carbon benefits project component A

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#### **Abstract**

The Carbon Benefits Project (CBP) is working to produce a standardized system for Global Environmental Facility (GEF) and other sustainable land management (SLM) projects to measure, monitor and model carbon stock changes and greenhouse gas (GHG) emissions. The project builds on existing C-inventory tools, of different methodological complexity, developed over the past 15 years at Colorado State University. The CBP will produce a modular, web-based system which allows the user to collate, store, analyze, project and report net C stock changes and GHG emissions for baseline and project scenarios in SLM interventions. Existing SLM projects in Brazil, China, Kenya and the transboundary area between Niger and Nigeria are being used as test cases.

## **Key Words**

Carbon sequestration, sustainable land management, climate change mitigation.

#### Introduction

Human activities currently emit greenhouse gases (GHG) equivalent to over 50 billion tonnes of CO<sub>2</sub>/yr. Approximately 30% come from land use and land use change. Sustainable land management projects have the potential to not only reduce GHG emissions, by reducing emissions from biomass burning, biomass decomposition and the decomposition of soil organic matter, but also to sequester C through practices that increase biomass production and promote the build up of soil organic matter. The GEF co-finance a wide range of SLM activities in developing countries from reforestation and agro-forestry projects, to projects that protect wetlands or foster sustainable farming methods. The carbon benefits of these and other non-GEF SLM projects are likely to be considerable. However at the moment it is difficult to compare the C benefits of different land management interventions as a wide range of different methods are used to measure them. Equally it is difficult for SLM activities in developing countries to benefit from financial incentives from emerging carbon markets. The aim of Carbon Benefits Project (CBP) is to produce a standardized system for GEF and other SLM projects to measure, monitor, model and forecast C stock changes and GHG emissions and emission reductions. The system being developed will be end-to-end (applicable at all stages of an SLM project cycle), cost effective and user friendly. The project consists of two components: A — being led by Colorado State University (CSU), with greater emphasis on cropland and grazing land, and B - led by the World Wildlife Fund (WWF), with special attention to forestry and agro-froestry.

This paper describes the activities, methods and projected outputs of component A of the CBP (http://carbonbenefitsproject-compa.colostate.edu/index.htm).

### Methodology

Premises

GEF and other SLM projects need to know if SLM interventions affect C stocks or GHG emissions and this involves measurement, modelling and verification for a baseline scenario (the stocks and fluxes that would have occurred in the absence of the intervention) a project scenario (stocks and fluxes that occur with the intervention) and the incremental change between the two. A protocol is therefore needed which guides the user through all stages of delivering an SLM intervention in terms of proving net C benefits, from

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forecasting at the planning stage, monitoring and verification at the implementation stage to long term projection of future impacts.

The CBP is developing a modular web-based system (Figure 1) which allows the user to collate, store, analyze, project and report C stock changes and GHG emissions for baseline and project scenarios in SLM interventions in a standardized and comprehensive way. Decision trees will guide the user to different options of varying complexity depending on the stage of the project and the level of detail required in terms of reporting net C benefits.

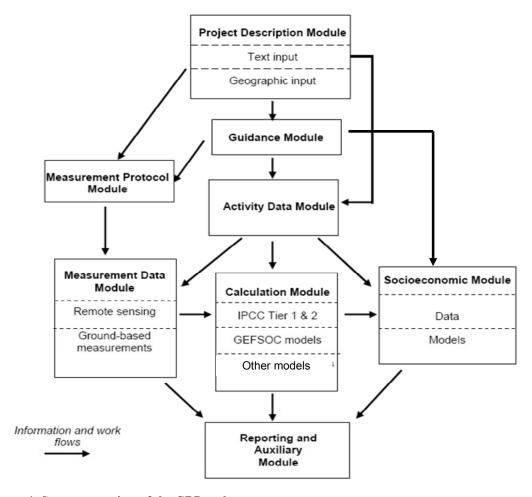


Figure 1. System overview of the CBP tool.

#### *Modeling approaches*

Carbon inventory assessments involve estimation of stocks and net fluxes of carbon from different land use systems in a given area over a given period and under a given management system. Ultimately, the scale of a project, the objective of the project (whether a C mitigation project or an SLM project with an interest in C) and the time and resources available for monitoring will determine the methods and data to be used for the carbon assessment (Ravindranath and Ostwald 2008).

The Carbon Benefits Project builds on more than 15 years of experience at Colorado State University of producing project and national scale carbon inventory tools for the agriculture, forestry and land use sector which represent IPCC Tier I, II and III approaches. The CBP is adapting and building on three tools in particular: The Agriculture and Land Use Tool (ALU), a national GHG inventory tool based on a Tier I/II approach (www.nrel.colostate.edu/projects/ghgtool/); COMET-VR a web-based decision support tool for the assessment of C stock changes at the field scale (Paustian *et al.* 2009, www.cometvr.colostate.edu); and the GEFSOC System (Milne *et al.* 2007; Easter *et al.* 2007), a Tier III tool for estimating national and subnational scale soil C stock changes in developing countries.

Socio-economic dimensions of SLM interventions are also being considered in the project to ensure that SLM activities with a positive impact on C and GHG mitigation do not have detrimental effects on society or livelihoods. Socio-economic considerations are often key determinants of possible success in terms of improved livelihood, for example through payment for environmental services.

#### Test case areas

The CBP system is being developed and tested, in close collaboration with five test case partners. These are helping to develop the CBP system by providing feedback on the C reporting needs of GEF SLM projects and testing parts of the system. The test cases include four GEF SLM projects and one non-GEF project:

- The Ningxia Integrated Ecosystem Management (IEM) and the Gansu IEM Projects, both part of the GEF PRC in China. These projects are located in the arid northwest of China and are implementing a number of measures to address land degradation such as shelterbelt establishment, conservation tillage and re-vegetation with drought resistant shrub species.
- The Kenya Agricultural Productivity and Sustainable Land Management Project (KAPSLM) which will
  promote sustainable land management in three watersheds in Kenya which cover humid to semi-arid
  areas of the country.
- The Niger-Nigeria Integrated Ecosystem IEM Project which is implementing a number of measures such as orchard establishment and rehabilitation of degraded rangelands to address land degradation in the transboundary area between Niger and Nigeria
- Also, one non-GEF Project, the Environmental Impact of Agricultural Expansion in South-west Amazonia project which is providing detailed data sets for the verification and testing of modeling components in the CBP system.

The test case areas vary in size, from landscape scale projects at 80,000 km² to pilot plot-scale at 12 km². They cover a range of SLM interventions, including conservation agriculture, agro-forestry, wetland protection, and grassland management. The projects are partners in the CBP to help develop a system that meets their C stock and GHG reporting needs; these range from very detailed - where GHGs are the main focus of the project to very broad based – where GHGs and C stocks are a minor part of the project. The SLM Project Partners will be implementing the CBP system by the end of Phase I of the project (May 2011). Phase II of the project will involve a series of workshops to role out use of the CBP system to other GEF networks of projects and non-GEF SLM projects.

#### Conclusion

A standardized C benefits protocol will allow a consistent comparison of different SLM projects by the GEF and other donors. It would also bring developing countries, and project managers, closer to being able to gain reward for land management activities that sequester carbon and reduce greenhouse gas emissions.

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## Flux of carbon dioxide and nitrous oxide across scales of two tillage systems in a California agricultural system

**Dennis E. Rolston**<sup>A</sup>, Juhwan Lee<sup>B</sup>, Kyaw Tha Paw U<sup>A</sup> and Johan Six<sup>B</sup>

#### **Abstract**

Using eddy-covariance and closed chambers, we quantified the flux of carbon dioxide ( $CO_2$ ) and nitrous oxide ( $N_2O$ ) under minimum tillage (MT) and standard tillage (ST) systems in two 15-ha neighboring fields in California. The eddy-covariance data showed that field level  $CO_2$  uptake in MT lagged behind that of ST for maize and sunflower, suggesting less photosynthesis in the MT crops compared to the ST crops.  $CO_2$  flux at the soil surface as measured by chambers was not significantly different by tillage and position. The level of  $CO_2$  flux rates varied annually depending on current crop type and soil carbon (C) inputs from a previous year. The  $CO_2$  flux from eddy-covariance, automated chambers, and portable chambers compared reasonably well. No significant overall effect of tillage and position on  $N_2O$  emissions was observed. However,  $N_2O$  fluxes in the side dress position were significantly greater than fluxes from other bed positions. Peak  $N_2O$  emissions appear to match with the times of N fertilization and irrigation. Process-based models were successful at predicting  $CO_2$  and  $N_2O$  emissions at our site. Simulations showed that annual differences in weather or management conditions contributed more to the variance in annual  $CO_2$  and  $CO_2$  emissions than did soil variability.

#### **Key Words**

Mediterranean climate, conservation tillage, DAYCENT, SOILCO2

#### Introduction

Estimates of agricultural greenhouse gas (GHG) emissions are needed to develop economically efficient as well as effective policies in mitigating and reducing GHG emissions in farming systems. Despite the importance of agriculture in California's Central Valley, the potential of alternative management practices to reduce soil GHG emissions has been poorly studied, and quantitative estimates across fields remain uncertain. Furthermore, the interactions between no or minimum tillage and irrigation practices have not been widely investigated. In addition, raised beds and furrows are typically formed for maintaining reasonable irrigation uniformity. Thus, soil properties controlling the rate of decomposition are expected to vary spatially across positions in the middle of the bed, the furrow, between plants, or across the fertilizer band. Accordingly, the spatial variability and intensity of  $CO_2$  and  $N_2O$  emissions would likely be position-specific, but have not been investigated.

The objective of this field study were to (i) quantify  $CO_2$  and  $N_2O$  emissions from an irrigated field under standard tillage (ST) and minimum tillage (MT), (ii) determine the temporal and spatial variations in  $CO_2$  and  $N_2O$  across a seed bed and at the field scale, and (iii) to improve and validate existing models in predicting soil C and N across farmer's fields following the implementation of MT.

#### Methods

Site description

The research site was a 30.8-ha irrigated field near Davis, CA (38°36′N, 91°50′E). The site has a Mediterranean climate with mean annual temperature of 16.1°C and mean annual precipitation of 564 mm, and irrigation is primarily by furrow irrigation. The site was managed under ST through Fall 2000 and then converted to no-till in Fall 2001. In October 2003 after harvest, the site was split into two fields, with the north half of the site under full tillage operations and the south half remaining under no-till. The standard tillage operations consisted of one pass each of deep ripping to 45 cm, stubble disking, disking to 15 cm, grading, and forming beds. In May 2005, stubble was chopped in both fields, with three shallow (7-10 cm), bed disc passes for ST and two passes for MT. Both fields also had one mulcher pass. From 2003 to 2006, the fields were planted to wheat, maize, and sunflower, respectively. At the initiation of the study in 2003, 30 sampling locations for gas samples were established in the field.

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### Greenhouse gas flux measurements

Three flux measurement methods were used. First, one eddy-covariance system was mounted on a mast in each treatment to measure field-scale CO<sub>2</sub> exchange. Measurements of vertical CO<sub>2</sub> fluxes were made using two 3-D sonic anemometers (CSAT-3) and two fast-response open path infrared gas analyzers (IRGAs). Secondly, two 0.62-m<sup>2</sup> auto-chambers were installed in the ST field with the capability of assessing the temporal pattern of CO<sub>2</sub> flux, and one auto-chamber was installed in the MT field. Lastly, the CO<sub>2</sub> and N<sub>2</sub>O fluxes were measured at 30 locations with portable chambers (covered 0.012 m<sup>2</sup> of soil surface) approximately monthly during the fallow seasons and biweekly during the growing seasons. The CO<sub>2</sub> concentration inside the chambers was measured at 0, 30, 60, 120, 180, 240, and 300 seconds after placement of chambers over the soil surface with an IRGA. We sampled N<sub>2</sub>O from the vented chambers in nylon syringes after 20 minutes and analyzed samples within 24 hours on a gas chromatograph.

At the position level,  $CO_2$  and  $N_2O$  fluxes from the portable chambers were normalized for the time of day of sampling by applying a  $Q_{10}$  function to the data. Based on 24-hr measurements of each flux, we used seasonal  $Q_{10}$  values ranging from 1.3 to 3.1 for  $CO_2$  and 1.68 for  $N_2O$ . A time-weighted average over a growing season was then computed. The effect of position on soil gas flux was determined by using the aggregated seasonal flux data. To extrapolate the flux at the position level to the whole field level, the  $Q_{10}$ -corrected flux was normalized by accounting for the percent of surface area each chamber position occupied in the field. The area-corrected data were used to determine the effect of tillage on soil gas flux at the field level

### Modelling approach

The DAYCENT model was used to estimate  $N_2O$  soil fluxes from these fields. Model performance was checked against measured  $N_2O$  fluxes. A Monte-Carlo analysis was performed for uncertainty estimation. Field scale  $CO_2$  fluxes were also evaluated using the one-dimensional process-based SOILCO2 module of the HYDRUS-1D software package.

### Statistical analysis of data

We selected a mixed model ANOVA for a coarse analysis of tillage and position effects on  $CO_2$  and  $N_2O$  fluxes, while accounting for confounding effects by changes in crops each year and the varying timing shifts of tillage, fertilizer, and irrigation management. The gas flux data were assumed to be independent each year at each plot. At each plot, gas flux measurements were considered as repeated over time and across positions within the plot.

At both position and field levels, data from November 2003 to February 2004 were not used in the mixed model ANOVA because flux measurements were made only on the bed positions during this period. Outliers were checked by visual inspection of the residual plot of the mixed model and then removed for a better model fit.

#### Results

Diurnal CO<sub>2</sub> patterns were evident in all months during the growing season, first related to a temperature dependence of soil respiration, and then later related to the light dependence of photosynthesis. Following the planting of maize in 2004, strong diurnal photosynthetic patterns (negative net ecosystem exchange) were observed by the young growing plants, with ST showing much more CO<sub>2</sub> uptake than in the MT treatment (Figure 1). It is notable that the maize plants in the ST tended to initially grow more vigorously than those in the MT during the early part of the growing season, although the photosynthetic C uptake rates subsequently became approximately equal. A similar difference persisted in 2005 under the sunflower crop, possibly due to poor crop growth in MT. In general, the eddy-covariance data suggest that tillage did not appear to increase soil CO<sub>2</sub> emissions, although the ST released slightly more CO<sub>2</sub> than the MT during the season in 2004 and 2005. Maximum mean, diurnal net ecosystem exchange (NEE) over the sampling period ranged from 16.3 to 111.7 for MT and 19.0 to 130.3 kg C/ha/d for ST. CO<sub>2</sub> emissions measured by chambers followed a similar trend of crop growth for the different years, ranging from 4.6 to 46.9 kg C/ha/d for ST and from 4.8 to 52.4 kg C/ha/d for MT (Lee et al. 2009). The flux from all three CO<sub>2</sub> flux measurement methods (eddy-covariance, automated chambers, and portable chambers) was compared. The flux values from these methods were all reasonably close to each other. Simulations showed that surface CO2 fluxes show a significant dependency on soil hydraulic properties (Buchner et al. 2008).

No significant overall effect of tillage and position on  $N_2O$  emissions was observed. However,  $N_2O$  fluxes in the side dress position were significantly greater than fluxes from other seed bed positions, and were further accentuated by a significant tillage effect. Peak  $N_2O$  emissions appear to match with the times of N fertilization and irrigation in 2004 and 2005. Generally, the range in modeled average daily  $N_2O$  fluxes at the site was comparable to the range in measured daily fluxes (Figure 2) (De Gryze *et al.* in press). However, the solitary  $N_2O$  flux peak measured on 22 May 2006 was not predicted by the model. In addition, the model underestimated  $N_2O$  emissions during May and June of 2004. The modeled variability around daily  $N_2O$  fluxes was in general smaller than the measured variability.

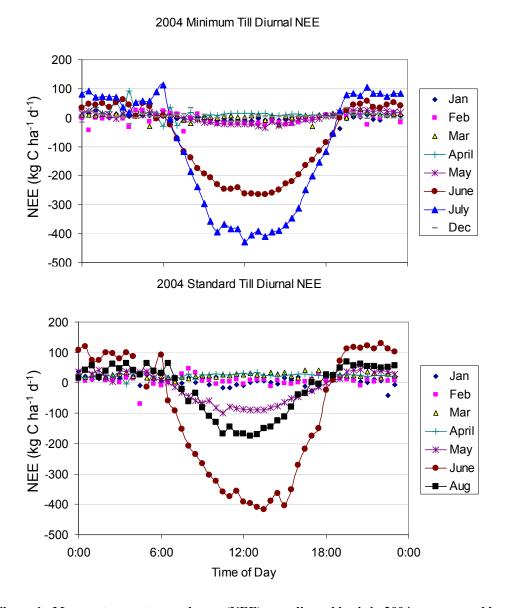


Figure 1. Mean net ecosystem exchange (NEE) on a diurnal basis in 2004 as measured by the eddy-covariance approach. Each plotted data point is the mean of data collected at 0.5 h intervals over the entire month.

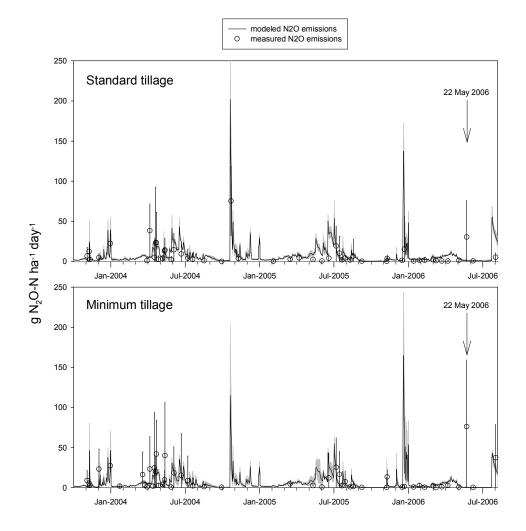


Figure 2. Modeled and measured  $N_2O$  emissions versus time for the standard and minimum tillage treatments. The vertical bars associated with each mean measured value is  $\pm$  1 standard deviation. The gray area around model results shows  $\pm$  1 standard deviation around the average, as calculated by a Monte Carlo analysis. From De Gryze et al. (2010), in press.

#### Conclusion

The eddy-covariance results show that MT did not lead to a decrease in soil respiration compared to ST at the field scale. Similarly, there was no gross effect of tillage or position on  $CO_2$  and  $N_2O$  flux measured by closed chambers. However, seasonal  $CO_2$  and  $N_2O$  emissions were significant across the scales and tended to differ temporally at a specific bed position. A comparison between the three flux measurement methods shows that  $CO_2$  fluxes were comparable across scales. The model showed that annual differences in weather or management conditions contributed more to the variance in annual GHG emissions than did soil variability. The SOILCO2 and DAYCENT models were successful at predicting  $CO_2$  and  $N_2O$  emissions of different tillage systems in California.

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## Gas emissions from the interaction of iron, sulfur and nitrogen cycles in acid sulfate soils

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### **Abstract**

Nitrous oxide is a powerful greenhouse gas, 298 times more potent than  $CO_2$ . Coastal lowland acid sulfate soils ( $\sim$ 18,000 ha; ASS) constitute only about 5% of Australia's sugarcane soils, but could contribute about 1/4 of the national  $N_2O$  emissions from sugarcane. It has been proposed by a number of authors that the large differences between the N-gas emissions from ASS and non-ASS is that in ASS nitrate oxidises reduced iron in the soil producing nitrous oxide and other N-gases. Here we report on laboratory studies that investigate the geochemical pathways that cause these gas emissions. The presence of pyrite enhanced gaseous nitrogen and  $SO_2$  emissions and the flux was also dependent on sample moisture content. This chemical denitrification pathway needs to be considered in fertiliser management and other crop nutrient models. Most of the gas evolution reactions are favoured by acid conditions and it is suggested that increasing surface soil pH and controlling water logging may decrease N-gas emissions.

#### **Key Words**

Pyrite, chemo-denitrification, nitrous oxide, nitrogen oxides, ammonia, sulfur dioxide, hydrogen sulphide.

#### Introduction

Acid sulfate soils used for sugarcane production relative emit large quantities of NO<sub>x</sub> and N<sub>2</sub>O (Denmead *et al.* 2005; 2007; 2006; 2008) relative to other cropping soils as well as SO<sub>2</sub> and H<sub>2</sub>S (Kinsela 2007; Macdonald *et al.* 2004). These acid soils are wet and have high organic carbon and clay contents, and either have high natural mineral N content or have significant quantities of N fertiliser, up to 160kg N/ha added at the start of each growing season. Such conditions favour the production of NO (see Serça *et al.* 1994; Blackmer and Cerrato 1986) and NO<sub>2</sub> (Slemr and Seiler 1984), collectively known as NOx as well as N<sub>2</sub>O. While NO<sub>2</sub> can be formed by the photochemical reaction of NO and O<sub>2</sub> in the atmosphere (Akyama and Tsuruta, 2003), it is also possible for NO<sub>2</sub> and NO to be formed in the surface layers of the soil (Slemr and Seiler 1984). N<sub>2</sub>O can also be produced during both nitrification and denitrification (eqns 2 and 5). It is noted that many of the N gas evolution reactions (eqns 2-5, 7-9) appear favoured by acid soil conditions.

In agricultural soils the full range of redox reactions for N fertiliser species are possible. This includes: nitrification:

$$\begin{array}{lll} NH_4^+ + 2O_2 & \rightarrow NO_3^- + H_2O + 2H^+ & [1] \\ NH_4^+ + O_2 & \rightarrow 0.5 \ N_2O + 1.5H_2O + H^+ & [2] \\ \text{denitrification:} \\ NO_3^- + 1.25c + H^+ & \rightarrow 0.5N_2(g) + 1.75H_2O + 1.25CO_2(g) & [3] \\ NO_3^- + 0.75\{CH_2O\} + H^+ & \rightarrow NO(g) + 1.25H_2O + 0.75CO_2(g) & [4] \\ NO_3^- + \{CH_2O\} + H^+ & \rightarrow 0.5 \ N_2O(g) + 1.5 \ H_2O + CO_2(g) & [5] \\ \text{and reduction:} \\ 2NO_3^- + 2\{CH_2O\} + 8H^+ & \rightarrow N_2 + 6H_2O + CO_2(g) & [6] \\ \end{array}$$

From eqns [3] to [6], acidic soils with high organic carbon content, favour denitrification, releasing  $N_2$ , NO and  $N_2O$  and possibly  $CO_2$ , provided soil water conditions are favourable. In acid sulfate soils, nitrate can also oxidise underlying sulfides producing further denitrification:

$$\begin{array}{c} NO_{3}^{-} + 0.7S^{-} + .03H^{+} \rightarrow 0.5N_{2}(g) + 0.7SO_{4}^{2-} + 0.1H_{2}O & [7] \\ NO_{3}^{-} + 0.4S^{-} + 0.6H^{+} \rightarrow NO(g) + 0.4SO_{4}^{2-} + 0.3H_{2}O & [8] \\ NO_{3}^{-} + 0.6S^{-} + 0.4H^{+} \rightarrow 0.5N_{2}O(g) + 0.6SO_{4}^{2-} + 0.2H_{2}O & [9] \end{array}$$

Again reactions [7] to [9] seem favoured by acidic conditions. In acid sulphate soils conditions appear optimum for the conversion of fertiliser N to gaseous N provided there is sufficient soil N, organic matter and water.

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It is also possible for NO<sub>3</sub> to interact with the iron cycle and under reducing conditions directly oxidise iron minerals or dissolved aqueous species.

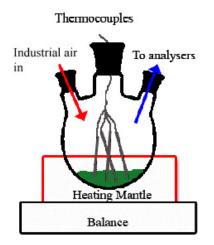
$$2\text{FeS}_2 + 6\text{NO}_3^- \rightarrow 3\text{N}_2 + 2\text{FeOOH} + 4\text{SO}_4^{2-} + 2\text{H}^+$$
 [10]

Reaction 10 proceeds through complex pathways with various nitrogen intermediates produced i.e. NO<sub>2</sub>, NO, N<sub>2</sub>, N<sub>2</sub>O. For example nitrite, NO<sub>2</sub> can be produced by denitrifying or nitrifying micro-organisms; nitrite may then react with ferrous iron to produce gaseous N compounds

$$Fe^{2+} + 2NO_2^{-} + 3H^+ \rightarrow FeOOH + N_2O + H_2O$$
 [11]

In acid sulfate soils there is a possibility for enhanced emissions of nitrogen gases due to the oxidation and reduction potential of ferrous and ferric iron present in the soil, and the presence of organic carbon and when the water filled pore space (WFPS) is greater than 60 %. Soil emissions could be generated during the reduction of ferric and the oxidation of ammonia (Clément *et al.* 2005) and/or by the reduction of NO<sub>3</sub><sup>-</sup> by the operation of the "ferrous wheel" (see Davidson *et al.* 2003) and the direct oxidation of reduced iron by NO<sub>3</sub><sup>-</sup> (see Postma *et al.* 1991). Our hypothesise is that the interaction of nitrate and iron sulfide minerals can cause emissions of nitrogen and sulfur gases. This paper aims to test this hypothesis using both a pure chemical system and a more complex soil incubation system.

#### Methods



## Experimental apparatus

A reaction vessel (Figure 1) was constructed from quick-fit glass ware and Teflon tubing. The 3 necked reaction flask was connected to industrial air stream (6 L/min; BOC Australia), temperature in and mass of the vesselwere measured every 10 seconds using thermocouples and a balance and the 1 minute average values recorded using a Campbell Scientific CR1000 logger. The air stream from the reaction vessel was then sent to a manifold and the air stream split; 1 L/min was sent to an ADC Nitrous Oxide Analyser and 5 L/min was sent to an ECOTECH Trace Gas Analyser Station. The ECOTECH Trace Gas Analyser Station consisted of 4 gas analysers, Sulfur Dioxide Analyser EC9850T; Hydrosulfide Analyser EC9850T with convertor; Ammonia Analyser EC9842 and NOx Analyser EC9841T. Gas concentrations in the air stream were recorded at one minute intervals.

Figure 1. Experimental Apparatus.

### Experimental Approach

Three different experimental runs were undertaken, using 5 mL 1 M KNO<sub>3</sub>, 1 g of reagent grade pyrite, or 1 g of pyritic soil. The pyritic soil was collected from McLeods Creek, on the Tweed River, Northern New South Wales Australia. This site is well characterised (see Smith and Melville 2004; White *et al.* 1996; Wilson *et al.* 1999) and the soils are classified as acid sulfate soils, which have 5-10% organic carbon in the surface soil and 3-5 % pyrite below the oxidation front at depths of 0.8 to 1.5m. The collected pyritic soil was placed in an insulated container, returned to the laboratory, freeze-dried and stored in a freezer until use. The gas analysers and hot-plate were switched on and allowed to warm up for 1 hour prior to the start of an experiment. The experimental apparatus was assembled and a background was run for 15 minutes, after which the sample was sealed in the reaction chamber and left for further 15 minutes. 5 mL of 1 M KNO<sub>3</sub> were then mixed with the sample within the sealed chamber and the experiment proceeded until all of the solution had evaporated.

#### Results

Small gas concentrations were detected during background runs (Figure 2a). The presence of reduced iron, in the pyrite greatly enhanced the emissions of NOx and NH<sub>3</sub> in the model system (Figure 2b). The interaction of NO<sub>3</sub> with the pyrite and the resulting de-nitrification must provide various nitrogen intermediates that

result in NOx formation. The enhance  $NH_3$  emissions that also occur during the NOx emission peak are possible due to ammonification caused by the ferric iron, acidity and evaporation. There is also enhanced emission of  $SO_2$  from the ideal system during the final phases of evaporation. Macdonald *et al.* (2004) found that field emissions of  $SO_2$  from acid sulfate soils were strongly correlated to evaporation.

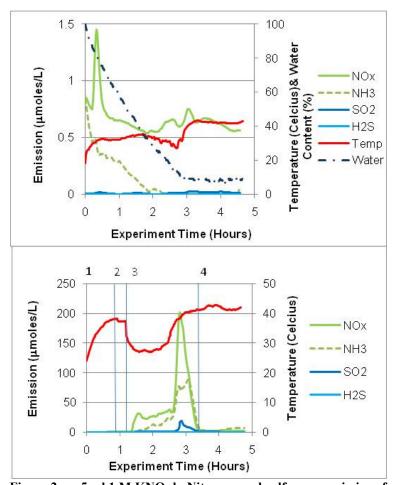


Figure 2. a. 5 ml 1 M KNO<sub>3</sub> b. Nitrogen and sulfur gas emissions from pyrite bathed in 5ml 1 M KNO<sub>3</sub> Period 1 represents the background emission, Period 2 is the emission when the pyrite is added. Period 3 is when the nitrate is added to the reaction vessel and Period 4 is the point where there is no more solution visible in the reaction vessel.

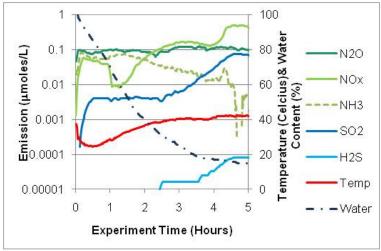


Figure 3. Gas emissions from pyrite sediments and 5 ml of 1 M KNO3

The production of the  $N_2O$ , NOx,  $NH_3$  from the pyritic soil was not as clear cut as the model experiments but the general emission trends werere similar (Figure 3). The low concentrations of the emission were most likely due to the amount of pyrite that was present in the pyritic soil sample that was used in the experiment.

The average pyrite content of the sample was 5 % w/w, which means that only 0.05g pyrite was present in the reaction chamber. Despite this there was clear evidence of the interaction of the pyrite with the applied nitrate from the emission of  $SO_2$  from the system. The emission of  $SO_2$  indicates that the pyrite within the reaction vessel was oxidised. The  $SO_2$  emission was strongly linked to evaporation and began when the water content reached 50%. The emission of NOx, had two periods of sustained emissions between hours 1-2 and at hour 4 these emissions were also correlated to changes in evaporation and water content.

Denmead *et al.* (2007, 2008) has shown that the emission factor for  $N_2O$  from fertilisers applied to acid sulfate soils is 29%. This is nearly 10 times greater than for non acid sulfate soils (Denmead *et al.* 2007, 2008). Results from the pyritic soil experiment shows that  $N_2O$  can be produced due to the interactions between nitrate and pyrite (Figure 3). While only 1.4 mg  $N_2O$  was produced, it is possible that the higher emissions that are seen in the field could be caused by the direct interactions of  $NO_3$  and N intermediaries with iron-monosulfides or soluble ferrous iron.

#### Conclusion

The interaction of the iron, nitrogen and sulfur cycles may explain the large emissions of  $N_2O$ , NOx, NH<sub>3</sub> and  $SO_2$  from acid sulfate soils. The laboratory experiments here clearly showed that the presence of pyrite increased the production of these gases relative to the control. The emission peaks were also clearly related to the water content of the reaction matrix. There were also clear emissions of  $N_2O$  and NOx from the pyrite soil sample but in future experiments the sample size will need to be increased by a factor of 10 to increase the pyrite content.

The oxidation of pyrite by NO<sub>3</sub> also caused the emission of SO<sub>2</sub>. This emission, like the nitrogen, was strongly correlated to moisture content of the reaction matrix. These results indicate that chemical denitrification caused by the interaction of nitrogen with iron and sulfur is an important soil process. This process can occur under ambient temperatures very likely occur in the surface soils. It is possible that increasing surface soil pH and controlling surface water logging may reduce these emissions.

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## Gaseous composition of smoke samples obtained at a tropical peatland fire

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#### **Abstract**

Tropical peatland in Indonesia is one of the most important atmospheric carbon sources due to rapid peat decomposition and frequent wildfire. To obtain a basic data to evaluate the influence of fire on carbon and greenhouse gas release from peatland, gaseous composition of smoke samples were analysed. The concentrations of carbon dioxide ( $CO_2$ ), carbon monoxide ( $CO_3$ ), methane ( $CO_4$ ) and nitrous oxide ( $CO_3$ ) were determined and compared with each other. The concentrations of  $CO_3$  and  $CO_4$  were highly correlated to that of  $CO_3$ . The ratio of  $CO_3$ :  $CO_3$ :  $CO_3$ :  $CO_3$ :  $CO_3$ :  $CO_3$ :  $CO_4$ :  $CO_$ 

#### **Kev Words**

Carbon monoxide, greenhouse gas emission, Indonesia, peatland fire, tropical peatland.

#### Introduction

Tropical peatland soil is one of the most vulnerable carbon sources in the world. In recent decades, huge area of tropical peatland has been developed, deforested, and degraded. For example, Page *et al.* (2002) evaluated that 13–40% of the mean annual global carbon emissions from fossil fuels was released from Indonesian peatland combustion. Compared to gas flux observation under normal condition, on-site gas emission measurement from a burning tropical peatland is still limited. In this paper, we report the composition of major gaseous components in smoke samples obtained from a latest peatland fire in Southeast Asia.

### **Materials and Methods**

Site description

The study site is located near Palangka Raya (2°S 114°E), Central Kalimantan, Indonesia. This area is the northern edge of the Mega Rice Project. During this project, many canals and ditches were constructed to drain peatland area. After the project was frustrated, vast devastated peatlands were left. Because of extremely dry conditions, peatland fire frequently occurs in dry season, especially in El Niño and Southern Oscillation (ENSO) years (Hirano *et al.* 2007). Incomplete burning of peat generates much smoke to cause dense haze, which has recently become a serious social problem. During the fieldwork of this study (late September to early October, 2009), the study site had many smoking spots and was covered by dense haze.

## Measurement of gas concentration

The concentration of major gaseous components released by peatland fire was measured. Smoke samples were collected to individual plastic bags in the field. The concentrations of carbon dioxide  $(CO_2)$  and carbon monoxide (CO) in these samples were determined in a laboratory of the Center for International Cooperation in Sustainable Management of Tropical Peatland (CIMTROP), University of Palangka Raya (UNPAR). A non-dispersive infrared sensor (ZFP9GC11, Fuji Electric, Tokyo, Japan) and a controlled potential electrolysis sensor (CO-85FL, Riken Keiki, Tokyo, Japan) were used for the analysis of  $CO_2$  and CO, respectively. Before this measurement, a small portion of each smoke sample was transferred into a preevacuated glass bottle. These bottles were then shipped to Hokkaido University, Japan to determine methane  $(CH_4)$  and nitrous oxide  $(N_2O)$  concentrations. Two devices of gas chromatography, GC-8A with a flame ionization detector (Shimadzu, Kyoto, Japan) and GC-14B with an electron capture detector (Shimadzu, Kyoto, Japan), were used for  $CH_4$  and  $N_2O$  measurement, respectively.

## Results

The result of the measurement is shown in Figure 1. The concentrations of CO,  $CH_4$ , and  $N_2O$  were plotted against that of  $CO_2$  because of their highly correlated relationships. The concentrations of  $CO_2$  and CO in smoke samples reached to 1000-2500 ppm, while those of  $CH_4$  and  $N_2O$  were less than 100 ppm and 1 ppm, respectively.

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The correlations between  $CO_2$  and the other gases are summarized in Table 1. The values of  $R^2$  were high (0.77–0.97) and all the correlations were statistically significant (P < 0.001). The X-intercepts of CO and CH<sub>4</sub> were similar to normal atmospheric concentration of  $CO_2$ , whereas that of  $N_2O$  was far from the value suggesting a different generation process for  $N_2O$ . Based on the slopes of the linear relationship, molar ratio of carbon was  $CO_2$ : CO:  $CH_4 = 1.0$ : 0.38: 0.026 = 71.0%: 27.1%: 1.9%. Such a high proportion of CO to  $CO_2$  reflects imperfect combustion of peat. In case of normal forest fire, for example, Statheropoulos and Karma (2007) reported 0–44 ppm of maximum CO concentration with 350–800 ppm of maximum  $CO_2$  concentration at the flame-front of a forest fire in Greece.

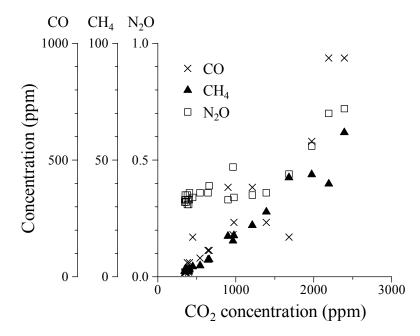


Figure 1. Concentration of major gases in peatland fire smoke samples plotted against that of CO<sub>2</sub>.

Table 1. Results of linear regression analysis between the concentration of  $CO_2$  and those of other major gases in peatland fire smoke samples.

Gas	n	Slope	Y-intercept (ppm)	X-intercept (ppm)	$R^2$
CO	23	$3.82 \times 10^{-1}$	-117.5	401.7	0.8290 ***
$CH_4$	24	$2.61 \times 10^{-2}$	-7.6	308.9	0.9676 ***
$N_2O$	24	$1.57 \times 10^{-4}$	0.3	-1091.1	0.7736 ***

<sup>\*\*\*</sup> Significant at the 0.001 probability level.

#### Conclusion

Burning of tropical peatlands releases much amount of CO as well as major greenhouse gases. The role of CO in chemical reactions in the atmosphere is complex and still unclear, so CO emission from peatland fire is important not only for health condition of inhabitants but for potential influences on atmospheric chemistry and the global climate. Continuous and multi-site observation is needed for more detailed understanding.

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## Genetic analysis of active $N_2O$ -emitting bacteria from tropical peat soils for their nitrous oxide reductase gene

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### **Abstract**

Tropical peat swamp forest is an important carbon deposit in terrestrial ecosystems, in which carbon is accumulated as a large mass of woody peat soil. Reclamation of the peat swamp forest into plantation led to degradation of peat soil to release a massive nitrous oxide ( $N_2O$ ) emission along with  $CO_2$ , both known as important greenhouse gases. Active  $N_2O$  emitting bacteria isolated from the reclaimed peat land soils and identified as *Burkholderia* spp. of  $\beta$ -proteobacteria were saprophytic denitrifiers more adaptable to nutrient-poor, medium-strongly acidic medium, than reference denitrifying bacteria, such as *Paracoccus denitrificans* NBRC 12442.  $N_2O$  emission by *Burkholderia* spp. from acidic peat soils was highly pH-dependent to be active at acidic regions, ranging from pH 4.0 to 4.5. In a nitrous oxide reductase ( $N_2OR$ ) inhibition assay using 10% acetylene gas for a specific  $N_2OR$  inhibitor, these active  $N_2O$  emitters showed no increase of  $N_2O$  emission under exposure to 10% acetylene gas, while normal denitrifiers possessing  $N_2OR$  produced a large amount of  $N_2O$  after injection of 10% acetylene gas. In genetic analysis, PCR using specific and degenerate primers for *NosZ* for the  $N_2O$  emitting *Burkholderia* spp. did not give any *NosZ* amplicons, while *P. denitrificans* NBRC 12442 and *Pseudomonas nitroreducens* NBRC 12694 clearly gave amplicons for *NosZ*.  $N_2O$  emission from reclaimed tropical peat soil is thus caused by the  $N_2OR$  gene-missing denitrifying bacteria of Burkholderiales.

#### **Key Words**

Nitrous oxide reductase, NosZ, nitrous oxide, N<sub>2</sub>O emission, tropical peat soil, *Burkholderia* spp.

#### Introduction

 $N_2O$  is an important greenhouse gas in global warming, mainly produced from agriculture farmland and sewage-treating plant, both of which are fundamental in human life (Crutzen 1981). Moreover,  $N_2O$  gas is chemically stable, with its half-life period of 114 years, and therefore this stability led to 298-fold higher greenhouse effect than  $CO_2$  (IPCC 2007). It was also warned that  $N_2O$  might be the worst gaseous principle to destroy  $O_3$  layer in stratosphere during  $21^{st}$  century (Ravishankara *et al.* 2009). To date, however, no effective manner to quench  $N_2O$  gas has been developed. Our recent studies revealed that active  $N_2O$  emitters inhabit in tropical peat soil of reclaimed fertilized farmlands including vegetable fields and oil palm plantation lands (Takakai *et al.* 2006, Hashidoko *et al.* 2009a). Major  $N_2O$  emitters from peat soil in Central Kalimantan and Sarawak were characterized as a group of *Burkholderia*.

#### Methods

Soil sampling and site description

Land use of each sampling site is as follows: *Acasia* pulp plantation site in peat soil (Riau, Indonesia), peat soil farmland reclaimed 2 y ago (Central Kalimantan, Indonesia), and oil palm plantation, 5 y old (Sarawak, Malaysia). Land soils were collected in mid-September 2008 from the sampling sites at depths of 5, 10 and 20 cm.

## $N_2O$ emission assay in the absence of soil

Basic ingredients of medium for culture assay (Hashidoko *et al.* 2008) are as follows: 5 mL of Winogradsky's mineral mixture (100 mg CaCO<sub>3</sub>, 3.7 g KNO<sub>3</sub> as 500 ppm N and 3 g gellan gum, all dissolved in 1 L of milli-Q water and pre-heated). To a 30-mL glass vial plugged with a butyl rubber and a screw cap (Nichiden-Rika Glass Co., Kobe, Japan), 10 mL of the medium afforded 22.6 mL of headspace volume. The medium autoclaved at 120°C for 15 min and cooled was inoculated with supernatant of the soil suspension and cultured for 5-7 days. N<sub>2</sub>O produced in headspace of the vials was analysed by a Porapak N (Varian, 1 m) column-connected gas-chromatography equipped with micro-electron ion capture detector. From the headspace gas, 1 mL of the gas was sampled and injected to the GC.

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Bacterial isolation and identification from soil

Soil samples that had emitted remarkable amounts of  $N_2O$  in the headspace were re-suspended in sterilized water (10 mg/10 mL) and the upper solution (100  $\mu$ L) was plated on Winogradsky's agar medium supplemented with 0.005% (w/v) yeast extract. Majorly emergent colonies were isolated (4-5 distinguishable colonies per plate), and these soil bacterial isolates were again tested in the  $N_2O$  emission culture assay.

Bacteria that have been characterized as active N<sub>2</sub>O emitters were shaking-cultured in nutrient broth (NB) medium at 25°C to over OD<sub>550</sub> 0.4, and the bacterial cells centrifuged, washed several times with sterilized water and subjected to extraction of chromosomal DNA using a DNA extraction kit, Isoplant II (Nippon Gene, Toyama, Japan), and PCR for 16S rRNA gene region were done using EX Taq HS (Takara, Kyoto, Japan) with universal 27F and 1525R primers. Resulting PCR amplicons (1.5 kbp) were each subjected to direct PCR sequence analysis, using an ABI Prism 310 genetic analyzer with a BigDye Terminator version 3.1 cycle sequencing ready-reaction kit (Applied Biosystems, Foster City, CA).

### Appropriate conditions for $N_2O$ emission

Using the  $N_2O$  emission assay, activity of the  $N_2O$  emitting soil bacteria isolated from the peat soil was all maximal in acidic pH. Moreover, these acidic soil-adapting  $N_2O$  emitters accelerated  $N_2O$  emission as 20-570 fold increase in the medium supplemented with 0.5% sucrose (Hashidoko *et al.* 2010). Optimum conditions for active  $N_2O$  production were acidic at pH 4.2-4.5. Supplemental 0.5% sucrose in the medium led to maximal 560-fold  $N_2O$  emission in some  $N_2O$  emitting *Burkholderia* spp. in the  $N_2O$  emission assay.

Inhibition Assay for  $N_2O$  reductase ( $N_2OR$ ) using acetylene gas as its specific inhibitor  $N_2O$  reductase is thoroughly inhibited by 10% acetylene gas in headspace. Hence, 10% acetylene gas was injected to the headspace immediately after the inoculation of bacterial cell suspension. After 7-day-incubation,  $N_2O$  in headspace was measured by ECD-GC and compared to that without acetylene injection (n=3 or 5). All the incubation was done at 25°C.

PCR for detection of nosZ region from chromosomal DNA of denitrifiers

As N<sub>2</sub>OR gene, nosZ is involved in denitrifying gene cluster of bacterial denitrifiers. Therefore, using specific nosZ gene primers (nosZ-661F, nosZ-1111F, nosZ-1527R, nosZ-1773R) (Scala and Kerkhof 1998), N<sub>2</sub>OR gene for bacterial denitrifiers were searched by PCR technique. PCR amplicons using the specific primers were purified by agarose gel electrophoresis, and sequenced for searching on Blastox program of DDBJ database. As reference denitrifiers, nosZ region of Paracoccus denitrificans NBRC 12442 and Pseudomonas nitroreducens NBRC 12694 were also amplified for database analysis.

## Results

Eight active  $N_2O$  emitters were isolated from three different sites of peat soils, and were all identified as genus *Burkholderia*, sub-division of  $\Box$ -proteobacteria. These  $N_2O$  emitting *Burkholderia* were grouped into three different clusters in phylogenetic classification using a partial 16S rRNA gene region. All these  $N_2O$  emitting soil bacteria showed the highest  $N_2O$  production in the soilless  $N_2O$  emission assay in acidic region (pH 4.2-4.6). We therefore tested  $N_2OR$  inhibition assay in the soilless culture medium of pH 4.5, of which pH values is close to of acidic peat soil and active in  $N_2O$  emission. In parallel, we did the same inhibition test at pH 6.0. At both pH 4.5 and 6.0,  $N_2O$  emission by the *Burkholderia* spp. was less affected. At pH 4.5,  $N_2O$  emissions were increased 15-30% under the presence of 10% acetylene from those without acetylene gas, while at pH 6.0,  $N_2O$  were increased 50-70% compared to those without acetylene. However, absolute amounts of  $N_2O$  that were increased by  $N_2OR$  inhibition at pH 6.0 were rather smaller than those at pH 4.5 (Hashidoko *et al.* 2009).

PCR detection of nosZ was unsuccessful. Two amplicons obtained from an active  $N_2O$  emitter isolated from Central Kalimantan were not nosZ gene but matched to that of function-unknown membrane-binding protein. In contrast, PCR amplicons obtained from complete denitrifiers (*P. denitrificans* NBRC 12442 and *P. nitroreducens* NBRC 12694, both used as the reference bacteria) were both characterized as those of nosZ.

#### Conclusion

In the  $N_2O$  emission assay for soil suspension and isolated bacteria from several sampling sites,  $N_2O$  emitting bacteria of highly pH-dependent (appropriate pH value for the most active  $N_2O$  emission was pH 4.2-4.5) activate nitrate respiration under acidic conditions. In neutral conditions,  $N_2OR$  recovery was not so clear, suggesting that both nitrate respiration and nitrous oxide reduction are repressed. Searching for *nosZ* in chromosomal DNA of *Burkholderia* sp. using PCR and DNA sequencing techniques led to temporal conclusion that  $N_2OR$  gene of these active  $N_2O$  emitters is missing or replaced with gene for another membrane protein.

In this study, all the active N<sub>2</sub>O emitters were identified as *Burkholderia* spp. by 16S rRNA gene sequence determination. Phylogenetic cluster analysis showed that these active N<sub>2</sub>O emitting *Burkholderia* spp. are composing three major groups, and these *Burkholderia* spp. probably most contribute to active N<sub>2</sub>O emission in reclaimed peat soil. As our other study also suggest positive correlation between nitrogen contents in soil and distribution of active N<sub>2</sub>O emitting bacteria. *Burkholderia* spp. also showed clear responses to supplemented sugar to activate N<sub>2</sub>O emission. Regarding it as organic carbon sources in soil, peat decomposition reasonably resulted in active N<sub>2</sub>O emission.

Taken together, active  $N_2O$  emitters in tropical peat soil are adapted to acidic peat soil, and during nitrate respiration in the acidic soil, they probably lost functionality of  $N_2OR$  encoding nosZ gene. From this genetic point of view, it is necessary to investigate gene structure in denitrification gene cluster in  $N_2O$  emitting bacteria, and should be further discussed genetic evolution of nosZ gene functionality in soil.

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## Grazing and GHG fluxes in steppe environments – how grazing reduces $N_2O$ emissions and $CH_4$ uptake

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#### **Abstract**

The interactions between grazing, livestock management and freeze/thaw and their impact on the exchange of  $N_2O$  and  $CH_4$  steppe soils in steppe soils of Inner Mongolia were examined. Increases in stocking rate in steppe environments do not necessarily lead to increased annual  $N_2O$  emissions. Livestock grazing reduces  $CH_4$  uptake significantly due to effects on soil aeration, and, thus  $CH_4$  diffusion to sites with an active methanotrophic bacterial population.

### **Key Words**

N<sub>2</sub>O, CH<sub>4</sub>, grassland.

#### Introduction

The greenhouse gas nitrous oxide (N<sub>2</sub>O) is estimated to contribute about 6% to global warming (IPCC, 2007). Its atmospheric concentration has increased by 20% since pre-industrial times, mainly due to increased agricultural production (Mosier et al. 1998: Kroeze et al. 1999). Livestock production and associated manure management has contributed about 38% with regard to anthropogenic N<sub>2</sub>O emissions. Temperate grasslands, such as steppe, cover approximately 8% of the terrestrial land surface and are widely used as pastures. High stocking rates as well as the addition of faeces have been reported to increase soil N<sub>2</sub>O emissions (Yamulki et al. 1998; Ma et al. 2006; Saggar et al. 2007). On the other hand, grazing has been reported to strongly reduce the uptake of atmospheric CH<sub>4</sub> (Liu et al. 2007), another greenhouse gas for which upland grassland soils act as a significant sink. Most temperate grasslands are characterized by cold winters giving rise to distinct freeze/thaw cycles. The latter episodes can endure from days to months, and freeze thawing periods have been shown to contribute significantly to annual budgets of N<sub>2</sub>O (Rover et al. 1998; Brumme et al. 1999; Papen and Butterbach-Bahl 1999). For CH<sub>4</sub>, it is assumed that winter fluxes in such regions are close to zero, i.e. do not contribute significantly to annual fluxes. However, N<sub>2</sub>O as well CH<sub>4</sub> flux measurements are often short term and periods with peak exchange rates may be missed. This study concentrates on the interactions of grazing, livestock management and freeze/thaw cycles on the exchange of N<sub>2</sub>O and CH<sub>4</sub> between steppe soils of Inner Mongolia and the atmosphere.

In our study we hypothesized that (i) freeze/thaw episodes dominate the annual  $N_2O$  budget, (ii)  $N_2O$  fluxes increase with increasing grazing intensity and (iii) feedlots are significant point sources for  $N_2O$  on regional scales. With regard to  $CH_4$  uptake we hypothesized (iv) that winter fluxes are not marginal and need to be considered for calculating annual fluxes.

### Materials and methods

Our experimental sites were situated in the Xilin river catchment, Inner Mongilia, PR China and managed by the Inner Mongolian Grassland Ecosystem Research Station, IMGERS (43°33'N, 116°42.3'E). The growing season is from May to October, with mean annual air temperature and precipitation of 0.7°C and 335mm (reference period 1982-2005), respectively. Most of the precipitation, fell between June and August. Our study focused on three ungrazed sites (UG99, UGfl, UGsl); two lightly, moderately and heavily grazed sites (Lfl, Lsl, Mfl, Msl, Hfl, Hsl); and one site which was grazed moderately during winter only (WG). Measurements were either performed using an automated system for estimating fluxes in sub-daily resolution or by a manual system using the static chamber method and gas chromatography for analysis.

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#### Results

Compared to ungrazed sites, grazing increased the amplitude of soil temperature and decreased the winter snow cover due to changes in the roughness length (Figure 1). As a consequence, soil moisture at the grazed sites was reduced during snow melt. Values on UG99 reached up to 90% water filled pore space (WFPS) while on WG values they did not exceed 60% (Figure 1). Differences in soil temperature and moisture regimes significantly affected soil microbial N cycling, with higher rates being found at the ungrazed sites.  $N_2O$  fluxes were mostly  $<5 \mu g \, N/m^2/h$  at all sites during the entire year. Higher fluxes were only observed either during freeze-thaw events or during periods with increased soil moisture contents during the vegetation period.  $N_2O$  fluxes during spring thawing period dominated the annual fluxes on the ungrazed sites while they were insignificant or entirely missing at grazed sites. This indicated that grazing decreases freeze/thaw fluxes. Observations at the lightly, moderately and heavily grazed sites revealed that freeze-thaw fluxes gradually decreased with increasing grazing intensity.

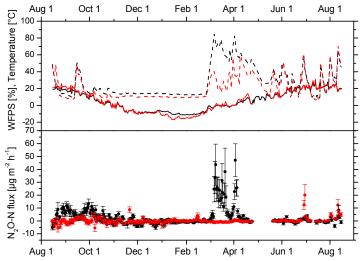


Figure 1. Top panel: temperature (solid) and moisture (dotted) for UG99 (black) and WG (red), bottom panel:  $N_2O$ -N fluxes for UG99 (black) and WG (red).

Based on our results a general mechanism can be identified which drives the interaction between grazing and freeze-thaw  $N_2O$  emissions. It is well established that under ungrazed conditions tall vegetation accumulates snow and that, with increasing snow cover, the soil is effectively insulated from low winter temperatures. The temperature effect is of importance for supporting microbial growth during winter, since a critical threshold seems to exist at approximately - $10^{\circ}C$ . Above this temperature a vital microbial community can survive, which is further activated by the onset of thawing in spring. This is consistent with our observations that microbial gross N turnover rates were significantly higher during winter and during spring-thaw at the ungrazed site as compared to the WG site. Our data as well as earlier studies (e.g. Koponen *et al.* 2004) demonstrate that freeze-thaw  $N_2O$  emissions increase with increasing soil moisture values and are highest around 60% WFPS. Since reduction of background emissions due to grazing are not considered in current IPCC methodology, our results suggest that  $N_2O$  emissions from semi-arid, cool temperate pasture systems may be severely overestimated.

With regard to  $CH_4$  fluxes, soils of typical semi-arid steppe are a significant sink for atmospheric  $CH_4$ , not only during the vegetation period, but also during winter when soil temperatures were well <-10°C. The seasonal variation of  $CH_4$  uptake was primarily determined by soil temperature. Soil moisture affected  $CH_4$  uptake of steppe soil only when temperature was suitable for  $CH_4$  oxidation and during spring thaw. Approximately one third of the annual  $CH_4$  uptake was not during the growing season and cannot be ignored in estimates of annual  $CH_4$  uptake in semi-arid steppe. However, grazing significantly reduced  $CH_4$  uptake by the soil and was associated with increased soil compaction and reduced soil aeration which contributed to reduced  $CH_4$  diffusion from the atmosphere to the soil layers with active  $CH_4$  uptake.

#### **Conclusions**

Our study indicates that increases in stocking rate in steppe environments do not necessarily lead to increased annual  $N_2O$  emissions. This is due to a decrease of freeze/thaw  $N_2O$  fluxes with increasing stocking rate. Current methodologies may systematically over-estimate the importance of grazing for  $N_2O$ 

emissions from cool temperate pasture systems. An integrated view of fluxes from livestock farming systems fluxes should be taken into account.

In our study the average difference in annual  $N_2O$  budgets between ungrazed and grazed sites is about 110g  $N_2O$ -N per ha/yr, whereas sheep related  $N_2O$  emissions from sheepfolds, urine patches and dry faeces were 36 g/(sheep yr). This indicates that net increases in emissions from grazed steppe systems as compared to ungrazed systems can be expected if stocking rates > 3 sheep/ha. With respect to  $CH_4$  it is important to estimate off-season fluxes to fully understand and calculate annual budgets. Livestock grazing reduces  $CH_4$  uptake significantly due to effects on soil aeration, and, thus  $CH_4$  diffusion to sites with an active methanotrophic bacterial population.

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## Greenhouse gas budget for terrestrial ecosystems in China

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#### **Abstract**

This paper reviews the literature on organic carbon (C) storage in Chinese terrestrial ecosystems, methane (CH<sub>4</sub>) and nitrous oxide (N<sub>2</sub>O) exchange rates between the terrestrial ecosystems and the atmosphere and estimates the integrated greenhouse gas budget for these ecosystems in China. The estimate indicated that Chinese ecosystems acted as a weak sink of greenhouse gas with a range of -0.01 to -0.26 Pg CO<sub>2</sub>-eq/y in 1980s and 1990s, mainly due to the increase in C storage. The ratios of anthropogenic to natural sources of CH<sub>4</sub> and N<sub>2</sub>O in China were substantially larger than the world average, reflecting more intensive disturbance in China than the rest of the world.

#### **Kev Words**

Biomass carbon, soil carbon, methane, nitrous oxide.

#### Introduction

Terrestrial ecosystems play an important role in the greenhouse gas balance of the atmosphere. Whether they act as a source or sink depends on land use and management. The stored carbon (C) is lost when natural ecosystems are converted for agriculture, however, with reforestation, afforestation and application of good management practices terrestrial ecosystems are able to regain the lost C. Land use change is also a critical factor which can shift terrestrial ecosystems from a source to a sink of atmospheric CH<sub>4</sub>. On the other hand the expansion of flooded rice to feed the increasing population has resulted in an increase in atmospheric CH<sub>4</sub>. In addition application of fertilizer nitrogen (N) and increasing N deposition has resulted in a reduction of atmospheric CH<sub>4</sub> oxidation by oxic soils and an increase in N<sub>2</sub>O emission. This paper reviews the current literature on greenhouse gas emission from Chinese terrestrial ecosystems and develops a greenhouse gas budget expressed in CO<sub>2</sub>-equivalents.

## Change in carbon storage

Organic C in terrestrial ecosystems is stored in two main pools, the biomass and soil. In China biomass C was estimated to range from 6.099 to 14.04 Pg C by various methods (Li *et al.* 2003; Fang *et al.* 1996). It is clear that, 1) biomass C is mainly distributed in forestlands, where C densities are much larger than those in grasslands and brushlands; and 2) the averaged biomass density in Chinese forests is only about one third of the global average.

Using the data from the Second National Soil Survey, which was conducted in the period from the late 1970s to the early 1980s, organic C storage in soils (SOC) of China was estimated to range from 50 to 185 Pg C. Excluding the extreme low and high estimates, the average storage over the 9 estimates is 85.76±10.49 Pg C with an SOC density of 9.55±1.17 kg C/m² for the average land area of 8.9821×10<sup>6</sup> km² in China. The SOC density of Chinese soils was also lower than the average global SOC density, which was attributed to the large proportion of soils located in arid and semi-arid regions, low percentage of forest coverage, intensive cultivation, and low return of crop residues into soils.

Accumulated evidence indicates that terrestrial ecosystems in China have increased organic C storage since the late 1970s (Piao *et al.* 2009). The increase in C storage mainly occurred in biomass and soils in forestlands and croplands. Fang *et al.* (2007) estimated that biomass storage increased from 4.3 to 5.9 Pg C in the period between 1981 and 2000, and attributed this to increases in forestland area (from 116.5 to 142.8×10<sup>6</sup> ha) and the density of biomass C (from 3.69 to 4.10 kg/m²). Organic C storage is increasing not only in forest ecosystems, but also in cropland soils, due to increases in return of crop residue to cropland soils, crop yields, and the area under conservation tillage. The change in SOC was not spatially homogenous in cropland soils in China (Huang *et al.* 2006). The net C sink of Chinese terrestrial ecosystems was estimated to be in the range of 0.19–0.26 Pg C/y, and accounted for 28–37% of the fossil C emissions during the 1980s and 1990s (Piao *et al.* 2009).

### Methane exchange

Methane emissions from wetlands varies greatly with wetland type. Marshes located in the Sanjiang Plain have the largest  $CH_4$  emissions with seasonal mean fluxes ranging from 10 to 20 mg  $CH_4/m^2/h$  during the growth period. The annual mean  $CH_4$  fluxes from other types of wetlands are usually less than 5 mg  $CH_4/m^2/h$  (Ding and Cai 2007). Assuming that  $CH_4$  emissions are in proportion to the area at the national scale then the total  $CH_4$  emissions in China are calculated to be 7.21 Tg  $CH_4/y$  in the natural wetland area of  $38.48 \times 10^4$  km<sup>2</sup>.

Field measurements showed that there are large spatial variations in CH<sub>4</sub> emissions from rice fields in China with a seasonal emission range of 0.3-205 g CH<sub>4</sub>/m<sup>2</sup> and the majority of Chinese rice fields emit the same amount of CH<sub>4</sub> during the rice growing period as those elsewhere in the world (Cai *et al.* 2000). The water regime in the off-rice season is a critical factor leading to large CH<sub>4</sub> emissions during the growing season (Cai *et al.* 2000). Total CH<sub>4</sub> emission from rice fields in China was estimated using various techniques and the emission varied from 3.73 to 41.4 Tg CH<sub>4</sub>/y. By applying 2006 IPCC Guidelines, CH<sub>4</sub> emissions from Chinese and global rice fields were estimated to be 7.41 and 25.55 Tg CH<sub>4/y</sub>, respectively, for the year 2000 (Yan *et al.* 2009).

Field measurements of  $CH_4$  oxidation were conducted on aerobic soils of forestlands, grasslands, and fruit gardens across China and the data showed that  $CH_4$  uptake rate varied from 1.86 to 7.8 kg  $CH_4$ /ha/y. On average, published data suggests  $CH_4$  uptake by grasslands was 3.39 kg/ha/y, significantly smaller than that by forestlands (4.94 kg/ha/y) (P<0.05). Measurements in the North Plain of China indicated that the cropland under conventional management took up  $CH_4$  at the rate of 1.56 kg  $CH_4$ /ha/y (Qi *et al.* 2002). Scaling up the rate for grasslands, forestlands and croplands, the total uptake by Chinese terrestrial ecosystems was estimated to be 2.45 Tg  $CH_4$ /y, being about 8.2% of the 30 Tg  $CH_4$ /y taken up by global terrestrial ecosystems (IPCC 2007a).

#### Nitrous oxide emission

Forests and grasslands are not fertilized in China, thus these ecosystems could be regarded as natural sources of  $N_2O$ . Published data showed that there were large variations in annual  $N_2O$  emission rates in the forestlands and grasslands of China with the maximum annual emission of 4.68 kg N/ha. The  $N_2O$  emission rate was significantly correlated with precipitation ( $R^2$ =0.5592, P<0.01). The average emission rate for grasslands was  $0.36\pm0.37$  kg N/y and for forestlands  $2.38\pm1.57$  kg N/y. There was a significant relationship between  $N_2O$  emission rate and  $CH_4$  uptake rate measured at the same sites simultaneously ( $R^2$ =0.4166, P<0.01). We used the average  $N_2O$  emission rates from grasslands and forestlands and the areas used for estimating  $CH_4$  uptake, to calculate  $N_2O$  emission. The total emission from China was estimated to be 456 Gg N/y, accounting for 7.59% of the global emissions (6.0 Tg N/y) from natural sources (IPCC 1997).

Available data indicates that  $N_2O$  emission factor (EF) for synthetic fertilizer N varies greatly, depending on water regime, N application rate, soil properties, etc. Overall average EF is very close to the default value of 1% in the 2006 IPCC Guidelines (IPCC 2007b). There is a trend for the EF to increase with increasing precipitation in uplands (Lu *et al.* 2007), in the same way as  $N_2O$  emission rates increased in forestlands and grasslands. Generally,  $N_2O$  emission from rice fields is smaller than that from uplands, but substantial  $N_2O$  emission has been observed in rice fields which were drained during the rice growing period, and emission increased with the number of times the fields were drained in mid-season (Zou *et al.* 2009). The average  $N_2O$  emission from croplands of China was 372.6±67.3 Gg N/y, of which, 9 to 35 Gg N/y cones from rice fields during growing period. Synthetic fertilizers dominate the sources for  $N_2O$  emissions. The estimated  $N_2O$  emission from Chinese croplands accounts for 11.3% of the total global emission (3.3 Tg N/y) from agricultural soils (IPCC 1997).

#### Integrated greenhouse gas budget

The individual exchange rates between terrestrial ecosystems and the atmosphere are summarized in Table 1. The C flux at the national scale was cited directly from the estimate made by Piao *et al.* (2009). Methane emission from natural wetlands,  $CH_4$  uptake by aerobic soils, and  $N_2O$  emission from natural sources were estimated in this work. The available estimates for  $N_2O$  emissions from farmlands were averaged. The estimate made by Yan *et al.* (2009) was used for the assessment of  $CH_4$  emissions from rice fields in China because it was made on the most comprehensive and newest dataset, and it also covered global rice fields. For comparison the exchange rates at the global scale are also given in Table 1. The global rates for C flux,

 ${\rm CH_4}$  uptake, and  ${\rm N_2O}$  emissions from natural sources and farmlands were taken directly from IPCC publications. For the rice fields, the estimate made by Yan *et al.* (2009) was used in the assessment with the reasons described above. For wetlands, the estimate made by Houweling *et al.* (1999) was used because it fell within the median of the estimates listed in the IPCC report (IPCC 2007a). For uniformity  ${\rm N_2O}$  and  ${\rm CH_4}$  exchange rates were converted into  ${\rm CO_2}$ -eq using the factors of 298 and 25 at the 100-year time scale (IPCC 2007a).

Table 1 Greenhouse gas budget of terrestrial ecosystems in China and globe

Sources	0 0	China	Reference	Glo	be	Reference
				1980s	1990s	
Change in C stor	rage (Pg C/y)	-0.19 to -0.26	Piao et al. 2009	-0.3 (-	-1.4 (-	IPCC, 2007a
		(-0.70 to -0.95)		1.10)	5.13)	
CH <sub>4</sub> emission	Wetlands	7.21 (0.18)	This work	145 (3.63)		Houweling et al.
$(Tg CH_4/y)$						1999
	Rice fields	7.41 (0.19)	Yan et al. 2009	25.55 (0.64	.)	Yan et al. 2009
CH <sub>4</sub> Uptake (Tg	$CH_4/y)$	-2.45 (-0.06)	This work	-30 (-0.75)		IPCC 2007a
$N_2O$ (Tg N/y)	Natural fields	0.456 (0.21)	This work	6 (2.81)		IPCC 1997
	Croplands	0.3726 (0.17)	This work	3.3 (1.55)		IPCC 1997
Budget (Pg CO <sub>2</sub> -eq/y)		-0.01 to -0.26		6.78	2.75	

Global warming potential for 100 year time-scale; CO<sub>2</sub> 1, CH<sub>4</sub> 25, N<sub>2</sub>O 298 (IPCC 2007a). Values in parentheses are Pg CO<sub>2</sub>-eq/y.

The total GWP from -0.01 to -0.26 Pg CO<sub>2</sub>-eq/y suggested that terrestrial ecosystems in China either made no substantial contribution to GWP or acted as a sink. In contrast, on the global scale, even though terrestrial ecosystems acted more likely as a C sink after 1980s (IPCC 2007a), they were still a substantial source of GWP (6.78 Pg CO<sub>2</sub>-eq/y in 1980s and 2.75 Pg CO<sub>2</sub>-eq/y in 1990s). The difference between China and the global situation was attributed mainly to 1) improvements in terrestrial ecosystems, such as reforestation and afforestation or re-growth of shrubs, which increased C densities in biomass and soils (Fang *et al.* 2007); 2) organic C densities in biomass and soils were low, thereby leaving space for C sequestration; and 3) the contribution of CH<sub>4</sub> emissions from wetlands to total GWP was relatively small in China, compared to the global average. However, the ratios of CH<sub>4</sub> emissions from rice fields (anthropogenic source) to that from the natural wetlands (natural source) and N<sub>2</sub>O from farmlands to that the natural source were 1.06 and 0.81, respectively, much larger in China than 0.18 and 0.55 for the globe, reflecting the fact that human disturbance was more intensive in China than that in the rest of the world.

For the overall budget, the uncertainties of the estimate mainly resulted from three sources. First, the individual sources and sinks were estimated for different years, while the emissions vary every year. Second, not all terrestrial ecosystem sources and sinks of greenhouse gas were taken into account in the budget. Third, the sources and sinks estimated in this work were based on very limited field. Therefore, further field measurements of greenhouse gas exchange are required and improvements are needed in the methods for estimating the total exchange rate at the national scale.

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# Greenhouse gas emissions from intensive pasture on ferrosol in Northern NSW, Australia: Impact of biochar amendment

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#### **Abstract**

An intensive field campaign was performed from April to June 2009 to assess the effect of biochar amendment on the emission of soil-borne GHGs from a sub-tropical pasture on acidic ferrosol. Over the whole measurement period high emissions of  $N_2O$  and high fluxes of  $CO_2$  could be observed, whereas a net uptake of  $CH_4$  was measured. Only small differences in the fluxes of  $N_2O$  and  $CH_4$  from the biochar amended plots  $(35.33 \pm 4.83 \ \mu g \ N_2O-N/m^2/h$ ,  $-6.76 \pm 0.20 \ \mu g \ CH_4$ - $C/m^2/h$ ) vs. the control plots  $(31.08 \pm 3.50 \ \mu g \ N_2O-N/m^2/h$ ,  $-7.30 \pm 0.19 \ \mu g \ CH_4$ - $C/m^2/h$ ) could be observed, while there was no significant difference in the fluxes of  $CO_2$ . However, it could be observed that  $N_2O$  emissions were significantly lower from the biochar amended plots during periods with low emission rates (<  $50 \ \mu g \ N_2O-N/m^2/h$ ). Only during an extremely high emission event following heavy rainfall  $N_2O$  emissions from the biochar amended plots were higher than from the control plots. Our results demonstrate that pastures on ferrosols in Northern NSW are a significant source of GHG and that the amendment of biochar can alter those emissions. However, more field and laboratory incubation studies covering prolonged observation periods are needed to clarify the impact of biochar amendment on soil microbial processes and the emission of soil-borne GHGs.

## **Key Words**

Greenhouse gas emissions, biochar amendment, Northern NSW, Australia.

#### Introduction

Land-use and agricultural practices affect the soil microbial carbon (C) and nitrogen (N) turnover and hence the biosphere-atmosphere exchange of greenhouse gasses (GHG), namely N<sub>2</sub>O, CH<sub>4</sub> and CO<sub>2</sub>. In Australia, the agricultural sector contributes to 15.7% of of the total emissions of GHGs and the agriculture produces about 59.5% of all CH<sub>4</sub> emissions (67.2 Mt CO<sub>2</sub>-eq.) and 85.3% of all N<sub>2</sub>O emissions (20.7 Mt CO<sub>2</sub>-eq.) (AGO 2007). When land-use changes involving biomass burning, soil degradation and deforestation are included in this estimate, the overall emissions account for one-third of the total national GHG release. At the same time agriculture is considered to have the highest GHG mitigation potential by reducing GHG emissions from soil and sequestering carbon in soils via modified land-use and management. A promising new mitigation approach of is the application of biochar to soils, which offers the potential of securely sequestering carbon in the soil since charcoal generally is protected from rapid microbial degradation (Lehmann et al. 2006). Moreover, it has been shown that biochar amendment to soils can significantly improve soil quality and plant growth (Chan et al. 2007; Chan et al. 2008) and at the same time reduce the emissions of GHG from soils (Yanai et al. 2007; Van Zwieten et al. 2009). However, to date only very few studies reported on the effect of biochar on soil soil-borne GHGs emissions and the impact of biochar amendment on soil microbial processes remains unclear. Therefore, this study aimed to investigate the effect of soil biochar amendment in pasture systems of Northern NSW upon the emissions of N<sub>2</sub>O, CH<sub>4</sub> and CO<sub>2</sub> over a 2 month intensive field campaign using a fully automated closed chamber monitoring system

#### Methods

Continuous trace gas flux measurement

The soil–atmosphere exchange of  $N_2O$ ,  $CH_4$  and  $CO_2$  was measured with a mobile fully automated measuring system. 6 acrylic measuring chambers ( $50 \, \text{cm} \times 50 \, \text{cm} \times 15 \, \text{cm}$ ; width x length x height) were fixed on stainless steel frames, which were driven approximately 10 cm into the soil. The lids of the chambers were opened and closed automatically with pneumatic devices. During the closing period air samples from each chamber were taken alternately and injected towards the analytical devices. Changes in  $N_2O$  and  $CH_4$  concentration after chamber closure were measured with a gas chromatograph (Texas Instruments SRI 8610C, Torrance/USA) equipped with a  $^{63}Ni$  electron capture detector (ECD) for  $N_2O$  analysis and a flame

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ionisation detector (FID) for CH<sub>4</sub> analysis. In addition, an infrared gas analyser (LI-COR 820, LICOR, Lincoln/USA) was installed to allow measurements of CO<sub>2</sub> concentrations in air samples. N<sub>2</sub>O, CH<sub>4</sub> and CO<sub>2</sub> fluxes were calculated from the linear increase or decrease in gas concentration, corrected for air temperature, atmospheric pressure and chamber volume to surface area ratio.

### Study site

The study site at Wollongbar Agricultural Institute (28°50′S, 153°25′E) in north eastern NSW, Australia was decribed by Sinclair *et al.* (2009) as a factorial experiment assessing the impacts of two different biochars upon fertiliser use efficiency and pasture biomass production. This study examined one treatment within this factorial experiment and compared it to the corresponding controls. A cattle feedlot biochar (analysis in Table 1 below) was applied at 10t/ha in November 2006 and was incorporated to a depth of 100mm. The site had a combination of Amarillo pinto peanut and annual ryegrass. Over the annual ryegrass season (summer), the plots received an equivalent 50kg N/ha each month, and twice yearly applications of P (28 kg/ha) and K 50 (kg/ha). These quantities of N application are common for intensive pasture production. Sinclair *et al.* (2009) found a significant response to both N and P uptake from the biochar amendment, as well as a significant increase in pasture biomass yield over 2 seasons, 2007 and 2008.

Table 1. Summary analysis of cattle feedlot biochar used in field trial.

Total	Total	Total	Total	рН	CaCO <sub>3</sub>	KCl NH <sub>4</sub> -	KCl NO <sub>3</sub> -	Bray 1 P	CEC
C	N	P	K	$(CaCl_2)$	eq.	N	N		
51%	0.43%	0.61%	1.8%	10.4	5.7%	0.16mg/kg	0.32mg/kg	61mg/kg	16cmol(+)/kg

#### Results

Basic soil analyses were conducted on the site at the commencement of the study period. These are shown in Table 2. It is clear from these analyses that there are no major differences in the soil properties, although as expected, soil C appears slightly higher in the biochar amended plots. The pH of the soil was 4.7 (CaCl<sub>2</sub>) and the CEC of the soils was very low at 5.1 cmol (+)/kg.

Over the whole measurement period high emissions of  $N_2O$  and high fluxes of  $CO_2$  could be observed, whereas a net uptake of  $CH_4$  was measured. Only small differences in the fluxes of  $N_2O$  and  $CH_4$  from the biochar amended plots vs. the control plots could be observed, but there was no significant difference in the fluxes of  $CO_2$  (Table 3).

Table 2. Analysis of soil in plots (n=3) prior to commencement of study.

	Biochar	Std dev	Control	Std dev
Total N	0.44	0.02	0.45	0.02
Total C	4.6	0.12	4.4	0.17
KCl extractable NH <sub>4</sub> -N	6.1	0.98	7.2	1.7
KCl extractable NO <sub>3</sub> -N	5.2	0.23	4.0	0.64

In general, a great spatial and temporal variability of the fluxes could be observed. Soil  $CO_2$  emissions ranged from 36 to 86 mg  $CO_2$ -C/m²/h and a positive correlation with soil water filled pore space (WFPS) could be observed. Average methane uptake from the pasture site was found to be 6.76 mg  $CH_4$ -C/m²/h for the biochar plots and 7.30 mg  $CH_4$ -C/m²/h for the control plots with highest values up to 18 mg  $CH_4$ -C/m²/h. Methane emissions up to 7.31 mg  $CH_4$ -C/m²/h occurred after periods of heavy rainfall under saturated soil moisture conditions. Highest spatial and temporal variability was measured for the  $N_2O$  fluxes with emissions ranging from 1.9 to 502  $\mu$ g  $N_2O$ -N/m²/h.  $N_2O$  fluxes were strongly correlated to WFPS and highest emissions were measured after an extreme rainfall event with 157 mm of rain over one day (May 22, 2009). During periods with constant WFPS a strong diurnal pattern of  $N_2O$  emissions could be observed with highest fluxes occurring in the late afternoon, which was explained by the daily temperature pattern in the topsoil.

Table 3: Mean N<sub>2</sub>O, CH<sub>4</sub> and CO<sub>2</sub> fluxes emissions from the biochar amended vs. the control treatments for measuring periods from April 19 to June 13, 2009.

	Biochar	Control
Mean CO <sub>2</sub> Flux [mg CO <sub>2</sub> /m <sup>2</sup> /h]	$67.70 \pm 0.82$	$67.88 \pm 0.99$
Mean CH <sub>4</sub> Flux [mg CH <sub>4</sub> -C/m <sup>2</sup> /h]	$-6.76 \pm 0.20$	$-7.30 \pm 0.19$
Mean $N_2O$ Flux [ $\mu g N_2O-N/m^2/h$ ]	$35.33 \pm 4.83$	$31.08 \pm 3.50$

Table4. N<sub>2</sub>O emissions from the biochar amended vs. the control treatments for different measuring periods.

Time Period	N <sub>2</sub> O emission biochar	
	$[\mu g N_2O-N/m^2/h]$	$[\mu g N_2O-N/m^2/h]$
19.5-15.5	$15.94 \pm 0.59$	$22.82 \pm 0.79$
20.5-26.5	$132.28 \pm 19.52$	$89.81 \pm 15.71$
1.6-13.6	$7.05 \pm 3.08$	$10.16 \pm 2.80$

During periods with low emission rates ( $< 50 \mu g N_2 O-N/m^2/h$ )  $N_2 O$  emissions were significantly lower from the biochar amended plots compared to the control plots. However, after the extreme rainfall event on May 22 significantly higher emissions were measured from the biochar treatment (Table 4).

#### Conclusion

Using a fully automated closed chamber monitoring system we could quantify emissions of  $N_2O$ ,  $CH_4$  and  $CO_2$  from intensive pasture with a high temporal resolution. Our results demonstrate that pastures on acidic ferrosols in Northern NSW are a significant source of GHG. Although a small overall uptake of  $CH_4$  was observed this could not offset the high emissions of  $N_2O$  and  $CO_2$ . The hypothesis that the application of biochar would lead to a reduction in emissions of GHG from soils was not supported in this field assessment. The overall GHG balance was slightly higher in the biochar amended treatment. However, our results demonstrate that biochar can alter those emissions. More field and laboratory incubation studies covering prolonged observation periods are needed to clarify and optimise the impact of biochar amendment on soil microbial processes and the emission of soil-borne GHGs.

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## Greenhouse gas emissions from soils under sugarcane for ethanol production in Brazil

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#### **Abstract**

This paper includes both an integrative view of global patterns on the distribution and trends in SOM as well as research in South America, specially in Brazil, focusing on the impact of land use change and management practices on SOM. Finally, this work presents the potential effects on SOM due to the cultivation of biofuel crops, especially ethanol from sugarcane in Brazil. Future directions are briefly discussed here. For instance, ethanol can be produced from cellulose and hemicelluloses that are present in feedstocks including fast-growing hays like switchgrass, short-rotation woody crops like poplar and also from crop residues.

### **Key Words**

Carbon dioxide, methane, nitrous oxide, soil, carbon footprint.

#### Introduction

The interactions of land use, management and environment create a varied picture of SOM dynamics across the globe. Globally, the amount of organic matter in soils, commonly represented by the mass of carbon, is estimated to be about 1500 Pg C (1 Pg C =  $10^{15}$  g carbon) in the top 1 m of soil, which is three times the amount present in the vegetation and twice the amount found in the atmosphere (IPCC 2007). The amount of carbon stored in soil is determined by the balance of two biotic processes-the productivity of terrestrial vegetation and the decomposition of organic matter. Each of these processes has strong physical and biological controlling factors. These include climate; soil chemical, physical, and biological properties; and vegetation composition.

#### Methods

This paper includes both an integrative view of global patterns on the distribution and trends in SOM as well as research in South America, especially in Brazil, focusing the impact of land use change and management practices on SOM. Land use change, mainly for previous agricultural practices, has often decreased in soil organic carbon (SOC) stocks due to enhanced mineralization of soil organic matter (mainly to  $CO_2$ ). A significant fraction of the  $\sim 32\%$  increase in atmospheric  $CO_2$  over the last 150 years stems from the breakdown of soil organic matter after forests and grasslands were cleared for farming. This process increases greenhouse gas concentrations in the atmosphere, exacerbating global warming. Conversely, adoption of "best management practices", such as conservation tillage, can partly reverse the process – they are aimed at increasing the input of organic matter to the soil and/or decreasing the rates at which soil organic matter decomposes. This mechanism has been called "soil carbon sequestration" and can be defined as the net balance of all greenhouse gases (e.g.,  $CO_2$ ,  $CH_4$  and  $N_2O$ ), expressed in  $C-CO_2$  equivalents or  $CO_2$  equivalents, computing all emission sources and sinks at the soil-plant-atmosphere interface. It must be noted that  $CO_2$  fluxes are evaluated trough C stock changes in the different compartments and  $CH_4$  and  $N_2O$  fluxes directly measured, or estimated with the best available estimates.

### **Results and discussion**

Finally, this work presents the potential effects on SOM due to the cultivation of biofuel crops, especially ethanol from sugarcane in Brazil (Figure 1). Depleting fossil fuel sources and the increasing demand for energy is currently worldwide fuelling the use of biomass as a renewable energy (IEA 2007). In Brazil, the largest exporter of ethanol in the world, the current trend is for growth in this sector, mainly due to geopolitical, economic and environmental issues further forcing the use of ethanol as alternative to fossil fuel. However, up to know it is not well understood how large scale intensive production of biomass for

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energy purposes and/or changes in agricultural management will feedback on the biogeochemical cycles of carbon, nitrogen and water. For instance, possible negative effects include enhanced greenhouse gas (GHG) emissions, especially of the potent GHG N<sub>2</sub>O, due to an increasing application of synthetic fertilizer to maximize biomass production. On the other hand a series of positive environmental consequences might result, e.g. if soil C and N stocks could be increased due to adaptation of agricultural management e.g. improved treatment of crop residues. Thus, biofuel production is/ will be an important component in any sustainable regional management strategy, requiring the balancing of ecological demands.

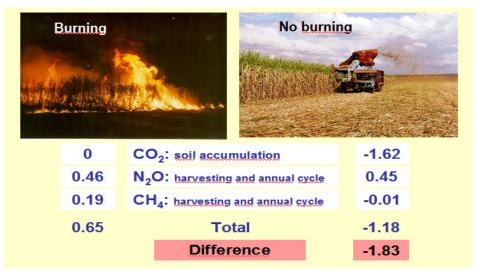


Figure 1. Carbon balance (Mg Ceq/ha/y) for sugarcane production with different harvesting systems (with or without burning sugarcane leaves).

Future directions are briefly discussed here. For instance, ethanol can be produced from cellulose and hemicelluloses that are present in feedstocks including fast-growing hays like switchgrass, short-rotation woody crops like poplar and also from crop residues. While not cost-competitive today, already observed advances in technology lead us to believe that in the next few years, ethanol made from these feedstocks, called second generation ethanol, will become commercially feasible. Taking into account the scarcity of arable land available to meet an increasing energy demand, it is expected that crop residues will be totally or partially removed from the field for ethanol production (Cerri *et al.* 2007). On the other hand, in the case of sugarcane, partial removal of litter may even be beneficial, since in some soil and climate conditions, excessive mulch might hinder planting, fertilizer application and irrigation operations, increase disease and pest occurrence (e.g. *Mahanarva fimbriolata*) and delay ratoon emergence resulting in lower crop yields. There might be a compromise in leaving part of the residues on the field while processing the other part into bioethanol, which would still be beneficial to the soil and to the crop, and allow for the production of renewable energy (Galdos *et al.* 2010).

While the negative impacts of complete litter removal are foreseeable, the impact of partial removal on soil organic carbon, soil physical quality, and crop productivity has not been fully resolved. It is well known that crop residues applied to soil are important for soil organic carbon, which is an important determinant of soil fertility and within limits; crop productivity is positively related to the soil organic matter content. More information about the maximum permissible rates of sugarcane litter removal under different soil and climate conditions is highly needed. Furthermore, it is essential to develop decision support systems for a judicious management of crop residue for essential but competing uses, since a potential reduction of carbon levels in soils can contribute to increased levels of greenhouse gases in the atmosphere.

#### **Conclusions**

Considering the increase in demand for alternative energy sources, and pressing issues such as global warming and the depletion of natural resources, there is a need for sustainable biofuel production. There are currently several initiatives for the establishment of specific criteria for environmentally sound biofuel production, including government standards and regulations. However, most sets of criteria for the agricultural phase of biofuel production focus primarily on greenhouse gas emissions and energy use. Taking into account the issues discussed here, soil quality should definitely be included in the sustainability assessments for bioethanol.

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## Have agronomic field trials provided sufficient data to predict soil carbon sequestration rates?

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#### **Abstract**

As nations debate whether and how best to include the agricultural sector in greenhouse gas pollution reduction schemes, the role of soil organic carbon as a potential large carbon sink has been thrust onto centre stage. Results from most agricultural field trials indicate a relative increase in soil carbon stocks with the adoption of various improved management practices. However, the few available studies with time series data suggest that this relative gain is often due to a reduction or cessation of soil carbon losses rather than an actual increase in carbon stocks. Based on this observation, we argue here that stock change data from agricultural field trials may have limited predictive power when the state of the soil carbon system is unknown and that current IPCC accounting methodologies based on these trial results may not properly credit these activities.

## **Key Words**

Carbon sequestration, greenhouse gases, soil organic matter, IPCC.

#### Introduction

Improved management of agricultural land has the potential to both greatly reduce net greenhouse gas (GHG) emissions (Smith et al. 2008) and to act as a direct CO<sub>2</sub> sink through soil carbon sequestration (Lal 2004). The recognition that agricultural soil carbon sequestration could be a successful "win-win" or "no regrets" policy, simultaneously reducing atmospheric GHG levels and increasing food security through improved soil health has thrust the issue onto numerous national political agendas. Existing agricultural field trials represent one of the greatest immediately available resources for the study of management impacts on soil carbon sequestration. These data sets have both informed soil carbon modelling efforts (i.e. Parton et al. 1987: Skiemstad et al. 2004) and formed the basis for the stock change factors used in current IPCC accounting guidelines (IPCC 2006). The measurement of soil organic carbon (SOC) content at the onset of a trial provides a baseline from which to calculate the impact of imposed management treatments on rates of SOC change. Initial SOC measurements can also be useful to verify that starting SOC values are similar between treatments, which are of critical importance for paired-plot studies where greater concern over spatial heterogeneity between sites exists. Unfortunately, the great majority of these studies were designed to define the influence of agricultural management practices on plant dry matter production, grain yields and other agronomic properties. Few long-term trials accurately measured SOC stocks at the onset of experimentation. Useful data on SOC stock changes have been and can still be gathered without the aid of the baseline data. However, without time series data, results from these trials have restricted predictive power and current IPCC accounting methodologies based on these trial results may not properly credit these management activities.

#### Discussion of typical results

As noted, only a small number of studies have actually followed a change in management through time, the remainder have compared SOC stocks in contrasting management practices after a defined number of years of implementation. Without the baseline data at the inception of a trial or a temporal sequence of measurements, it is impossible to determine whether or not a current measured difference in SOC between two treatments has resulted in a net sequestration of atmospheric CO<sub>2</sub>-C. A second consideration involved in defining the influence of applied management practices on soil carbon change and carbon sequestration is whether SOC has stabilised at a new steady state value indicative of the applied management practice or is still changing and progressing towards a new equilibrium value. Evidence suggests that the imposition of agriculture on previously undisturbed soil will result in a 20-60% loss of SOC (Mann 1986; Davidson and Ackerman 1993; Lal 2004) with the rate of loss being greatest initially and then diminishing with time (dashed line in Figure 1). If two management practices (conventional (CP) and best management practice (BMP) in terms of SOC accumulation) are initiated at different times after clearing (points A, B and C)

different SOC sequestration outcomes are obtained (Figure 1). Results from replicated field trials with time series data in Australia indicate that Australian agricultural soils are typically somewhere between scenario A and B in **Error! Reference source not found.**. The relative change between treatments consistently showed a large net gain in SOC, but this was due to the conventional practice typically losing SOC and the conservation or BMP losing SOC but at a smaller or insignificant rate.

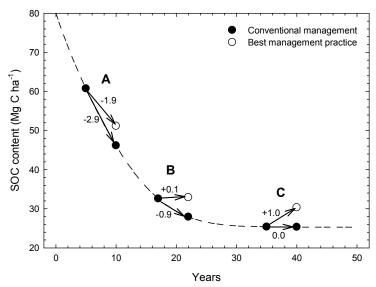


Figure 1. Results from a hypothetical field trial comparing CMP and BMP initiated at three times (A, B and C) after initial clearing. If the initial conditions were unknown, all 3 trials would show a relative gain of 5 Mg C/ha in the BMP over the 5-year trial period. The actual rate of change in SOC stocks (given next to each arrow) is entirely dependent upon the initial state of the system: A) the soil is still responding to the initial land clearing and is losing SOC at a rapid rate and both management scenarios result in a net emission of CO<sub>2</sub>; B) the rate of SOC loss has moderated and little net change in SOC is noted in the BMP while the conventional management system continues to lose SOC; and C) the soil has reached steady state with respect to the CMP and the BMP results in a net sequestration compared to the SOC content present at the time the experiment was initiated.

#### Predictive value of these results?

Does the observed difference in a paired-site study or single point-in-time measurements in a trial translate to the case of adopting the new management? If the CMP trial was at steady state at the beginning of the trial (e.g. point C in Figure 1), then we can reasonably assume that the difference was due to increased soil carbon stocks under the BMP system and adoption of this practice at some point in the future will result in these gains. However, if the CMP trial was not at steady state and was continuing to lose SOC (i.e. **Error!**Reference source not found. and points A and B in Figure 1) and the relative gain in the BMP trial was really due to a reduction or cessation of losses, then it is uncertain whether this data will give us an answer to the posed question because the accumulation and loss of SOC may not be symmetrical processes.

There is evidence from both mechanistic and modelling studies that SOC is typically lost more rapidly than it is gained. First, the formation of stable aggregates that retard SOC decomposition may be much slower than their destruction during tillage (Jastrow *et al.* 1996; Six *et al.* 2000), thus SOC stocks may not build nearly as rapidly as they appear to be lost (Balesdent *et al.* 2000). This concept of hysteresis was nicely demonstrated by Pankhurst *et al.* (2002) by switching management practices after 14 years of a trial and then re-sampling 3 years later. Applying tillage to the previously no-till plots resulted in large losses of C from the upper 10 cm of soil, however, applying no-till to previously tilled plots resulted in non-significant SOC changes after 3 yrs (Pankhurst *et al.* 2002). In a second example, studies of rangeland management have shown that reestablishment of healthy, diverse and productive plant communities takes much longer (up to 5-10 times longer) than the degradation of these systems (Harrington *et al.* 1984; McKeon *et al.* 2004) leading to potential rapid loss of SOC but gradual gains (Hill *et al.* 2006). Third, most multiple-pool soil carbon models will show greater loss rates than sequestration rates when modelling input changes over decadal timescales because changes typically take on the order of a century to fully propagate through all the various SOC pools. These examples all suggest that reducing SOC loss rates may be easier than actually increasing stocks.

# **Accounting implications**

Carbon emissions and removals for Article 3.4 of the Kyoto Protocol (UNFCCC 1992) activities most pertinent to the agricultural sector need to be accounted for on a "net-net" basis; meaning that net emissions and removals from activities during a commitment period are to be compared to net emissions and removals in a base year (Schlamadinger *et al.* 2007). Accounting for net uptake or release of CO<sub>2</sub> from soils presents a unique challenge for the AFOLU (Agriculture, Forestry and Other Land Uses) sector because accurate measurements are extremely difficult, thus necessitating monitoring changes in SOC stocks instead of net emissions. While the net change in SOC stocks will give a measure of the overall emissions or removals during a commitment period, comparing stocks only in 2 years does not yield any information on whether or not the net emissions rate has changed throughout the commitment period. Currently, the agreed-upon IPCC Guidelines for National Greenhouse Gas Inventories (IPCC 2006) outline accounting methodology into a 3 tiered system depending on the level of desired detail and availability of suitable information.

Tier I & II Accounting. In these accounting approaches, SOC stock changes are calculated by multiplying a reference stock value (IPCC default values for Tier I and country/region specific values for Tier II) by a series of stock change factors, which are assumed to have linear effects for 20 years before reaching a new equilibrium (IPCC 2006). The stock change factors, which essentially represent the relative difference between two management practices, have been derived from data sets composed of primarily paired-site studies (i.e. West and Post 2002; Smith et al. 2008). As discussed earlier, these data cannot distinguish between sequestration and avoided emissions, with the result being that a country would get credit for an activity regardless of the actual SOC outcome. An advantage of this accounting methodology is that nations will correctly get credits for avoided emissions regardless of whether the actual SOC trajectory was more like scenarios A or B versus C in Figure 1. However, these credits may be artificially high in many situations because of the hysteresis problem outlined in the previous section.

Additionally, under a stock change factor accounting system, a change in land-use, management or inputs is needed to induce a SOC stock change. Thus, a farm that has been steadily increasing SOC stocks due to continuous good management since the baseline year would not get any credits for these activities despite actually decreasing the atmospheric burden of  $CO_2$  on an annual basis. Furthermore, this accounting methodology makes no consideration for when the change in management occurred, as long as it occurred between the accounting year and the baseline year, with the result being all land area that falls within one management change category will get the same amount of credits.

*Tier III Accounting*. The highest order accounting system is a spatially explicit detailed modelling- or inventory-based system (IPCC 2006). From a modelling standpoint, knowledge of only the relative difference between management wouldn't be good enough to predict actual SOC stock changes. In the case of scenarios A and B, we would also need to know if the baseline, if projected into the commitment period, is changing which would be extremely difficult to verify let alone model. In a Tier III national inventory-based approach, SOC stocks would only be followed through time so the relative SOC gains (i.e. emission reductions) found in many field trials would not be "seen" and only the actual change in stocks over time will be reported.

Thus, under current IPCC recommended accounting guidelines, there may be a perverse situation where Tier I and II approaches will yield emissions reduction credits for all management shifts regardless of whether the shift results in net sequestration or simply a reduction in SOC losses, while SOC accounting under the more detailed Tier III approach would result in net liabilities for a country if the change in management only resulted in a reduction in SOC loss rate. Given that even a reduction in the loss rate of SOC is of value in terms of meeting GHG abatement targets and is consistent with the goals of net-net accounting (Schlamadinger *et al.* 2007), this analysis suggests that inventory-based accounting methods, while being able to correctly track changes in SOC stocks, may not be the most appropriate choice for emissions inventories and efforts should perhaps be focused on improving the stock change factor and modelling approaches.

## **Conclusions**

Results from agronomic field trials generally show a relative gain in carbon stocks with implementation of management practices that return or retain more of the carbon captured by growing plants. However, much of the data used to support such a conclusion has been derived from point-in-time measurements which are

ambiguous as to whether the relative difference was due to net sequestration or simply a cessation of losses during the trial (i.e. an avoidance of emissions). While most field trial evidence suggests a real net benefit to GHG abatement, we have argued here that 1) the predictive power of results from most agronomic field trials to alternative situations where these management practices have been implemented is questionable without detailed knowledge of the state of the soil carbon system; and 2) the current recommended IPCC accounting methodologies may not properly credit these activities and may indeed result in contradictory results when accounted for using Tier I or II versus Tier III approaches.

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# Hippuric acid effect on $N_2O$ emissions from cow urine patches at a range of soil temperatures

Janet Bertram<sup>A</sup>, Tim Clough<sup>A</sup>, Leo Condron<sup>A</sup>, Rob Sherlock<sup>A</sup> and Maureen O'Callaghan<sup>B</sup>

#### **Abstract**

Urine patches deposited by ruminant grazing animals are a source of the greenhouse gas nitrous oxide ( $N_2O$ ). Reductions in emissions of  $N_2O$  have been measured following amendment of cow urine with additional hippuric acid, a natural constituent of the urine. Since the previous studies all used relatively high incubation temperatures, a range of temperatures were used in this study to test the potential effect of hippuric acid under differing conditions. Unlike the earlier studies, there was no inhibition of  $N_2O$  emissions due to urinary hippuric acid content during this experiment. The incubation temperature, however, greatly affected  $N_2O$  emissions, with fluxes increasing with increasing temperature (13.36 mg  $N_2O$ -N at 20°C vs. 0.31 mg  $N_2O$ -N at 5°C). Increasing the urinary hippuric acid content also had no effect on the soil pH, nitrogen dynamics, or ammonia ( $NH_3$ ) emissions. Higher emissions of  $NH_3$  from the 5°C than from the 10°C treatment meant that total gaseous N losses were lowest from the 10°C soil. The lack of effect of hippuric acid in this experiment may have been due to the low soil moisture content allowing aerobic soil bacteria to degrade the acid, or may indicate that hippuric acid does not inhibit nitrification.

## **Key Words**

Greenhouse gas emissions, nitrogen dynamics, ammonia emissions, nitrification, denitrification.

## Introduction

Nitrous oxide ( $N_2O$ ) is a potent greenhouse gas, which is produced in urine patches during the nitrification and denitrification of urinary-N. Globally, 40% of anthropogenic  $N_2O$  emissions are agriculturally derived. Hippuric acid (HA), a naturally occurring minor constituent of ruminant urine, was shown in previous studies (Bertram *et al.* 2009; Kool *et al.* 2006; van Groenigen *et al.* 2006) to reduce emissions of  $N_2O$  from synthetic and real cow urine applied to soil, when the hippuric acid content of the urine was increased. However, the previous experiments were all carried out at relatively high temperatures (16–21°C) which do not occur throughout the year in the field. Therefore this current experiment was instigated to investigate the inhibitory effect of hippuric acid at a range of temperatures representative of those occurring at the soil collection site at 10 cm soil depth.

# Methods

Soil collection and urine amendment

Temuka silt loam soil (Gley soil, NZ Soil Classification (Hewitt 1998)) from 0-10 cm depth was sieved (< 4 mm) and packed in PVC tubes to a depth of 6 cm at a bulk density of 0.79 g/cm<sup>3</sup>. Dairy cow urine was amended with urea, and the high hippuric acid treatment (HHA) received additional hippuric acid, while the low hippuric acid treatment (LHA) underwent no further amendment (Table 1). Each soil core had 15.0 mL of urine pipetted onto its soil surface.

Table 1. Concentrations of nitrogen and hippuric acid (HA) and HA content as a percentage of total urinary N in the low hippuric acid (LHA) and high hippuric acid (HHA) urine treatments.

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Treatment	N concentration	HA concentration	HA content	N application rate			
	(g/L)	(mmol/L)	(% urinary N)	(kg N/ha)			
LHA	10.0	35	4.9	764			
HHA	10.6	75	9.9	810			

## Experimental design

The experiment was a 2 x 4 factorial design, with two urinary hippuric acid treatments (LHA and HHA, as detailed above) and four temperature treatments (5, 10, 15 and 20°C) to give a total of eight treatments. Four replicates of each treatment (a total of 32 cores) were destructively sampled on 5 sampling occasions, and the

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set of soil cores used for the final destructive sampling was also used for gas sampling throughout the study. The soil moisture content was initially held at 0.45 g water/g soil to encourage nitrification, as an earlier study had shown evidence of hippuric acid inhibition of nitrification (Bertram *et al.* 2009). From day 17, the soil moisture content was altered to 0.55 g water/g soil to promote denitrification as no effect of hippuric acid had been observed by this time.

# Soil, microbial and gas analyses

Sub-samples of soil were analysed for surface and bulk soil pH, and for ammonium  $(NH_4^+)$ , nitrite  $(NO_2^-)$  and nitrate  $(NO_3^-)$  concentrations. The set of 32 cores used for gas sampling were placed into 0.5 L Mason jars on each sampling occasion to allow headspace sampling of soil emissions of  $N_2O$ , and ammonia  $(NH_3)$  emissions were measured at the same time using acid traps.

## Results

In contrast to the results of the previous studies, there was no indication of inhibition of  $N_2O$  emissions due to increased levels of urinary HA over the course of the experiment (Figure 1a). There was, however, an increase in  $N_2O$  emissions with increasing incubation temperature (Figure 1b), with the highest flux of  $> 11000 \mu g N_2O-N/m^2/h$  measured in the  $20^{\circ}C$  treatment. These results were reflected in the concentrations of soil inorganic N, with  $NH_4^+$  decreasing more rapidly and  $NO_3^-$  increasing more rapidly at higher temperatures, while being unaffected by HA concentration. Since pH in urine patches is linked to N dynamics, the measured pH values remained elevated for longer at the lower temperatures.

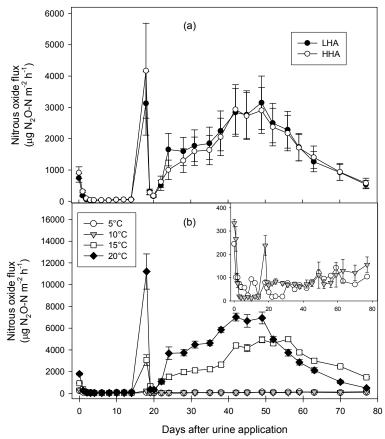


Figure 1. Nitrous oxide emissions measured from (a) hippuric acid treatments and (b) all temperature treatments, with (inset)  $5^{\circ}$ C and  $10^{\circ}$ C temperature treatments only (Error bars = SEM, n = 16 (a) or 8 (b)). NOTE: differing scales on y axes.

As seen previously (Bertram *et al.* 2009), there was no effect of HA amendment on NH<sub>3</sub> emissions, but an increase in incubation temperature reduced emissions of NH<sub>3</sub>. Thus, overall, HA amendment did not affect gaseous N emissions from the applied urine, but an increase in incubation temperature caused emissions of nitrogenous GHGs to increase from < 12% of the total N applied in the 5 and 10°C treatments to > 17% of the total N applied in the 20°C treatment (Table 2).

Table 2. Cumulative emissions of N<sub>2</sub>O-N and NH<sub>3</sub>-N as total N emitted (mg) and percent N applied. Means

followed by same letter in each column do not differ significantly.

Treatment	Mean cumulative N emitted per core							
	mg N			%	% total N applied			
Temperature	$N_2O-N$	NH <sub>3</sub> -N	Total <sup>#</sup>	$N_2O-N$	$NH_3-N$	Total <sup>#</sup>		
5°C	0.31 c	18.18 a	18.48 c	0.20 c	11.76 a	11.96 c		
10°C	0.37 c	14.75 b	15.12 d	0.24 c	9.56 b	9.80 d		
15°C	9.96 b	14.17 b	24.13 b	6.45 b	9.18 b	15.63 b		
20°C	13.36 a	13.67 b	27.03 a	8.67 a	8.84 b	17.51 a		
significance	***	***	***	***	***	***		
Acid								
LHA	6.07	14.93	21.00	4.05	9.95	14.00		
HHA	5.93	15.45	21.38	3.73	9.72	13.45		
significance	NS	NS	NS	NS	NS	NS		

<sup>\*\*\*</sup> P < 0.001, NS = not significant

## Conclusion

In this experiment, amendment of real cow urine with additional HA did not result in inhibition of  $N_2O$  emissions from soil. This was in contrast to the results of previous studies, which used similar differences between HA concentrations. Since, in this current experiment, the soil moisture content was lower than was the case in the earlier experiments, it is possible that the acid was degraded in the soil by aerobic bacteria capable of utilising the benzoic acid produced by hydrolysis of HA (Gescher *et al.* 2002; Philippe *et al.* 2001; Pumphrey and Madsen 2008). Alternatively, this experiment may indicate that HA does not affect nitrification, despite the indications seen in the previous study (Bertram *et al.* 2009). Increasing the soil temperature resulted in increases in total gaseous N emissions, due to large increases in  $N_2O$  emissions as the temperature increased. Nitrous oxide emissions in the 5 and 10°C treatments were very low, and enhanced NH<sub>3</sub> emissions from the 5°C treatment, probably due to the continued elevation of soil  $NH_4$  concentrations, meant that gaseous N emissions were higher from the 5°C soil than from the 10°C soil.

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<sup>#</sup>Sum of N2O-N + NH3-N

# How do microaggregates stabilize soil organic matter?

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#### **Abstract**

Microaggregates play a key role to protect soil organic matter (SOM) from microbial decomposition. Several physical, physico-chemical and biochemical mechanisms have been proposed to describe the SOM stabilization in soil. However, no scientific consensus exists about a range of hypotheses. The aim of this review is to consolidate common notions and hypotheses on physical and physico-chemical protection mechanisms. The key notion of physical protection is exclusion of microbes and enzymes from microaggregate pores. Recent investigations showed higher microbial diversity and presence of accessible pore networks in microaggregates. The physico-chemical protection mechanism is more robust but monolayer or patchy adsorption of SOM onto clay surfaces requires further detailed research. The adsorption of SOM and exo-enzymes on pore walls and clay surfaces has been identified as a plausible concept of SOM stabilization.

# **Key Words**

Microaggregation, physical protection, physico-chemical protection, intercalation.

### Introduction

Stabilization of soil organic matter (SOM) in soil aggregates is on the global climate change agenda and viewed as an antidote to rapid carbon dioxide release from soil by human induced management practices. Scientific discussion over the past decade emphasizes the potential of soil to sequester atmospheric carbon dioxide through several stabilization mechanisms. Oades (1988) and Sollins *et al.* (1996) published comprehensive reviews of organic matter retention and stabilization in soil. The pivotal role of soil structure and texture was discussed in detail by Van Veen and Kuikman (1990). The authors presented experimental evidence of the effect of soil architecture on organic matter decomposition. In recent years a number of reviews were published to crystallize the stabilization mechanisms of SOM (Baldock and Skjemstad 2000; Kaiser *et al.* 2002; Krull *et al.* 2003; Von Lutzow *et al.* 2006; Kögel-Knabner *et al.* 2008a,b). However, the hypotheses put for some protection mechanisms such as physical and physico-chemical processes still lack a substantial body of experimental evidence and explanation. Advances in instrumentation for directly viewing inside microaggregates (<250 µm) would offer one such opportunity for further detailed research on SOM protection mechanisms. This review will attempt to consolidate the current understanding on physical and physico-chemical protection mechanisms of SOM in microaggregates.

# Stabilization of SOM in microaggregates

Physical protection

Occlusion into microaggregates during its formation is one of the most important processes by which SOM can circumvent decomposition. The exclusion of microbes and enzymes from pores is the key protection mechanism for occluded SOM in microaggregates (Sollins et al. 1996). There is a sharp increase of pore volume that has diameters between 0.1 μm and 1 μm within microaggregates. The pore volume at diameters <0.1 µm is about 21% of the total pore volume present in microaggregates (McCarthy et al. 2008). The accessibility of bacteria and fungi to the occluded SOM is restricted due to the ratio between dimensions of the microhabitat and the size of the organisms. However, the diversity of microbial population is reportedly higher in silt and clay fractions, which may be due to higher nutritional availability and exclusion of protozoan grazing (Sessitsch et al. 2001). The methodological discrepancies regarding separation of aggregates between the investigations by McCarthy et al. (2008) and Sessitch et al. (2001) were considered not 'out of the range' for comparison by the current authors. If microaggregates are a protective space for SOM then these two findings must be complementary. Looking at the different approaches we can assume that the microbial community in microaggregates is less active due to inactivation or inaccessibility of extracellular enzymes in pore networks. Small mineral mesopores (0.002-0.01 µm) are not accessible to exoenzymes, and organic matter in mesopores is protected against mineralization or decomposition (McCarthy et al. 2008; Zimmerman et al. 2004a). However, Mayer et al. (2004) and McCarthy et al. (2008) proposed that the arrangement of pore networks in microaggregates, rather than simple exclusion of exo-enzymes, is

responsible for protection of SOM. Although some pores in microaggregates are habitable for small bacteria and accessible to exo-enzymes, the production of enzymes to decompose SOM might not be 'physiologically profitable' due to tortuosity of the pore network. The development of computerized microtomography has allowed us to look inside the microaggregates by non-destructive means. Recent studies based on synchrotron microtomographic imaging showed highly interconnecting micropore networks in soil aggregates (Lindquist 2002; Peth *et al.* 2008). The interconnected pore networks enable the transport of oxygen and soil solution to the center of aggregates, where SOM can be stabilized by organo-mineral complexes (Park *et al.* 2007; Peth *et al.* 2008) or by interacting with the pore walls (Zimmerman *et al.* 2004b). Further research is required to explore the relationship between microbial diversity, exclusion and/or activity of exo-enzymes, and the connectivity of pore networks to resolve the nature of physical protection of microaggregates to SOM.

Among the proposed SOM protection mechanisms the intercalation of SOM between silicate clay layers has received less attention than other mechanisms such as soil wettability. The principal reason behind this is likely related to uncertainty of intercalation of SOM. SOM is generally composed of complex macromolecules and structurally not fitted in interlayer space of clays. However, solubility and flexibility of the organic molecules and the presence of efficient metal complexers has been found to determine the extent of SOM intercalation (Schnitzer et al. 1988). Organic macromolecules such as enzymes, proteins, fatty acids or organic acids can be intercalated into 2:1 expandable phyllosilicates at pH <5 (Violante and Gianfreda 2000). Moreover, the penetration of small organic molecules into the smectite interlayer with conformational change and their subsequent polymerization into larger molecules are catalyzed by Al<sup>3+</sup> or Fe<sup>3+</sup> (Schulten et al. 1996; Kennedy et al. 2002), Generally, the intercalated materials are depleted in ligninderived aromatic compounds (Schulten et al. 1996). The stability of interlayer complexes depends on the isomorphic substitution in tetrahedral sheets of phyllosilicates due to the localization of a negative layer charge near the reaction sites. This statement leads to the conclusion that minerals such as vermiculite and mica, having isomorphous substitution in the outer silicate sheet, are able to form the most stable interlayer complexes (Tunega et al. 2007). Some researchers consider that there exist no specific methods to determine intercalated organic carbon, and hypothesize that chemical characterization and quantification of intercalated SOM are highly unreliable (Eusterhues et al. 2003). Clearly, the contribution of intercalation in SOM stabilization requires further detailed scientific dialogue and research.

# Physico-chemical protection

Physico-chemical protection of soil organic matter arises from the interaction of different types of organic carbon with clay particles. The types of organic matter that are adsorbed on the clay particles can range from simple organic acids to complex bio-macromolecules, such as extracellular enzymes, suberins, DNA etc. The main causes of such interaction are large surface area and charged surfaces on clay particles. The surface area of the minerals is not a good predictor of organic matter and mineral interaction in soil because of its discontinuous coverage by SOM (Kögel-Knabner *et al.* 2008a). A term 'monolayer equivalent' is proposed by Mayer (1994) with the caution that organic matter should be distributed across the whole clay surface in a single layer. The author held the view that the surface area of clay controls the organic matter preservation. However, Ransom *et al.* (1997) rejected this hypothesis and presented evidence of patchy distribution of organic matter on clay. In accordance with Ransom *et al.* (1997) several other investigators proposed patchy surface adsorption of organic matter (Kaiser and Guggenberger, 2003; Curry *et al.* 2007). However, in recent work of Wagai *et al.* (2009) it was shown that the surface area of clay of most of the studied soil surface horizons developed on acidic metasedimentary and ultrabasic igneous rocks is completely covered by organic matter, except of a few with 'painted' clay surfaces.

The interaction of organic matter and clay particles is further determined by the architecture of clay minerals. The neutral siloxane surfaces or tetrahedral sheets of 2:1 and 1:1 phyllosilicates, where no isomorphous substitution has occurred, do not strongly participate in reactions, whereas the permanent charge sites within the tetrahedral sheets are very active. The reactivity of the siloxane surface increases if the major isomorphism substitution occurs at the octahedral sheets of phyllosilicates (Schoonheydt and Johnston, 2006). The hydroxyl surfaces where octahedral sheets are exposed also act as reaction sites for SOM interaction. It is clear from the above that physico-chemical protection of SOM needs to take into account the distribution of charge in clay mineral surfaces and its origin. Since the presence of the neutral siloxane surface can impair continuous strong organic matter coating on clay surfaces, the straightforward measurement of protection capacity of soil by relating it with percent clay content may not be judicious.

Moreover, if clay adsorbs SOM in a 'monolayer', the question of its maximum thickness and hence protection capacity will need to be worked out. Organic matter protection can be explained as either (i) physical protection due to adsorption on clay surfaces or (ii) protection due to adsorption of enzymes on clay (Theng 1979). Experiments on nuclease activity on DNA in the presence of kaolinite, illite and montmorillonite showed that adsorption on clay surfaces provided physical protection against decomposition. The adsorption of nuclease on clay surfaces separates the enzyme from the substrate, and the conformation of the enzyme and adsorption strength also plays a significant role. However, part of the adsorbed DNA remained accessible to bacteria (Demaneche *et al.* 2001). The nucleic acid molecule adsorbed on the external surface of montmorillonite is subject to more rapid bacterial decomposition compared to that adsorbed inside the interlayer (Khanna *et al.* 1998). Fiorito *et al.* (2008) observed less bioavailability of clay bound proteins. The conformational change of protein molecules inhibits the protease-substrate reaction. However, there is a report of higher activity of clay bound enzymes due to exposure of more active sites of enzymes by 'allosteric regulation' as in biological systems (Fiorito *et al.* 2008). The diversity of results regarding clay-enzyme interaction clearly indicates the necessity of more detailed investigation rather than generalization.

## Conclusion

The understanding of protection mechanisms of SOM in microaggregates with its protective capacity is crucial for adopting better soil management practices and to inform soil policy makers. Undoubtedly, microaggregates have the capacity to significantly slow SOM decomposition. However, recent findings on pore connectivity and microbial diversity in microaggregates indicate simple physical exclusion of exoenzymes and microbes may not solely be responsible for SOM protection. The protection of SOM by occlusion in microaggregate pores, in an absolute sense, is related to the adsorption of SOM on the pore walls or on exposed facets of clays. Moreover, interlayers of clay minerals have the capacity to stabilize SOM by adsorption and complexation. The adsorption of SOM and exo-enzymes on clays with conformational change may be a better explanation of its protection against decomposition because conformational change interferes with enzyme-substrate recognition. The capacity of clays to protect SOM depends on its adsorption coverage and thickness of monolayers. An integrative research approach is required linking microbiology, clay mineralogy, chemistry and physics to further advance our understanding on protection mechanisms of SOM in microaggregates.

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# Impact of addition of various resource quality inputs on soil CO<sub>2</sub> flux and C balance in a tropical dryland agroecosystem

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### **Abstract**

Management strategies in agroecosystems may influence C balance in soil through variation in C input to soil and also by causing variation in C output from soil. In a two year study we evaluated the effect of application of soil inputs with varying resource quality viz: high quality (C:N 16; HQR), low quality (C:N 82; LQR) and mixed quality (HQR +LQR; MQR) inputs having equivalent amount of N, on the soil CO<sub>2</sub> flux, % C build-up, soil C balance and crop productivity in a tropical dryland rice-barley-summer fallow agroecosystem. Addition of LQR singly resulted in high probability of C retention capacity compared to other treatments, however lower levels of soil C build-up, and crop productivity was observed. On the other hand, although in HQR treatment the C balance approached almost unity, the C build-up and crop productivity was comparable to that of the LQR treatment. Combining the two inputs resulted in significant build-up of soil C and enhancement of crop productivity and also indicated high C sequestration capacity. It is concluded that for sequestration of C, the resource quality of the input i.e., the form of C, labile or recalcitrant, is more important than the absolute amount of C added to the soil through exogenous inputs.

# **Key Words**

Resource quality, agroecosystem, soil CO<sub>2</sub> flux, C balance, C build-up, crop yield.

### Introduction

Agroecosystems has become very important not only for its role in achieving food security but also in mitigation of the climate change due to atmospheric enrichment of CO<sub>2</sub> and other greenhouse gases (IPCC 2001). The mechanism and potential of C sequestration in soil are still not well understood, and predictions made for world-wide carbon (C) balance remain uncertain (Rustad 2006). Since soil can serve both as a source or sink for atmospheric CO<sub>2</sub> depending upon the agricultural management practices employed, any change in management strategies may influence soil C cycle (Lal 2004). Maintenance of soil organic C is essential for the long-term sustainability of agroecosystems in general and particularly dryland agroecosystems. Achieving agricultural sustainability is the prime need for India where about 68% of total agricultural land (85 x 10<sup>6</sup> ha) is under dryland farming conditions, receiving moisture supply only through highly seasonal rainfall. In the contemporary global change scenario, the evaluation of the impact of agricultural management practices on both the emission of CO<sub>2</sub> from soil and C sequestration capacity in soil has been emphasized. However, limited information is available on the maintenance and sequestration of C in soils of rice field in general and particularly in tropical dryland agroecosystems (Singh et al. 2009). In drylands the application of soil organic amendments (e.g. crop residues, green manures), among other measures, is generally recommended for efficient management of soil organic matter and moisture availability (Singh et al. 2007). It is important to emphasize on not only the quantity of organic amendments, but its resource quality as well. There is a need to evaluate the impact of management strategies, which manipulate the quality of exogenous inputs, on soil CO2–C flux in tropical dryland agroecosystems, an aspect scantily explored so far. The broad objective of the present work was to examine the influence of resource quality on soil CO<sub>2</sub> flux in the context of agricultural sustainability and global change. The specific objectives of the present study, carried out in a Indian tropical dryland agroecosystem having rice-barleysummer fallow annual sequence, subjected to varying quality soil inputs, were: (1) to evaluate the effect of quality of exogenous inputs on soil CO<sub>2</sub> flux, microbial biomass and crop root biomass, (3) to quantify soil C build-up and increment in crop yield and (4) to estimate the C balance in soil through C input and C output.

### Material and method

The experiments were conducted in Banaras Hindu University campus at Varanasi (25°18' N lat. And 83°1' E long., 76 m above the mean sea level. This region has a tropical moist sub-humid climate, characterized by strong seasonal variations with respect to temperature and precipitation. The long term average annual rainfall is about 1100 mm. The soil belongs to the order inceptisol, showing pale brown colour, sandy loam

texture and a neutral reaction. The experimental design involved application of various soil amendments having equivalent amount of N (80 Kg N) but with contrasting chemical composition viz. chemical fertilizer (FER) and three organic inputs in form of high quality resource (*Sesbania aculeata* shoot, N 3.03%, C:N 16, lignin:N 3.2, polyphenol + lignin:N 4.2, HQR),low quality resource (wheat straw, N 0.61%, C:N 82, lignin:N 34.8, polyphenol + lignin:N 36.8, LQR), and high and low quality resource combined (*Sesbania*+wheat straw, MQR) besides control (cropped, no inputs, CON). Every year the exogenous inputs were applied only once, 1 or 2 d before the sowing of the rice crop. The experimental plots were laid down in a random block design using three replicates per treatment. The plot size was 3 m \_3 m. A strip of 1 m was left to separate each block.

During the two year study the flux of  $CO_2$  from soil surface was determined 32 times at regular intervals under field condition using alkali absorption method. (Singh and Shekhar 1986). Each year the flux was estimated seven times during the both the crop periods which corresponded with seedling, pre-grain-forming, grain-forming, post-grain-forming and maturity stages of crops and twice during summer fallow. Cumulative soil  $CO_2$  flux was calculated as the sum of  $CO_2$  evolved during different sampling intervals. The sum of rice and barley yields was represented as annual crop yield (CY). Crop yield increment (%) was estimated as: (CY of treatment – CY of control) x100 / CY of control. Soil organic C (SOC) was estimated by dichromate oxidation and titration method during summer fallow. C build-up (%) was estimated as: C build-up (%)= (SOC in treatment – SOC in control) x 100 / SOC in control. C content of plant materials were estimated by CHN Analyzer. Soil C balance was estimated as: C input in soil - C output from soil, where, C input was accounted as sum of C added through exogenous inputs, crop roots and crop stubbles and C output was accounted from soil  $CO_2$  flux (using conversion formula,  $C = CO_2 / 3.67$ ).

### Result and discussion

A distinct seasonal variation in  $CO_2$  flux was recorded in all treatments, flux being higher during rice period, and much reduced during barley periods (Table 1). During rice period the mean  $CO_2$  flux was greater in LQR and MQR treatments; however, during barley and summer fallow periods differences among treatments were small. The variability in annual cumulative soil  $CO_2$  flux was strongly related to various indices of resource quality of the exogenous inputs, i.e. C:N (r=0.96), lignin:N (r=0.92) and polyphenol+lignin:N (r=0.92) ratios.

Table 1. Variation in soil CO<sub>2</sub>-C flux and Cumulative CO<sub>2</sub>-C flux following various soil amendments.

		Cumulative CO <sub>2</sub> flux			
	(r	$(g CO_2/m^2/y)$			
Treatments	Rice	Barley	Summer Fallow	Annual	
	(112 days)	(139 days)	(60 days)		
1 <sup>st</sup> Annual Cycle					
CON	$180.7 \pm 15.5$	$94.2 \pm 6.0$	$129.4 \pm 4.5$	$972 \pm 30.3$	
FER	$138.1 \pm 11.3$	$94.8 \pm 7.3$	$131.7 \pm 5.3$	$889 \pm 20.2$	
LQR	$427.1 \pm 28.2$	$91.4 \pm 6.5$	$132.8 \pm 7.5$	$1606 \pm 6.6$	
HQR	$164.8 \pm 15.6$	$98.7 \pm 7.0$	$138.5 \pm 9.2$	$982 \pm 21.3$	
MQR	$361.6 \pm 22.1$	$100.2 \pm 6.7$	$135.3 \pm 4.5$	$1480 \pm 6.1$	
2 <sup>nd</sup> Annual Cycle					
CON	$142.3 \pm 10.9$	$86.8 \pm 5.2$	$133.8 \pm 8.2$	$889 \pm 14.0$	
FER	$151.2 \pm 17.8$	$94.1 \pm 5.8$	$139.5 \pm 3.0$	$944 \pm 19.2$	
LQR	$406.7 \pm 25.8$	101.3±5.3	$141.8 \pm 5.6$	$1633 \pm 9.0$	
HQR	$213.3 \pm 18.2$	$92.1 \pm 5.2$	$132.8 \pm 4.7$	$1083 \pm 12.5$	
MQR	$366.1 \pm 24.7$	$99.7 \pm 5.2$	$143.6 \pm 4.3$	$1518 \pm 7.7$	

Although, the cumulative  $CO_2$  flux was higher in LQR and MQR treatments yet, on considering  $CO_2$  flux per unit C added the ratio was lower indicating the possibility of high C retention in soil despite of huge loss of C (in terms of  $CO_2$ ) from these treatments. A reverse trend was found in CON, FER and HQR treatments with lower cumulative  $CO_2$  flux with an overall net loss of C (Table 2).  $CO_2$  flux per unit C added may give a better indication of C dynamics compared to cumulative  $CO_2$  flux alone.

Table 2. Variation in total C input to soil, CO2 flux per unit C added, C build up and crop yield increment as

influenced by various soil amendments.

Parameters	Treatments					
	CON	FER	LQR	HQR	MQR	
C input $(g C/m^2/y)$	$108 \pm 1.9$	$163 \pm 1.8$	$819 \pm 9.2$	$292 \pm 6.0$	$566 \pm 2.1$	
Cumulative CO <sub>2</sub> flux per unit C added (g CO <sub>2</sub> /gC/y)	$2.2 \pm 0.14$	$1.6 \pm 0.08$	$0.5 \pm 0.05$	$1.0 \pm 0.03$	$0.7 \pm 0.05$	
C build up (%)		8	18	15	33	
Crop yield increment (%)		45	32	38	49	

In any system when C input to the soil exceeds the C output from the soil, a positive imbalance occurs which subsequently results in sequestration of C in soil (Jastrow et al. 2007). In our study difference between C input and output in soil was found to be positive in the treatments where LQR was added either singly or in combination (Figure 1). Jacinthe et al. (2002) reported that soil mulching through the incorporation of wheat straw has beneficial effect on soil C sequestration. Paustian et al. (1997) also suggested that crop residues with higher C:N ratio play important role in C sequestration. Although LQR showed high C sequestration capacity in terms of C balance yet, the huge input of C in soil could not be translated to C storage either in the form of soil organic C build-up, or crop productivity (Table 2). Due to the slow rate of its decomposition of wheat straw C and other nutrients remained immobilized in undecomposed or partially decomposed portions of wheat straw (Singh et al. 2007), and was perhaps not available immediately after its application. The recalcitrant component of LQR may be incorporated in the passive pool of soil organic matter in long term as indicated by the balance of C input and output.

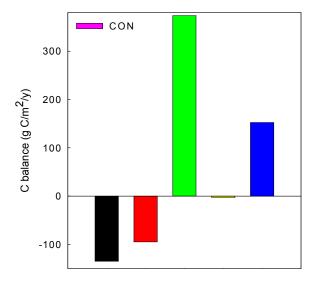


Figure 1. Impact of soil inputs on C balance during second annual cycle.

On the other hand, although in HQR treatment the C output was almost balanced by C input, the C build-up and crop productivity was comparable to that of the LOR treatment inspite of one-third C input (cf. wheat straw). Rapid decomposition of HQR resulted in release of the readily mineralizable labile C and other nutrients which perhaps were utilized for the accumulation of labile pool of soil organic matter and not for build-up of C or enhancement of crop productivity. Since C balance is near unity, this level of C may be maintained for long time. Addition of HOR to LOR altered the rate of decomposition resulting in prolonged release of nutrients which in turn supported the enhanced crop productivity and so also the C build up. In addition, some C which remained in the soil as recalcitrant partially decomposed mass may lead to C sequestration in the long term as evident from balance between C input and output. In case of CON and FER treatments the system seemed to be most unbalanced as the input of C exceeded C output.

### Conclusion

In this two year study combining the high and low quality inputs resulted in significant increment in C buildup and crop yield in addition to high C balance. The soil C retention capacity however varied significantly, mostly influenced by the recalcitrant or labile nature of the inputs. It is suggested that appropriate mixing of high and low quality inputs may contribute to improved crop productivity and soil fertility in terms of soil C sequestration, which in turn will help mitigate atmospheric CO<sub>2</sub>.

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# Impacts of soil moisture on trace gas emissions from grassland: a case study on grassland in Northern Ireland

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### **Abstract**

The impacts of soil moisture on trace gas emissions from grassland were investigated by an *in situ* measurement conducted over two sampling periods from 2008–2009 in a typical agricultural ecosystem of Northern Ireland. Gas samples were taken with the closed chamber technique and analysed for carbon dioxide (CO<sub>2</sub>), nitrous oxide (N<sub>2</sub>O) and methane (CH<sub>4</sub>). Wet soil conditions led to high emissions of CH<sub>4</sub> and N<sub>2</sub>O and a loss of applied nitrogen (N) fertilizer. These results are valuable toward the development of practical measures for reducing greenhouse gas emissions from agriculture.

# **Key Words**

Grasslands, greenhouse gases, fertilizer.

### Introduction

With rising global demand for food production, the area of land under cultivation and inputs of chemical fertilizers into agricultural ecosystems are expected to further increase (Galloway *et al.* 2008). As a result, the emission of greenhouse gases (GHGs) from agriculture may be intensified and their impact on global climate may become more serious. Therefore, greater understanding of the processes of trace gas emissions from agriculture must be developed (Batjes and Bridges 1992). This understanding will result in the development of practical measures for reducing trace gas emissions from agriculture.

Agriculture is estimated to contribute approximately 25%, 65% and 90% of global anthropogenic emissions of CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O, respectively (Duxbury 1994). Carbon dioxide is taken up by plants during photosynthesis and released through respiration processes from vegetation and soil organisms (Byrne *et al.* 2007). The CO<sub>2</sub> released from respiration depends on decomposition processes, which are affected by soil water status (Parton *et al.* 1987). Methane is commonly oxidized into CO<sub>2</sub> in unsaturated soils leading to an uptake of atmospheric CH<sub>4</sub> (Del Grosso *et al.* 2000). Soil production of CH<sub>4</sub> is associated with poorly drained areas (Gregorich *et al.* 2005). Synthetic N fertilizer application is the main source of N<sub>2</sub>O emissions from agriculture (Smith *et al.* 1997). N<sub>2</sub>O is produced via nitrification and denitrification processes (Wrage *et al.* 2004).

The impact of soil moisture on  $N_2O$  and  $CH_4$  emission from grasslands and forest soil has been well discussed (Zheng *et al.* 2002) and is considered a significant factor for regulating  $N_2O$  emissions. However, land management can affect sources and sinks of GHGs in grasslands in opposing manners. For example, increased fertilizer input generally leads to an increase in  $N_2O$  emissions, but can also contribute to increased C sequestration in the soil (Conant *et al.* 2005). Therefore, it is important to examine the impact of soil properties on all significant GHGs simultaneously to determine a net GHG effect from various agricultural management practices. The objective of this study was to determine the effect of soil moisture on trace gas emissions from a grassland system in Northern Ireland.

### Methods

Site and Experimental Design

The experimental field site was located in Crossnacreevy, Northern Ireland (54°32' N, 05°52' W; 390 m above sea level) as part of the Agri-Food and Bioscience Institute in Northern Ireland (AFBINI). The soil is a medium loam soil. Two nitrogen fertilizer treatments, high (420 kg N/ha/y) and low (105 kg N/ha/y), were applied to three replicates of three different grass species (*Lolium perenne*, *Phleum pratense*, *Dactylis glomerata*) combined with clover (*Trifolium repens*). Each year fertilizer was applied directly after harvest (nine times on high N, three times on low N). The data described in this paper were obtained during the last fertilizer application (40 kg N/ha) for the high N site in September of each year (2008 and 2009). Measurements were taken simultaneously at the low N sites, though no fertilizer was applied to these sites at that time.

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# Sampling and flux calculation

For obtaining the gas samples the closed chamber technique (Hutchinson and Mosier 1981) was used (chamber size: 40x40x10 cm). Three samples were taken with 60 ml plastic syringes, closed with a 3-way stopcock over a period of 30 minutes immediately ( $t_0$ ), 15 minutes ( $t_{15}$ ), and 30 minutes ( $t_{30}$ ) after the chamber was closed. Air pressure was obtained from the Aldergrove weather station (Latitude: 54.65; Longitude: -6.217), approximately 30 km from the field site. Temperature in the chambers was measured with a thermometer. Soil moisture was measured by soil probes buried at approximately 7 cm depth at the low N site. Analysis for  $CO_2$ ,  $N_2O$  and  $CH_4$  was carried out on a gas chromatographer (Shimadzu GC-2024) with automated injection system (Loftfield *et al.* 1997). The flux rates were calculated by using the ideal gas law and linear regression with chamber temperature and average air pressure during cover period. An exponential equation (Hutchinson and Mosier 1981) was used if R-squared was greater than 0.985 but less than 1.

### **Results**

Data from all three grass varieties were averaged for the high and low N sites because there was no significant difference in emissions between grass species. Figure 1a presents the fluxes for  $CO_2$ , which were in 2008 higher on high N plots (mean =  $173.6 \pm 30.1$ mg  $CO_2$ -C/m²/h) before and after cutting compared to low N sites (mean =  $144.1 \pm 26.9$  mg  $CO_2$ -C/m²/h). Similar results, though slightly lower, were found for 2009 after harvesting the plots.

Figure 1b presents high  $N_2O$  emissions after fertilizer application on high N plots in both years. In both 2008 and 2009, the highest fluxes were measured one day after fertilizing the site. The maximum  $N_2O$  emissions from the high N plots were  $1280.7 \pm 606.7~\mu g~N_2O-N/m^2/h$  and  $2015.2 \pm 763.4~\mu g~N_2O-N/m^2/h$ , for 2008 and 2009 respectively.

Figure 1c presents soil moisture and  $CH_4$  emissions which were both lower in September 2009 than in September 2008. In 2008, the highest average value of methane production was higher on the low N site  $(50.5 \pm 42.9 \ \mu g \ CH_4 - C/m^2/h)$  compared to the high N site  $(18.3 \pm 17.5 \ \mu g \ CH_4 - C/m^2/h)$ . This correlation, though lower, was also observed in 2009. Due to heavy rainfall in September of both years, the soil was completely saturated to the soil surface during the measurement period. Therefore, soil moisture data should also apply to the soil layers above 7 cm depth as the spot for main microbial activity was found to be in the top soil layers just a few centimeters thick (Koschorreck and Conrad 1993). Slightly higher soil moisture was observed in 2008, due to heavier rainfall in the weeks before the sampling period (data not shown).

# Conclusion

# N<sub>2</sub>O fluxes

As in previous research, the present study found that  $N_2O$  production was enhanced by reduced aeration via soil saturation (Wrage *et al.* 2004) and large N-input. This emission can be caused not only by denitrification via microbial activity but also by fungal denitrification (Laughlin 2002). Due to the Nitrates Action Programme Regulations for Northern Ireland (DOE 2006), the fertilizer in this experiment had to be applied before the  $15^{th}$  of September even though the site was very wet. Therefore, it was hypothesised that the site would lose high amounts of N. Glatzel and Stahr (2001) found lower emissions of  $N_2O$  (50 and -20  $\mu$ g  $N_2O-N/m^2/h$ ) after application of cattle slurry (200 kg/ha/y) on a well aerated grassland site. Lower fluxes than in the present study (489  $\mu$ g  $N_2O-N/m^2/h$ ) were also found by Lampe *et al.* (2006), who investigated the effect of mineral fertilizer and slurry application on  $N_2O$  emissions (489  $\mu$ g  $N_2O-N/m^2/h$ ) on aerated grazed grassland.

# CH<sub>4</sub> fluxes

In this experiment, temporarily high rainfall events caused anaerobic soil conditions leading to CH<sub>4</sub> emissions. Well-aerated grassland usually shows a net uptake of CH<sub>4</sub> (Mosier *et al.* 1991, Kammann *et al.* 2001). Induced CH<sub>4</sub> emission in grassland has also been observed in 5cm soil depth after autumn rainfall (Kammann *et al.* 2001). In addition, lab experiments have verified an increase in CH<sub>4</sub> production after a long lag phase either due to flooding (Wang and Bettany 1997) or anaerobic incubation (Peters and Conrad 1995). Similar results were observed in the present study during the first measurement period in 2008, when a slight but steady increase in CH<sub>4</sub> production on already CH<sub>4</sub> emitting plots was found over 12 days of sampling. The effect of higher emissions from the low N plots could be a reason of higher water content on the low N site, as this effect is enhanced under slightly higher soil moisture in 2008.

### CO<sub>2</sub> fluxes

A correlation was observed between higher CO<sub>2</sub> emissions and lower CH<sub>4</sub> emissions on the high N site and

conversely lower  $CO_2$  efflux and higher  $CH_4$  production on the low N site. This could also be explained by higher soil moisture content on the low N site which could be observed indirectly through the higher production of methane. This effect was more distinct in 2008 with slightly higher measured water content. High water content leads to a limitation of soil respiration through a slower diffusion rate of oxygen in water (Conant *et al.* 2004).

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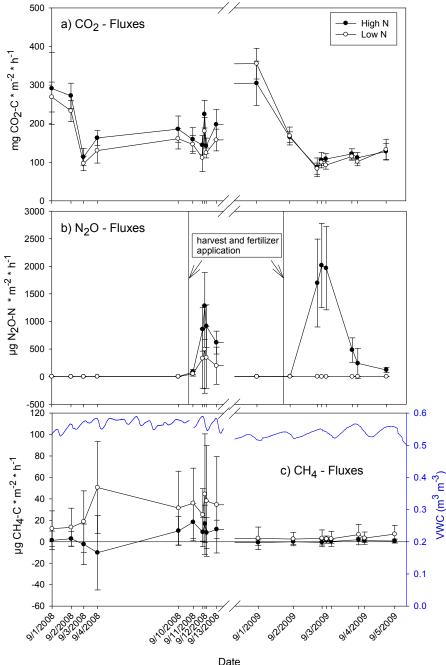


Figure 1. Fluxes for a) carbon dioxide (mg  $CO_2$ -C/m²/h), b) nitrous oxide (µg  $N_2O$ -N/m²/h) and c) methane (µg  $CH_4$ -C/m²/h) from Crossnacreevy, Northern Ireland during measurement periods in September 2008 and 2009 compared to c) vwc, volumetric water content (m³/m³)

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# Influence of pore size distribution and soil water content on N<sub>2</sub>O response curves

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#### **Abstract**

A laboratory study was conducted to determine nitrous oxide ( $N_2O$ ) response curves against water filled pore space, volumetric water content and volumetric gas content using intact cores collected from two soils with contrasting drainage characteristics. While both soils had similar total porosities, the soil considered to be poorly drained was found to have a higher macroporosity (pores  $> 30~\mu m$ ) mainly due to a larger volume of very large ( $>100~\mu m$ ) pores, resulting in this soil draining more rapidly at low tensions. Consequently, pore size distribution had a significant effect on the drainage characteristics. Volumetric water content was found to be the independent variable that related best to the measured  $N_2O$  emissions. An empirical relationship between  $N_2O$  emissions and volumetric water content, rather than water filled pores space, is applicable to soils with different bulk densities. This may provide a method for predicting  $N_2O$  emissions from a soil water balance model at a national level.

# **Key Words**

Volumetric water content, water filled pore space, gas diffusivity, intact cores, emission factors, nitrous oxide inventory.

# Introduction

Urine deposition onto pasture is New Zealand's largest source of nitrous oxide ( $N_2O$ ) emissions, representing c. 80% of the  $N_2O$  emissions inventory including direct and indirect emissions. Presently, an IPCC Tier 1 methodology is followed, where a single country-specific emission factor (EF<sub>3</sub>) of 1%, an average weighted according to soil drainage classes, is used for estimating emissions from excreta deposited onto grazed pastures within the national  $N_2O$  inventory (Ministry for the Environment 2009). However, a series of seasonal EF<sub>3</sub> field trials has shown that EF<sub>3</sub> varies throughout the year (Kelliher *et al.* 2005a) primarily due to varying soil water status at the time of field experiments. The development of seasonal and regional EF<sub>3</sub> values that reflect differences in soil water status will provide an important step towards a Tier 2 methodology for national  $N_2O$  inventory reporting.

Beneath a urine patch, where soil N concentrations are high, oxygen diffusion has a dominant influence on  $N_2O$  emissions. As oxygen diffusion rate in soils is difficult to measure, soil water content is often used as a proxy. Water filled pore space (WFPS) has been widely used to express soil water content in incubation and field studies. However, soils with different bulk densities will have different volumes of air and water at any given value of WFPS, resulting in considerable variation in relationships based on WFPS and  $N_2O$  fluxes. Thus it may be more appropriate to use other descriptors such as volumetric water content (VWC) or volumetric gas content (VGC) for estimating  $N_2O$  emissions across landscapes with varying bulk densities (Farquharson and Baldock 2008).

In a previous study, a water balance model was combined with an empirical relationship between  $N_2O$  emissions and soil gas content to develop a method to estimate  $N_2O$  emissions in the field from weather data (Kelliher *et al.* 2005b). This approach provides a potential method for determining spatial and temporal EF3 values for a Tier 2 inventory structure. In their study, the relationship between  $N_2O$  and soil gas content was determined in a laboratory study using re-packed cores from a single soil type. The aim of this trial was to determine which measure of soil water may be most suitable for predicting  $N_2O$  emissions from intact soil cores using two soils with contrasting soil physical properties.

## Methods

Experimental design

The main treatment of the experimental design was 5 different soil water tensions (-0.5 kPa, -1 kPa, -3 kPa, -5 kPa and -10 kPa), with a sub-treatment of soil type (well drained and poorly drained) and nitrogen addition

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(0N and +N). A poorly drained Otokia silt loam (Fragic Perch-gley Pallic soil, NZ soil classification) and a well drained Wingatui silt loam (weathered Fluvial Recent soil, NZ soil classification) were used for this laboratory study, as these soils have been extensively studied in previous seasonal EF3 field trials (e.g. de Klein *et al.* 2004, Sherlock *et al.* 2003). The physical nature of these soils is of interest because in some trials higher N<sub>2</sub>O emissions were observed from the well-drained Wingatui soil compared to the poorly-drained Otokia soil. Sixty intact soil cores (5 cm height, 10 cm diameter) were collected from each site using stainless steel rings. Soil bulk density, moisture release curves and the pore size distribution were determined for each core in addition to volumetric water and gas contents and WFPS. Cores were trimmed and the top soil surface "peeled" off to provide an unsmeared natural soil surface. The bottom of the cores were trimmed evenly and fitted with a fine gauze cloth. Earthworms were extracted from the cores using several approaches including saturation of cores, placing black plastic over cores and applying a mild electric shock to the cores for 15 seconds using a 9 V battery.

The trial was designed so that  $N_2O$  emission and moisture release data would be collected in parallel. This was accomplished as follows: 1) as soil water tension increased from 0 kPa to -10 kPa, all cores were weighed at each critical tension for determining moisture release curves; 2) as each batch of cores reached its assigned moisture tension for  $N_2O$  measurements, nitrogen treatments would be applied to the core surface and cores were allowed to equilibrate at the prescribed tension prior to the first  $N_2O$  emission measurement. 3) on completion of measurement of gas fluxes (at about 8 weeks after application of N), collection of moisture release data continued until all cores had reached -10 kPa. As denitrification is considered the primary source of  $N_2O$  emissions from pastoral land in New Zealand, nitrogen was applied to the "+N" cores as dissolved potassium nitrate at a rate equivalent to 500 kg N/ha. The "+N" and "0N" treatments were replicated 8 and 4 times, respectively.

## Nitrous oxide measurements

N<sub>2</sub>O emissions were measured on six occasions from each core, until emissions from '+N' treatments returned to levels measured from the '0 N' treatments. Emissions were determined by removing soil cores from the tension table and placing them in a plastic container. Headspace gas sample volumes of either 1 or 2 ml were removed from the container via rubber septa positioned in the lid. Gas samples were collected at 30 and 60 minutes following closure, while background air samples were used to represent 0 minutes. Gas samples were injected into 6 mL Exetainer vials containing ambient concentrations of N<sub>2</sub>O at atmospheric pressure, resulting in a pressurised vial containing 1 or 2 mL of container headspace air and 6 mL of ambient air. This allowed dilution of the sample, necessary due to the high headspace concentrations. The variation in the actual volume collected was required to adjust sample dilution. Following gas sampling, cores were weighed and returned to the appropriate tension. Gas samples were analysed for N<sub>2</sub>O concentrations by gas chromatograph using a SRI 8610 automated gas chromatograph.

The  $N_2O$  fluxes were calculated for each container from the increase in head space  $N_2O$  concentrations over the sampling time. The hourly  $N_2O$  emissions (mg N /m<sup>2</sup>/h) were calculated as follows:

$$N_2Oflux = \frac{\delta N_2O}{\delta T} * \frac{M}{Vm} * \frac{V}{A}$$

where,  $\delta N_2O$  is the increase in head space N<sub>2</sub>O concentrations over time ( $\mu$ L/L);  $\delta T$  is the enclosure period (hours); M is the molar weight of N in N<sub>2</sub>O; Vm is the molar volume of gas at the sampling temperature (L/mol); V is the headspace volume ( $m^3$ ); and A is the area covered ( $m^2$ ).

N<sub>2</sub>O response curves against increasing WFPS, VWC and VGC were generated for each soil type and for combined soil data and analysed using Genstat 10.

# Results

Pore size distribution

Total porosity was similar for the two soils while pore size distribution differed (Table 1) due to the Wingatui soil having a higher measured clay content of 37% compared to 32% for the Otokia soil. Soil bulk density was also higher for the Wingatui soil, at 0.88 Mg/m³ compared to 0.82 Mg/m³. Micropores (pores less than 30  $\mu$ m) represented 43% and 50% of the total soil volume for the Otokia and Wingatui soils, respectively. Consequently, the macropores (pores greater than 30  $\mu$ m) represented a larger soil volume in the Otokia (25%) than in the Wingatui (16%) mainly due to a greater proportion of very large pores (>100  $\mu$ m, equivalent to 0.1 mm) (Table 1). Because of this, Otokia soil will drain readily thereby decreasing the water content more rapidly with increasing tension during a drying phase following saturation.

Table 1. Pore size distribution of the Otokia and Wingatui soils.

Porosity and pore size distribution (% of soil volume)	Otokia	Wingatui
Total porosity	68.4	66.1
Microporosity	43.3	50.4
Macroporosity	25.1	15.7
pores between 30 & 60 μm	4.6	4.1
pores between 60 & 100 μm	2.6	1.7
pores between 100 & 300 μm	7.6	3.5
pores > 300 μm	10.2	6.0

# *N<sub>2</sub>O response curves*

 $N_2O$  emissions were greatest from the first gas sampling, conducted 4 days following equilibration at the prescribed moisture tension. Emissions declined rapidly as the moisture tension increased from -0.5 to -3 kPa, with emissions from the Otokia soil initially declining more rapidly compared to the Wingatui soil, presumably due to the Otokia soil containing a larger volume of very large pores (>300  $\mu$ m; Table 1) which drain rapidly.

 $N_2O$  response curves to soil water or gas content were most distinct when data was restricted to the first gas sampling occasion from the "+N" cores when nitrogen was not limiting. An analysis of the scatter grams of  $N_2O$  emissions against increasing water or gas content revealed that the data better fitted a broken line model rather than a curvilinear model. When relating WFPS, soil water or gas content to  $N_2O$  emissions across both soils, the strongest relationship was obtained when VWC was the independent variable ( $R^2 = 79\%$ , P < 0.0001; Figure 1). The intersection of the two lines occurs at  $0.55 \text{ cm}^3/\text{cm}^3$  (s.e.m. = 0.006). There was no significant difference in the relationships based on VWC for each soil type, allowing the data to be combined. The associated residual variance was 140, while the corresponding residual variance for VGC and WFPS was more than double, at 397 and 375, respectively, suggesting weaker relationships against  $N_2O$  emissions. Furthermore, in contrast to VWC, using either WFPS or VGC as a proxy of oxygen diffusion rates revealed significantly different broken line models for each soil type, which made impossible to combine the data for the two soil types.

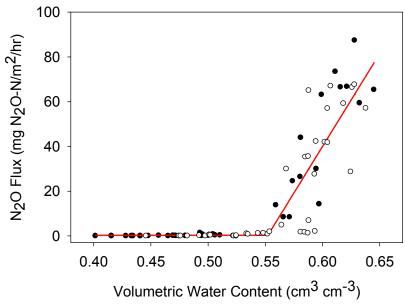


Figure 1. Scattergram of volumetric water content plotted against  $N_2O$  emissions, where  $\bullet$  = Otokia soil and  $\circ$  = Wingatui soil. Data is limited to emissions measured on first sampling occasion only. Broken line model fitted to pooled data has  $R^2$  = 79% (P < 0.0001). Y-intercept of the straight line = 0.3 mg  $N_2O$ -N/m²/hr (sem = 1.9) while the slope of the increasing line = 831 (sem = 88) and the intersection of the two lines occurs at 0.55 cm³ water /cm³ soil (sem = 0.006).

### Discussion

While both soils exhibited similar total porosities with values of approximately 66-68% v/v, it is the <u>distribution</u> of the pore size that influences the soil gas content of these soils above field capacity. The large proportion of very large pores in the Otokia soil will drain rapidly following rainfall or irrigation events resulting in a more rapid increase in soil gas content during a drying phase. This will allow greater oxygen diffusion which, in turn, will reduce  $N_2O$  production via denitrification. In practice this suggests that when the Otokia and Wingatui soils are subjected to the same tension during a drying phase following rainfall, the Wingatui soil will remain wetter for a longer duration, which may partly explain the higher  $N_2O$  emissions observed from this soil during earlier field trials.

The slower drainage and associated higher  $N_2O$  emissions from the Wingatui soil suggest that, in the top 50 mm, this soil is a poorer draining soil than the Otokia soil. However, the 'poorly drained' soil drainage classification for the Otokia soil relates to the whole soil profile, which is characterised by water perching on a slowly permeable subsurface fragipan restricting drainage to lower depths. This suggests that the current use of soil drainage status for weighting a national EF3 value may not be appropriate, considering the majority of  $N_2O$  production occurs in the topsoil and that previous studies using these soils have shown  $N_2O$  emissions from the 'well drained' Wingatui soil are often greater than those measured from the 'poorly drained' Otokia soil.

Volumetric water content was found to be the best independent variable relating to the measured emissions. This work has also demonstrated that, in contrast to WFPS and VGC, employing VWC as a key variable to potentially predict  $N_2O$  emissions allows data from soils with different bulk densities to be pooled to develop an empirical relationship that is applicable across soil types. For predicting emissions, this is currently one of the limitations of WFPS, a term that is used universally by many researchers studying  $N_2O$  emissions from soils. These results provide support to the suggestion that VWC may be a more appropriate predictor of  $N_2O$  emissions due to denitrification (Farquharson and Baldock 2008).

### Conclusion

While total porosity was similar for the two soils, the Otokia soil was found to have a higher macroporosity, mainly due to a larger volume of very large (>100  $\mu$ m) pores, resulting in this soil draining more rapidly at low tensions. Consequently, pore size distribution had a significant effect on the drainage characteristics in the top 50 mm (core height). VWC was found to be the independent variable that related best to the measured  $N_2O$  emissions: this was also the only variable where data from the two soils types could be combined. An empirical relationship between  $N_2O$  emissions and volumetric water content is applicable to soils with different bulk densities. Combined with a water balance model this may provide a method for predicting  $N_2O$  emissions at a national level

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# In situ determination of NO and N<sub>2</sub>O from cow-urine applied to a pasture soil under summer conditions

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### **Abstract**

A field experiment was performed during summer using bovine urine at 0, 500 and 1000 kg N/ha to study the effect of urine-N rate on  $NO_x$  ( $NO + NO_2$ ) and  $N_2O$  emissions. A Templeton silt loam soil (pH 5.2) was used (Typic Immature Pallic, New Zealand soil classification). The experimental design was a randomized complete block. The main objective of the study was to obtain  $NO_x$  data from pasture under bovine urine patches for New Zealand conditions. The experiment was run for 3 months with measurements of some pH, moisture, temperature and inorganic-N and gas ( $NO_x$  and  $N_2O$ ) fluxes, taken over this time. It was found that the emission factors after 3 months for NO-N in the summer were 0.15 and 0.20% of the urine-N applied for the 500 and 1000 kg N/ha rates respectively while the respective  $N_2O$ -N fluxes were 0.14 and 0.16%. Multiple regression analyses were used to predict the best regression model for NO-N flux at 500 and 1000 kg N/ha treatment. The best regression model was obtained at 1000 kg N/ha using the soil moisture and the rate of NO-N depletion as significant variables. In contrast, the best regression model for  $N_2O$ -N fluxes was obtained at 500 kg N/ha treatment using surface soil pH, logNO-N,  $N_2O$ -N:NO-N ratio and soil moisture as significant variables.

# **Key Words**

Nitric oxide (NO), nitrous oxide (N<sub>2</sub>O), bovine urine, season, multiple regressions.

### Introduction

Anthropogenic endeavours have led to changes in the global nitrogen cycle. As a consequence gaseous emission of nitric oxide (NO), nitrogen dioxide (NO<sub>2</sub>) (hereafter referred to as NO<sub>3</sub>), and nitrous oxide (N<sub>2</sub>O) have increased. Scientific interest in these gas emissions from agricultural soils has increased due to their adverse environmental effects, both globally and locally. Nitrous oxide is a gas that contributes to greenhouse warming and also a gas that can undergo oxidation in the stratosphere to form NO<sub>x</sub> which in turn can participate in photochemical processes. These processes have adverse effects on stratospheric ozone (O<sub>3</sub>) concentrations. The emission of NO<sub>x</sub> from soils is of significance due to its potential effect on tropospheric O<sub>3</sub> formation. Increasing levels of NO<sub>x</sub> can adversely affect air quality, which has implications for the health of humans, plants and animals. The economic loss of N fertilizer as NO<sub>x</sub> gas may represent 1-10% of the N applied (Veldkamp 1997). These NO<sub>x</sub> gases are also responsible for the atmospheric acidity and nitrogen to downwind ecosystems. In soils, the microbial processes responsible for NO<sub>x</sub> and N<sub>2</sub>O gas emissions are known to be nitrification and denitrification, while abjotic production also occurs to a lesser and unknown extent (Venterea and Rolston 2000). The majority of studies on NO<sub>x</sub> gas emissions have focused on fertilizer applications with very few studies (ca. 5) examining the potential for NO<sub>x</sub> emissions from urine patches in grazed pastures. Studies that have examined NO<sub>x</sub> gas emissions from urine have used unrealistically low rates of N, for New Zealand systems, or concentrated on soils with high moisture contents where NO<sub>x</sub> gas emissions might be expected to be low. Of these, none have examined urine-N rates and/or seasonal effects on urine-N NO<sub>x</sub> fluxes. There are no in situ studies in New Zealand temperate pastures that have examined the potential for NO<sub>x</sub> emissions from bovine urine.

The main objectives of this experiment were: To obtain the  $NO_x$  emission data from pastures under two rates of bovine urine, under New Zealand summer conditions; To examine the relationships between NO and the  $N_2O$  fluxes and between NO fluxes and the measured soil variables from urine treated soils.

# Methods

A field experiment was conducted in which urine, collected from the Lincoln University dairy farm, with urinary-N concentration of 10.5 g N/L was applied to experimental plots. Experimental plots were either gas chamber plots (0.029 m²) or soil sampling plots (0.16 m²). The experimental design consisted of three

treatments (500 kg N/ha, 1000 kg N/ha and a control) replicated 3 times. Gas sampling for  $NO_x$  and  $N_2O$  was conducted periodically for nearly 3 months using chemiluminescence and gas chromatography methods respectively. The soil  $NH_4^+$ -N and  $NO_3^-$ -N concentrations were measured concurrently with the gas sampling events over a depth of 0-7.5 cm but the soil  $NO_2^-$ -N concentration was determined for 3 soil depths of 0-2.5, 2.5-5.0 and 5.0-7.5 cm.

### Results

Results showed that urine-N rate significantly affected the inorganic-N concentrations. Maximum NH<sub>4</sub><sup>+</sup>-N and NO<sub>3</sub>-N concentrations were recorded at the highest urine-N rate (1000 kg N/ha) followed by the subsequent urine-N rate (500 kg N/ha) (Figures 1 and 2). The soil NO<sub>2</sub>-N concentrations did not show any significant differences between depths due to treatments. When data from the 3 soil depths were pooled the soil NO<sub>2</sub>-N concentrations were negatively correlated with soil pH (r = -0.22, P < 0.01). The NH<sub>4</sub><sup>+</sup> depletion rate was 1.8 fold higher in the 1000 kg N/ha than the 500 kg N/ha treatment. No significant differences in terms of surface soil pH were observed in urine-N treated soils. However, the urine-N treated soils had higher soil pH values than the control treatment. Fluxes of NO-N varied over time and with urine-N rate (Figure 3). Maximum NO-N fluxes were observed at the high urine-N rate of 1000 kg N/ha treatment. Cumulative NO-N losses for the 500 and 1000 kg N/ha treatments were 0.15 and 0.20% of the applied urine-N respectively. NO-N fluxes were positively correlated with surface soil pH, NO<sub>3</sub>-N, NH<sub>4</sub><sup>+</sup>-N, net ammonium depletion rates and net nitrate accumulation rates. Urine-N rate also significantly affected the N<sub>2</sub>O-N fluxes over time (Figure 4). Maximum cumulative N<sub>2</sub>O-N fluxes (0.16%) were recorded at 1000 kg N/ha followed by the 500 kg N/ha treatment (0.14%). When the N<sub>2</sub>O-N flux data from all sampling dates were pooled N<sub>2</sub>O-N fluxes were significantly correlated with surface soil pH and NH<sub>4</sub><sup>+</sup>-N concentration. Soil temperature and WFPS during the experimental period ranged from 14-30°C and 17.5-35.6% respectively.

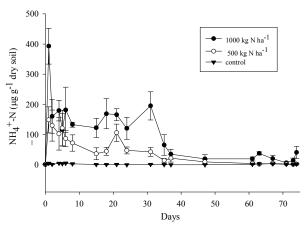


Figure 1 Soil  $NH_4^+$ -N concentrations over time (n = 3, error bars are  $\pm$  s.e.m.).

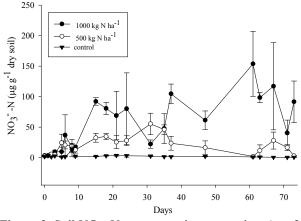


Figure 2. Soil  $NO_3$ -N concentrations over time (n = 3, error bars are  $\pm$  s.e.m.).

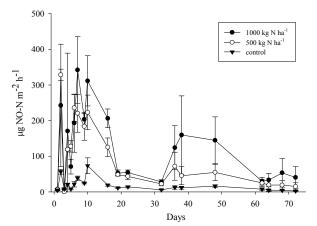


Figure 3. NO-N fluxes over time following urine treatment application (n = 3, error bars  $\pm$  s.e.m.).

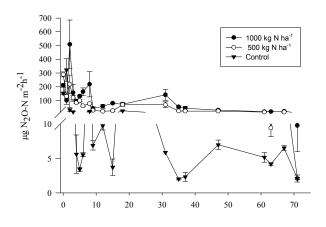


Figure 4. Soil  $N_2O$ -N fluxes over time following urine treatment application (n = 3, error bars  $\pm$  s.e.m.).

### Conclusion

The cumulative NO-N flux from the 500 kg N/ha treatment was very comparable with the maximum flux attained in the other field studies where bovine urine has been applied under summer conditions. No other in situ studies have been performed using 1000 kg urine-N/ha and the current study represents the first at this rate. No previous in situ urine studies have attempted to examine the relationships between the net NO-N flux, the soil  $NO_2$ -N pool and soil pH. Despite the presence of  $NO_2$ -N in the soil, no relationship was found between theoretical  $HNO_2$  concentrations and the NO-N flux. Thus net NO-N emissions are believed to have been predominately from microbial sources. Further evidence of biological production of NO was seen with the strong relationship between  $log N_2 O$ -N and log NO-N emissions. The gaseous N losses observed in the present study were not significant in agronomic terms, but assist in assessing the contribution of such losses to the atmospheric budget for  $log NO_2$ . Further studies are required to elucidate in-situ production mechanisms of NO and the relationship to  $log NO_2$  in the urine patch.

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# Kolbjörk: Carbon sequestration and soil development under mountain birch (Betula pubescens) in restored areas in southern Iceland

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### **Abstract**

Iceland has suffered from severe soil erosion since settlement with losses up to 60% of pre-settlement vegetation. Large land remediation projects are underway using *Betula pubescens*. A huge potential for carbon sequestration exists by this revegetation of degraded areas. Little is known about soil development when using native forest vegetation for land restoration. This study aims to both estimate the carbon storage and sequestration rate in these systems and establish constrains on the pedogenetic factors and their influence on soil development. A chronosequence of afforested areas, both natural succession from sown plots and planted areas, reaching 60 years back has been established and compared to natural old-growth forests in the same area. 3 subplots were identified for each age group and soil sampled along transects in each plot. Soil profiles were described, sampled and water content sensors installed at representative sites. Profiles showed stronger horizonation with age with a slight lowering of soil pH in the topsoil.

# **Key Words**

Pedogenesis, restoration, Andisol, erosion, Iceland.

#### Introduction

# Climate and scene setting

Iceland is an active volcanic island located on the North Atlantic ridge just below the Arctic Circle (~63°-66° N, 13°-24°W). Total land area is 103 000 km². The climate is humid and cool-temperate, characterized by cool summers and mild winters. Shifts between frost and thaw are common. Annual mean temperature ranges from 2-6°C with mean July temperature about 6-10°C (Einarsson 1976). Mean annual precipitation ranges from 600-2000 mm in lowland areas and >400mm in the interior (Einarson 1976). The growing season is short, 89-144 days per year (Friðriksson and Sigurðsson 1983)

### Icelandic soils

The soils in Iceland are predominantly volcanic in origin belonging to the Andisol order (Arnalds 2004). The soils are young, having mostly developed since the younger Dryas period around 10 000 years ago. They are heavily influenced by aeolian deposition, in part due to volcanic activity but also due to severe wind erosion in large parts of the country. Other influential factors are the cold maritime climate with intense cryoturbation (Arnalds *et al.* 2000; Arnalds 2008; Arnalds and Kimble 2001). The main broad categories of Icelandic soils are freely drained brown Andisols, both mineral and organic wetlands soils and soils of the barren deserts (Arnalds 2008). The desert soils are typically sandy Andisols with low water holding capacity, limited sources of macronutrients, rich in volcanic glass and have low amounts of allophane clay and organic C compared to vegetated areas (0.08-0.5 kg C/m² in desert soils compared to 40-90 kg C/m² in brown Andisols) (Arnalds and Kimble 2001). The deserts are erosional surfaces once covered with vegetation (Arnalds and Kimble 2001).

# Vegetation and land degradation

The vegetation cover at the time of settlement (AD 874) is estimated to have been about 50-60% with birch woodlands (*Betula pubescens*) covering about 25-30% of the country. (Anonymous 2001). Today, only about 25% of Iceland is covered with continuous vegetation of which only 1% is original birch woodland. Total loss of soil organic carbon (C) is estimated to be 120-500 x 10<sup>6</sup> Mg since settlement; representing a serious environmental problem still on-going with estimated yearly losses 50-100 x 10<sup>3</sup> Mg C year-1 (Óskarsson *et. al.* 2004). In response to severe land degradation Iceland has a long history of concern for the land, and restoration efforts have continued for more than 100 years. Carbon sequestration is a major benefit of land restoration and revegetation programs, particularly in the severely degraded desert areas. The carbon

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storage is 0.01 to 0.5 t C/ha for vegetation, both above and below ground (Aradóttir *et al.* 2000) and the sequestering rate 0.6 t C/ha/yr in soils for reclaimed areas a rate maintained for >50 years (Arnalds 2000). Both numbers are for unforested reclaimed areas.

# Kolbjörk (CarbBirch) project

### Overview

Kolbjörk is a 3-year project focusing on ecosystem development and potential for carbon sequestration using mountain birch (*Betula pubescens*) for land restoration on severely degraded areas. In view of government plans to reforest large parts of the country with native mountain birch further research on the ecosystem development in afforested areas is essential. Only one study is available for carbon sequestration in afforested areas (Snorrason *et al.*), and none were directed at afforestation of severely degraded land. The Kolbjörk project is a comprehensive study of ecosystem changes, carbon sequestration and carbon flux in reclaimed mountain birch areas. The project covers changes in understory vegetation community composition, carbon fluxes and productivity of plant biomass, colonization of mycorrhizal fungi and soil development in a chronosequence of established tree plots dating back 60 years with comparison to natural old growth forests in the area. Typically restoration efforts are directed at areas that are distant from remnant natural forests. Few studies have analyzed the rate and characteristics of the old growth ecosystem development.

# Study area

The research sites are in a severely degraded area close to an active volcano, Hekla in south Iceland (Figure 1). The landscape has been badly eroded since settlement times. The land is inundated on a regular basis with volcanic ejecta from nearby volcanic systems, covering vegetation and causing destabilisation of surfaces by both directly killing vegetation and subsequent erosion due to aeolian movement of tephra cutting and covering above ground biomass. Mature forested systems appear to be tolerant to tephra fall as several oldgrowth forests still exist in the area and probably have survived since before settlement times (Aradóttir 2007). In order to stabilize the area and prevent further erosion due to volcanic events a large reforestation project is underway. The aim is to establish forests over approximately 900 km² using native species, both mountain birch and willows (Aradóttir 2007).

# Research sites

Three reclaimed forested areas were picked for study and compared to two old growth forests (Figure 2). Reclamation at two sites, Gunnlaugsskógur and Stóri Klofi, commenced about 1940 on severely degraded land that had been devoid of tree cover for a long time. The vegetation has since spread from original plots onto the sand-covered lava. To get two complete chronosequences a third site, Bolholt, was needed, at Bolholt, where planting started in the 80's, also on sand covered lava. The chronosequences are the compared to two natural old growth forests, Hraunteigur and Búrfell.

# Sampling scheme

Within each age group in each area, three 20x10m plots were randomly chosen. Each plot was split into two 10x10 subplots, one for sampling and one for monitoring. Soil samples were taken on transects on the plots with 5 sub-samples taken at 2 m intervals combined into one and two replications. Each sample was split into three depth increments 0-5, 5-15 and 15-30 cm. Bulk density was determined both by inner diameter of the soil corer and in small profiles taken close to the areas. In addition soil profile descriptions and horizon sampling was done close to oldest reclaimed plots, pioneering stage plots and unforested plots in the Stóri Klofi area along with Hraunteigur old growth area, with two profiles for each age group. Stóri Klofi was picked as an intensive sampling site due to minimal spatial variability within the area compared with other sites.



Figure 5. Location of study area

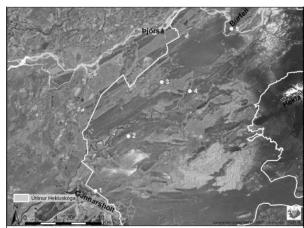


Figure 6. Distribution of study sites. 1 is Gunnlaugsskógur, 2 Bolholt, 3 Stóri Klofi, 4 Hraunteigur and 5 Búrfell. From Halldórsson *et al.* 2009)

# Soils in the sample areas

Due to intensive soil erosion and subsequent movement of material with wind and water, the spatial variability of the soils is very great inside each area. In many areas the old soil can be found at less than 30 cm depth from current surface with aeolian and fluvial sand in between. Soils in the old growth areas show effects of aeolian deposition, but limited erosion.

# Field description

Soil morphology and horizons were described according to the US Soil Taxonomy. Profiles were sampled by horizon, for analysis and for bulk density measurement. Tephra layers within the profiles were described and sampled. Water content sensors were placed in representative profiles to monitor changes in soil water.

# Chemical analysis

All samples: Total organic C and N, was determined by dry combustion. Clay content was determined by flushing with oxalic acid and subsequent analysis with ICP. CEC and AEC measured. pH was measured in KCl, water and NaF. Chosen samples are flushed with pyrophosphate for determination o organic matter in OM-metal complexes. Water retention was also measured on profile samples.

# **Discussion**

By determining the carbon stored in the sites, carbon sequestration rates and potential can be estimated for planned restoration programs. With the large sequestering potential of Andisols this will help achieve the goal of carbon neutrality for the country. Determining rate and extent of soil development after restoration from 'zero', i.e. from severely degraded areas largely devoid of vegetation, in the last 60 years increases understanding of the pedogenetic processes in Iceland and may help understand the revegetation and soil development after the last Ice Age. Stronger horizon formation with time has already been determined visually in the field and the extent of this difference will be further determined in the lab analysis. The amount of amorphous clay in the soils along with variable charge CEC can be used as an indicator of the extent of soil formation (Dahlgren *et al.* 2004). Soil organic matter (SOM) in Andisols is bound up in metal-hummus and amorphous clay-hummus complexes (Dahlgren *et al.* 2005) making the OM recalcitrant and not readily available for decomposition greatly increasing the stability of the SOM.

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# Links between emissions of nitrogen and sulfur gases from acid sulfate soils: field evidence

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# **Abstract**

Field scale emissions of nitrous oxide, nitrogen oxides and sulphur dioxide, measured by micrometeorological techniques, were examined to investigate a suggestion from laboratory studies that reduction of nitrate by pyrite could explain the very large emissions of nitrogen gases and sulphur dioxide from acid sulphate soils (ASS). All three of the target gases were emitted simultaneously from a bare ASS in the field, as they were in laboratory experiments in which nitrate solutions were added to pyrite or pyritic soil. However, the presence of a crop made it difficult to decide if chemodenitrification was at work in the field because of effects on soil evaporation and possible foliar absorption of emitted gases. The possibility remains that reaction between nitrate and pyrite might contribute to very high N2O emissions from ASS. More work on bare field soils is needed.

# **Key Words**

Nitrous oxide, sulphur dioxide, nitrification, denitrification.

### Introduction

In a whole-of-season study of emissions of greenhouse gases from an acid sufate soil (ASS), Denmead  $\it{et~al.}$  (2009) found that emissions of nitrous oxide (N2O) were extraordinarily large and prolonged. For the whole year they were the equivalent of 21% of the 160 kg of nitrogen (N) applied to the crop as fertiliser. The authors suggested that the porosity and high carbon content of the ASS at their experimental site coupled with frequent rainfall leading to high water filled pore space (WFPS) were important drivers of the large emissions, but also suggested that alternative mechanisms be explored. Macdonald  $\it{et~al.}$  (2004) demonstrated that ASS also can be significant sources of SO2, perhaps accounting for about 3% of known anthropogenic emissions of sulfur (S). The SO2 emissions seemed coupled to evaporation of soil water containing sulfite. In a companion paper to this Congress, Macdonald  $\it{et~al.}$  (2010) report laboratory studies which indicate that interactions between iron and nitrogen cycles also might explain the large emissions of SO2 from ASS. They suggest that in ASS, nitrate interacts with reduced iron in the soil profile, producing nitrous oxide (N2O) and oxides of nitrogen (NOx) as well as sulfur dioxide (SO2). Here, we report field studies on an ASS of the simultaneous emissions of these three gases, which, while not conclusive, confirm at least some of the laboratory findings.

### Methods

Site

The experimental sites were in sugarcane fields on the farm of W. Stainlay on coastal lowlands near Murwillumbah, NSW. Soils in the region are sulfuric and are classified formally as Sulfaquets and Humaquets (Soil Survey Staff 1998), commonly referred to as ASS. During periods of high rainfall, they are often inundated. They are characterised by a surface organic horizon 0.2-0.3 m deep (a clay loam with 10% organic carbon and pH  $\sim$ 5), a strongly acidic A2 horizon (pH < 4) extending to around 0.5 m, a reduced B horizon and often, a water table at depths of 0.5-0.7 m. The acidic A2 horizon is formed from the oxidation of pyrite.

# Studies

All three target gases were measured simultaneously in 3 campaigns, the first in 2003 and the last in 2007. The first campaign was conducted in a fallow sugarcane field, and the second and third were in a sugarcane crop at different stages of its growth. The field where the crop was growing was within 200 m of the first

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field. The first measurements were made when the crop was starting to ratoon after harvest and was between 0.4 and 0.9 m high and the second were made 11 months later, shortly before the crop was due for harvest again and was 4 m high. Rain occurred in all 3 campaigns. Particularly heavy falls occurred during the first and second campaign and persistent rain in the third. The rainfalls and the water filled pore space and temperature of the top 10 cm of soil along with evaporation rates are shown in Figure 1a.

## Emission measurements

Micrometeorological techniques were employed to measure gas emissions using a flux-gradient technique in which fluxes were calculated as the product of a transfer coefficient derived from aerodynamic theory and the difference in gas concentration between two heights above the soil surface (Denmead 2008). The necessary measurements to derive the transfer coefficient were the wind speeds and air temperatures at the two heights in the first campaign and turbulence statistics provided by a 3D sonic anemometer in the other two. The concentrations of N<sub>2</sub>O were measured with a Fourier transform infrared (FTIR) spectrometer, those of SO<sub>2</sub> by a pulsed fluorescence SO<sub>2</sub> analyser (Monitor Labs 9850), and those of NO<sub>3</sub> by a chemiluminescence gas analyser (Monitor Labs 9851), all instruments measuring on-line in the field and returning one-minute averaged concentrations. Temperatures and moisture contents of the soil down to a depth of 20 cm were measured as well. All measurements were processed as ½-h means. The first campaign was conducted between 27 November and 14 December, 2003. Urea fertiliser was drilled into the soil at a rate equivalent to 50 kg N/ha mid-way through the observation period on October 8. The 2<sup>nd</sup> campaign was conducted between 18 October 2005 and 2 November 2005 and the 3<sup>rd</sup> conducted in the same cropped field between 13 and 19 September 2006. Urea fertilizer at 160 kg N/ha was applied to the field on 18 October 2005. Some results of these campaigns, but not all, have been included in previous conference proceedings, but as reports of individual gas emissions and not in the context of exploring links between sulfur and nitrogen processes in ASS.

### Results and discussion

 $N_2O$ 

Average daily emission rates in the 3 campaigns are shown in Figure 1b. These exhibit a classical dependence on available soil N and the WFPS. In the first campaign, they virtually doubled after 8 December when recent rain had increased the WFPS from around 40% to the critical level for nitrification and N<sub>2</sub>O production of 60% (Davidson and Schimmel 1995). In the 2<sup>nd</sup> campaign, the WFPS was always between 60 and 80%, available N was plentiful, and N<sub>2</sub>O emission occurred at an increasing rate throughout. In the 3<sup>rd</sup> campaign, the WFPS was close to saturation level at which N<sub>2</sub>O is produced through denitrification, and significant amounts of the gas were emitted. Since the supply of fertiliser N was exhausted by then (Wang *et al.* 2008), N<sub>2</sub>O production may have been augmented by reaction between nitrate and pyrite in the ASS. This possibility exists for the other campaigns as well since the rates of N<sub>2</sub>O emission in all of them were much greater than typical literature values. The default emission factor for soils in many greenhouse gas inventories, including the Australian inventory is 1.25%, whereas that for only 3 days after fertilisation in the 1<sup>st</sup> campaign was 2.6% and for the whole growing season in 2005-2006 was 21%.

#### $SO_2$

Average daily emission rates are shown in Figure 1c. Macdonald  $et\ al.\ (2004)$  noted that  $SO_2$  emission was coupled to evaporation, but also that emissions were higher from a drying soil than a wet one, presumably because the gas stayed in solution until the wet soil had dried sufficiently. This was observed in the laboratory studies by Macdonald  $et\ al.\ (2010)$  and was very clear in the field studies reported here. For instance, in the  $1^{st}$  campaign,  $SO_2$  emissions were twice as large when the soil was dry before 63 mm of rain fell as they were afterwards. This behaviour says nothing about the mechanism of  $SO_2$  production, however, but it does mask any link between  $N_2O$  and  $SO_2$  production because  $N_2O$  is not highly soluble and its production appears to be linked positively with soil wetness. We note that the data presented in Figure 1c confirm the early observations of  $SO_2$  production in ASS by Macdonald  $et\ al.\ (2004)$ . In the present study, the soil was a source rather than a sink on 28 of the 32 days of data available.

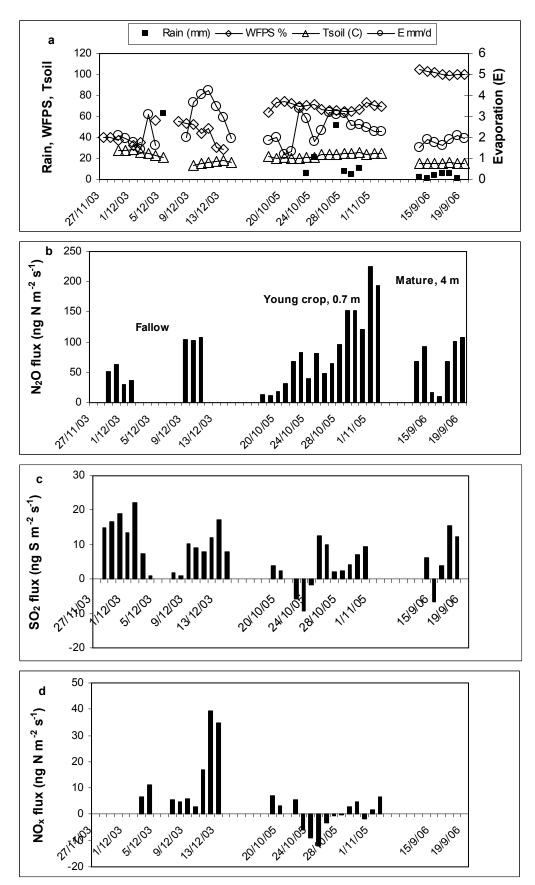


Figure 1. (a) Rainfall, water filled pore space and temperature in surface soil, and daily evaporation during 3 campaigns; (b) Average daily rates of emission of  $N_2O$ ; (c) Average daily rates of emission of  $SO_2$ ; (d) Average daily rates of emission of  $NO_x$ .

 $NO_r$ 

Average daily emission rates are shown in Figure 1d. Macdonald *et al.* (2010) found that  $NO_x$  was emitted in all their laboratory studies. This was also the case in the study on the fallowed field (1<sup>st</sup> campaign) reported here. Emission rates were a substantial fraction of those measured for  $N_2O$  and were highest after rain and fertiliser application. However, they were much smaller and sometimes negative in the 2<sup>nd</sup> campaign when a crop cover was present. Plants are known to act as sinks for  $NO_x$  (and  $SO_2$  also), particularly when the foliage is wet. Again, this is a complicating factor in linking N and S emissions.

### **Conclusions**

Field measurements of emissions of  $N_2O$ ,  $SO_2$  and  $NO_x$  from an ASS substantiate the laboratory findings of Macdonald *et al.* (2010) in confected systems combining nitrate solutions and pyrite or pyritic soils in as much as they demonstrate that all 3 gases can be produced and emitted simultaneously. This was seen most clearly in a field campaign on bare soil. However, the presence of a crop makes it difficult to demonstrate links between N and S production, not only because it influences evaporation from the bare soil, but also because the foliage can absorb both  $SO_2$  and  $NO_x$  as they diffuse through the crop canopy to the atmosphere. Not all the production of the N gases can be attributed to reduction of nitrate by pyrite because their production appears to occur mostly during nitrification, the process of nitrate formation. However, it is possible for chemodenitrification through nitrate reduction by pyrite in ASS to augment the formation of  $N_2O$  through classical pathways. Certainly the extraordinarily large emissions of  $N_2O$  from ASS warrant further research along these lines.

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# Loss of nitrogen by ammonia volatilization and NOx emission after application of urea to irrigated maize in Shanxi Province, China

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### **Abstract**

An experiment, using emerging micrometeorological techniques, was conducted on a urea fertilized maize crop in Shanxi Province in northern China to determine the importance of ammonia volatilization and  $NO_x$  emission as indirect greenhouse gases. The results showed that 6% and 1.2% of the applied N was lost as ammonia and  $NO_x$ , respectively.

### **Key Words**

Nitrification, denitrification, backward Lagrangian dispersion.

## Introduction

Most of the maize produced in China is grown in the northern part of the country (~70% of the total area planted) where yields in the last 50 years have increased from 1180 kg/ha to 5000 kg/ha mainly as a result of the application of fertilizer nitrogen (N) (Zhen et al. 2006). However, due to the lack of direction many farmers have applied too much fertilizer which has resulted in low N use efficiency (Goa et al. 2009). The reason for the low efficiency is that much of the N applied is lost from the plant-soil system by ammonia (NH<sub>3</sub>) volatilization, during nitrification, and by leaching, erosion, runoff, and denitrification (Yan et al. 2003; Zhu and Chen 2002). The N may be lost as NH<sub>3</sub>, nitrogen oxide and nitrogen dioxide (collectively referred to as NOx), the greenhouse gas nitrous oxide (N<sub>2</sub>O) and dinitrogen, and the amounts lost are influenced by the ecosystem, soil characteristics, cropping procedure, fertilizer techniques, and prevailing weather conditions. While not regarded as greenhouse gases, NH<sub>3</sub>, and NO<sub>x</sub>, play important roles in the greenhouse story through the formation of secondary aerosols which affect the earth's radiation balance. As the formation of secondary aerosols is expected to have significant effects on the variability and intensity of the Asian Monsoon (MAIRS 2008) it is important that reliable data are available for assessing the impact of increased fertilizer N use on the emission of these gases. The accuracy of the values obtained for NH<sub>3</sub> and NO<sub>x</sub> emission from monsoon Asia have been questioned (Wang et al. 2004; McElroy and Wang 2005). The values obtained for NO<sub>x</sub> emission from soil are uncertain (Yan et al. 2005) and one reason may be that most have been obtained as spot measurements with chambers (Veldkamp and Keller 1997). Consequently an experiment was conducted on a urea fertilized maize crop in Shanxi Province in northern China to determine the importance of NH<sub>3</sub> volatilization and NO<sub>x</sub> emission using the best available emerging micrometeorological techniques.

#### Material and methods

The experiment was conducted in a farmer's field at Yongi, Shanxi Province, China in July 2008. The cultivated horizon (0-20 cm) of the soil at the site contained 16.6% sand, 46% silt and 37.4% clay. It had a pH (1 soil: 5 water) of 8.5 and contained 9.6 g/kg organic C, 1.09 g/kg total N, 6.3  $\mu$ g N /g soil as ammonium and 5.1  $\mu$ g N /g soil as nitrate. The bulk density of the soil was 1.23 g cm³. Maize (variety Nongda 108) was seeded on June 6 after harvesting wheat. Prilled urea (60 kg N/ha) was applied by the traditional point deep placement technique at a depth of 5-10 cm on July 9 (33 days after seeding) between 0900-1100, and 1600-1830. The technique used by the farmer involved removal of a small amount of soil to the required depth with a hoe, addition of a calculated amount of urea to the hole by hand and covering the urea with soil.

Ammonia volatilisation was determined through application of a micrometeorological backward Lagrangian stochastic (bLs) dispersion technique (Flesch and Wilson, 2005) that infers rates of emissions of gases from defined source areas from measurements of gas concentrations upwind and downwind of the area. The bLs

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technique uses a Lagrangian dispersion model to simulate the trajectories of air parcels arriving at the gas sensors and traces the parcels backwards from the sensors. The numbers of touchdowns of parcels in the source area and outside it provide the means to attribute the gas flux to emissions from the source and background areas. The simulated ratio of the atmospheric gas concentration measured by the sensor  $C_g$  to the rate of emission from the source area  $F_0$  is given by

$$\left(C_g/F_0\right)_{sim} = (1/n)\Sigma[2/w_0], \tag{1}$$

where n is the number of simulated trajectories (50,000 in the present application) and  $w_0$  is the vertical velocity of particles at touchdown. Then the actual emission rate is given by

$$F_0 = (C_g - C_b)/(C_g/F_0)_{sim},$$
 (2)

where  $C_b$  is the background (upwind) concentration. The calculations required to evaluate Eq. (1) and (2) as well as the specification of source and background areas and the type and location of sensors are facilitated by use of the interactive software package WindTrax (WindTrax, 2006). The simulations require measured statistics of the atmospheric turbulence as well as the height and locations of the sensors and the wind speed and direction. Turbulence statistics were measured with a 3-D sonic anemometer (Campbell Scientific CSAT-3) installed in a neighbouring maize field. Ammonia concentrations were measured with a chemiluminescence analyser (Model EC9842T; Ecotech, Melbourne, Australia) installed near the centre of the fertilized plot and sample lines (6 mm diameter polyethylene tubing) were run to the analyser from intake points at the plot centre and 10 m upwind of the plot boundary. Measurements of NH<sub>3</sub> concentrations were made initially at 1.5 m above the ground increasing to 2 m as the crop grew. The same analyser was used to determine the concentration of NO<sub>x</sub>. The analyzer measures NO concentrations in the air stream directly and NO<sub>2</sub> concentrations after the stream has passed through a converter to change NO<sub>2</sub> to NO.

The fertilized area was divided into 3 blocks representing the western, central and eastern sections, and field moist soil samples were collected at intervals after fertilizer application using a soil corer with an external diameter 4.46 cm. Six replicate cores at depths of 0-15, 15-30, 30-45, 45-60, 60-75 and 75-90 cm were taken from each block and the individual layers were combined for analysis. On each occasion 10 g moist soil was extracted with 20 mL of 2 M KCl containing 5 mg/L phenylmercuric acetate solution for determination of urea, ammonium, and nitrate. Urea in the soil extracts was determined using a modified diacetymonoxime method (Mulvaney and Bremner 1979), and ammonium and nitrate were determined by a colorimetric procedure using a Technicon Autoanalyser (Rayment and Higginson 1992). The denitrification rates at the six different depths in the soil were determined by an acetylene inhibition method (Aulakh *et al.* 1991).

# **Results and discussion**

One day after fertilizer application (10 July), when 14 mm rain fell, the moisture content of the 0-15 cm surface soil was 16% and it decreased to 13.3% on 14 July. Following rain on 14, 17 and 21 July the moisture content increased to 22.4%. The water filled pore space decreased from 36.8 on 10 July to 30.4% on 14 July and increased to 51.5% on 22 July. After the rain on 10 July there was sufficient water for hydrolysis to occur and the concentration of urea decreased rapidly from 585 to around 100 µg N/g soil on 12 July and remained at that level until 19 July. Most of the urea had been hydrolyzed by 22 July. The ammonium concentration increased from 6.3 to ~74 μg N/g soil on 10 July and remained high until 19 July. By 22 July the ammonium concentration had decreased to 5 μg N/g soil. The nitrate concentration increased from 5.1 to 9.6 µg N/g soil on 10 July and remained close to 9 µg N/g soil throughout the experimental period. The relatively constant ammonium concentrations and low values for nitrate up to 19 July suggest that the nitrification rate in this soil was slow. The denitrification rates determined by the procedure of Aulakh et al (1991) were low (range 2.9 to 115.9 g N<sub>2</sub>O /ha/day) in line with the low water filled pore space (well below the 80% critical level for denitrification, Linn and Doran 1984). Denitrification varied with time and depth in the soil profile, but in general most of the denitrification took place in the 0-15 cm surface layer of soil. The rate of denitrification increased towards the end of the experimental period when the water filled pore space increased due to heavy rain.

# Ammonia loss

Overall NH<sub>3</sub> loss rates were slow and very little NH<sub>3</sub> was lost until 2 days after rain fell on 10 July (Figure 1). Ammonia volatilization is controlled by pH and the ammoniacal N concentration in the surface soil, temperature and wind speed (Sherlock *et al.* 1995). The pH of the unfertilized soil was high (8.5) and this would have been increased in the vicinity of the urea prills after urea hydrolysis so that some of the ammoniacal N would have been in the NH<sub>3</sub> form with the potential to be lost. However, placement of the

urea below the soil surface would have ensured that the ammoniacal N concentration at the soil surface would have been low and NH $_3$  would have had to diffuse to the soil surface before any loss could occur. Some diffusion obviously occurred and the rate of loss increased from  $\sim 0.1~\mu g~N/m^2/s$  on 12 July to 2.3  $\mu g~N/m^2/s$  on 14 July (Figure 1). Loss rates then gradually decreased until 17 July when the rate of loss increased to 1.8  $\mu g~N/m^2/s$ . Loss rates were again reduced by the rain late on 17 July. The variation in loss rates after 14 July seems to be due to changes in wind speed and temperature. On 17 July the higher wind speeds ( $\sim 4~m/s$ ) and temperatures ( $\sim 38$ °C) combined to produce a faster loss rate. The total loss of 6% of the applied N was much lower than the 11-12% loss observed in other experiments with deep placement on the North China Plain (Zhang *et al.* 1992; Cai *et al.* 2002). The higher losses in those experiments may have been due to the higher rates of fertilizer application.

# $NO_x$ loss

The rates of loss of  $NO_x$  varied throughout the day and throughout the experimental period (Figure 1) and averaged  $0.1\mu g\ N/m^2/s$ . Emission commenced at a slow rate on 12 July and increased gradually to a maximum of  $0.5\ \mu g\ N/m^2/s$  on 16 July. The total loss of  $NO_x$  during the experiment was 1.2% of the applied N. This is far greater than the fertilizer derived emission derived by others. Veldkamp and Keller (1997) evaluated measurements obtained with different fertilizers, soils and climates and concluded that on average 0.5% of fertilizer N was emitted as  $NO_x$ . Stehfest and Bouwman (2006) summarized 189 emission measurements for agricultural fields and developed a statistical model to simulate  $NO_x$  emission from soil taking into account the influence of factors such as N application rate, soil N content and climate. They calculated the fertilizer induced emission from soil to be 0.55% of the nitrogen applied. Yan et al (2005) using a similar technique arrived at a value of 0.7%.

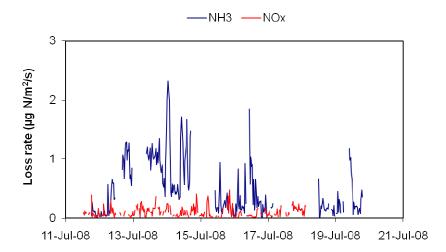


Figure 1. Ammonia and NO<sub>x</sub> emission following application of urea to maize in China.

 $NO_x$  can be produced in soil as a by-product of nitrification and denitrification, but at low water filled pore space it is generally accepted that nitrification is the important process (Ludwig *et al.* 2001). As the water filled pore space in this study was between 30% and 37% until rain fell on 19 July it might be assumed that  $NO_x$  was formed mainly by nitrification. The relatively constant ammonium concentrations in the surface soil for the first 10 days after fertilization and the low nitrate concentrations indicate that nitrification, while slow, did occur. However, the results of the denitrification study suggest that denitrification was also occurring in the surface soil, presumably in anaerobic microsites. Consequently we are not able to determine the mechanism for the production of the  $NO_x$  in this study.

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# Management practices impact on soil nitrous oxide emission in the northern Great Plains, USA

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#### **Abstract**

Management practices may influence soil N<sub>2</sub>O emission, a greenhouse gas responsible for global warming. The effects of irrigation, tillage, crop rotation, and N fertilization were evaluated on soil surface N<sub>2</sub>O flux and soil temperature and water content at the 0- to 15-cm depth from April to November in 2008 and 2009 in eastern Montana, USA. Treatments were two irrigation practices (irrigated and non-irrigated) and five cropping systems [conventional-tilled barley with N fertilization (CTBFN), conventional-tilled barley with no N fertilization (NTB-PN), no-tilled barley with N fertilization (NTB-PN), no-tilled barley with N fertilization (NTB-PN), and no-tilled barley with no N fertilization (NTBON)]. The N<sub>2</sub>O flux varied with changes in soil temperature and water content, peaking immediately following substantial precipitation and/or irrigation (>30 mm) over 7 d period. Cumulative N<sub>2</sub>O flux from April to November was greater in non-irrigated than in irrigated practice in 2008 and greater in CTBFN than in CTBON, NTB-PN, and NTBON in 2009. The flux was greater with N fertilization than without in 2009 and greater in 2008 than 2009. Increase in N substrate availability due to N fertilization and soil water availability due to irrigation and precipitation probably increased soil microbial activity that increased soil N<sub>2</sub>O emission.

# **Key Words**

Crop rotation, irrigation, nitrogen fertilization, nitrous oxide, soil temperature, soil water, tillage.

### Introduction

Nitrous oxide, although emitted in trace amount, is one of the most potent greenhouse gas responsible for global warming because it is 296 times more powerful than  $CO_2$  in terms of global warming potential (IPCC 2001). Agriculture is the main source of anthropogenic  $N_2O$  emission due to N fertilization to crops, manure application, atmospheric N fixation, and soil organic matter mineralization (IPCC 2001). Although tillage and N fertilization influence soil  $N_2O$  emission (Dusenbury *et al.* 2008), little information is available about the effects of soil and crop management practices on  $N_2O$  emission in the northern Great Plains, USA. The objective of this study was to evaluate the individual and combined effects of irrigation, tillage, crop rotation, and N fertilization on soil surface  $N_2O$  flux from April to November in 2008 and 2009 in the northern Great Plains, USA.

# Materials and methods

Soil surface N<sub>2</sub>O flux was measured from 9 A.M. to 12 A.M. twice a week to once in every two weeks from April to November in 2008 and 2009 from a static chamber (Hutchinson and Mosier 1981). A chamber made of polyvinyl chloride. 20 cm diameter by 15 cm tall, was installed to a depth of 7.5 cm in the soil in each treatment. A cover, 20 cm diameter by 10 cm tall, was placed at the top of chamber, and gas samples were collected at 0, 20, and 40 min by injecting a needing in the chamber and transferring them in Extainers. The N<sub>2</sub>O concentration in the gas sample was measured with a gas chromatograph in the laboratory. At the time of gas sampling, soil temperature at the 0-to 15-cm depth was measured with a temperature probe and soil water content was determined gravimetrically by collecting field-moist soil sample and oven drying at 105°C. The experiment was conducted in western North Dakota, USA in a sandy loam soil in 2008 and 2009. Treatments consisted of two irrigation practices (irrigated and non-irrigated) as main plot and five cropping systems [conventional-tilled barley with N fertilization (CTBFN), conventional-tilled barley with no N fertilization (CTBON), no-tilled barley-pea with N fertilization (NTB-PN), no-tilled barley with N fertilization (NTBFN), and no-tilled barley with no N fertilization (NTBON)] as split-plot treatments in a randomized block design with three replications. Malt barley and pea were planted in April and harvested in August. In NTB-PN, both malt barley and pea phases were present in every year. At planting, N fertilizer was applied at 67 kg N/ha to malt barley in both irrigated and non-irrigated practices. After 1 month, another N fertilizer at 67 kg N/ha was top dressed to malt barley in the irrigated practice. No N fertilizer was applied to pea. Both malt barley and pea received P fertilizer at 25 kg P/ha and K fertilizer at 21 kg K/ha at planting. After harvesting grains, biomass residue (stems + leaves) were returned to the soil.

### Results and discussion

The N<sub>2</sub>O flux varied with changes in precipitation and soil temperature and water content from April to November in 2008 and 2009 (Table 1, Figures 1-3). While the trend in N<sub>2</sub>O flux generally followed to that of soil temperature, fluxes peaked immediately following substantial precipitation and/or irrigation (>30 mm) over a period of 7 d. During these periods, N<sub>2</sub>O flux was greater in non-irrigated than in irrigated practice in 2008 but was variable between irrigation practices in 2009 (Figure 2). Similarly, the flux was greater in CTBFN and NTBFN than in other cropping systems in 2008 and 2009 (Figure 3). Cumulative N<sub>2</sub>O flux from May to November was greater in non-irrigated than in irrigated practice in 2008 and greater in CTBFN than in CTBON, NTB-PN, and NTBON in 2009 (Table 1). Tillage and cropping system did not influence N<sub>2</sub>O flux but N fertilization increased the flux compared with no N fertilization in 2009.

Table 1. Effect of irrigation and cropping system on cumulative soil surface N<sub>2</sub>O flux from April to November and mean soil temperature and water content at the 0- to 15-cm depth in 2008 and 2009.

Irrigation	Cropping system†	N <sub>2</sub> O flux (kg N/ha)		Soil temperature (°C)		Soil water (g/kg)	
	J ,	2008	2009	2008	2009	2008	2009
Irrigated		0.96b‡	0.44a	15.9a	15.2a	74.0a	90.8a
Non-irrigated		1.21a	0.41a	15.9a	15.8b	70.8a	86.4b
C	TBFN	1.06a	0.57a	15.6b	15.4bc	75.3a	91.6a
C	TBON	1.08a	0.37b	16.9a	16.1a	73.8a	83.1b
N	TB-PN	1.19a	0.43b	15.6b	15.3bc	74.8a	89.8a
N	TBFN	1.08a	0.46ab	15.5b	15.2c	69.9a	87.1ab
N	TBON	1.00a	0.32b	15.8b	15.7ab	68.3a	91.5a
Contrast							
Till vs. no-till		0.03	0.08	0.56*	0.25	5.4	-1.9
N fert. vs. no N fert.		0.02	0.17**	-0.79*	-0.61*	1.6	2.0
Cont. barley vs. barley pea in no-till		-0.15	-0.04	0.14	0.12	-5.7	-0.5

<sup>†</sup> Cropping systems are CTBFN, conventional-tilled malt barley with 67 to 134 kg N/ha; CTBON, conventional tilled malt barley with 0 kg N/ha; NTB-PN, no-tilled malt barley-pea rotation with 67 to 134 kg N/ha applied to malt barley; NTBFN, no-tilled malt barley with 67 to 134 kg N/ha; and NTBON, no-tilled malt barley with 0 kg N/ha.

<sup>\*</sup> and \*\* Significant at  $P \le 0.05$  and 0.01, respectively.

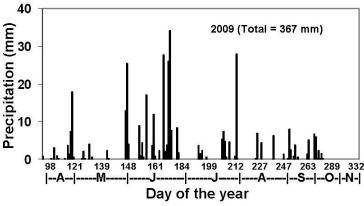


Figure 1. Daily precipitation from April to November in 2009 at the study site.

Sharp increases in  $N_2O$  flux following substantial precipitation during spring and summer suggests that precipitation increased soil microbial activities and organic matter mineralization during increased soil temperature due to greater soil water content. However, irrigation to an amount of 30 mm did not increase the flux, although it increased soil water content. Rather flux was lower in irrigated than in non-irrigated practice in 2008. In contrast, greater  $N_2O$  flux in CTBFN than in other cropping systems, except in NTBFN, suggests that tillage, followed by N fertilization probably increased the flux as a result of increased soil organic N mineralization and/or N substrate availability. Increased  $N_2O$  flux with increase in N fertilization rates have been reported by several researchers (Mosier *et al.* 2006; Dusenbury *et al.* 2008). Greater soil temperature but lower  $N_2O$  flux in CTBON indicates that soil temperature probably has minimal effect on

<sup>‡</sup> Numbers followed by different lower case letters within a column and upper case letter within a row in a set are significantly different at  $P \le 0.05$  by the least significant difference test.

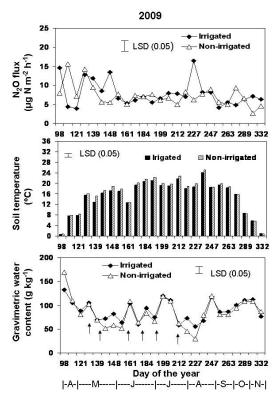


Figure 2. Effect of irrigation on soil surface  $N_2O$  flux and soil temperature and water content at the 0- to 15-cm depth from April to November in 2009. Arrows indicate time of irrigation. LSD (0.05) is the least significant difference between treatments at P=0.05.

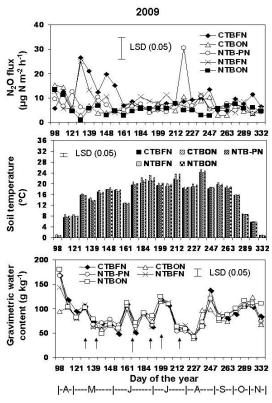


Figure 3. Effect of cropping system on soil surface  $N_2O$  flux and soil temperature and water content at the 0- to 15-cm depth from April to November in 2009. Arrows indicate time of irrigation. CTBFN denotes conventional-tilled malt barley with 67 to 134 kg N/ha; CTBON, conventional tilled malt barley with 0 kg N/ha; NTB-PN, no-tilled malt barley-pea rotation with 67 to 134 kg N/ha applied to malt barley; NTBFN, no-tilled malt barley with 67 to 134 kg N/ha; and NTBON, no-tilled malt barley with 0 kg N/ha. LSD (0.05) is the least significant difference between treatments at P=0.05.

 $N_2O$  flux. The non-significant effect of crop rotation on the flux shows that inclusion of legumes, such as pea, in the crop rotation also has minimum effect on  $N_2O$  flux. Although total precipitation from May to November was greater in 2009 than in 2008, the reasons for greater  $N_2O$  flux in 2008 than in 2009 were not known but probably due to differences in soil  $NO_3$ -N content among years which was not measured in this study.

### **Conclusions**

Soil  $N_2O$  flux usually increased following substantial rainfall over a period of 7 d due to increased soil water content. Irrigation <30 mm during dry period, however, did not increase the flux compared with no-irrigation, although it increased soil water content. Tillage, followed by N fertilization increased  $N_2O$  flux compared with other cropping systems probably due to increased soil organic matter mineralization and N substrate availability. For reducing  $N_2O$  emission, no-tilled continuous cropping with adequate N fertilization with or without irrigation can be used in the northern Great Plains, USA.

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# Modeling long-term soil organic carbon dynamics in forage-based crop rotations in Subarctic Sweden (62-63 °N)

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## **Key Words**

Boreal zone, long-term experiments, agro-ecosystems, land use change, initial site characteristics.

### Introduction

For carbon sequestration estimates it is necessary to evaluate effects of management practices on soil organic carbon (SOC) dynamics in a wide range of production systems and climatic zones. At higher latitudes with cold temperate climate, crop rotations dominated by forage are common and often highly productive – and the climate as well as the forage cropping systems favours large stocks of SOC. The objective of this study was to estimate and describe SOC stock dynamics in the arable topsoil layer (0 to 25 cm depth) for different 6-yr forage-based rotations using sampling data from three long-term field experiments in "Norrland", i.e., North Sweden.

#### Methods

The continuous forage rotation ('A'), received ca.  $1 \text{ kg C/m}^2$  as cattle manure per year, and rotation 'B' had 4 years of forage and two years of annuals, receiving the same amount of manure. Rotation 'C' had 3 years of forage and received  $0.7 \text{ kg C/m}^2$  of manure. Rotation 'D' had only annuals and no manure application. We used plant C allometric functions developed for forage crops together with *The Introductory C Balance Model* (ICBM; Andrén and Kätterer 1997; Andrén *et al.* 2007, 2008ab) to describe SOC dynamics for the continuous forage rotation ('A') without parameter tuning. Then we adapted the ICBM soil climate and decomposer activity parameter ( $r_e$ ) to account for the major effects of increased tillage in rotations 'B' to 'D' (see e.g. Andrén *et al.* 2007; Bolinder *et al.* 2007). The  $r_e$  parameter usually is calculated from subparameters based on climate, soil type, crop type, intensity of cultivation etc. and in this case the effects of forage crops vs. annuals on cultivation intensity are of special interest – can cultivation effects in these extreme conditions be described following normal assumptions?

## **Results and discussion**

At the site with the lowest, but still comparatively high, initial amount of SOC (8.2 kg C/m<sup>2</sup> in topsoil down to 25 cm), SOC stocks increased by 12 g C/m<sup>2</sup>/yr over a 50-year period for the continuous forage rotation ('A'). At the same site, SOC stocks were more or less at steady-state in rotation 'B', receiving the same amount of manure. For rotation 'C' with more annuals and less forage and manure, SOC stocks decreased by 18 g C/m<sup>2</sup>/yr, while the SOC stocks for rotation 'D' (no forage, no manure) decreased by 24 g C/m<sup>2</sup>/yr. At the other two sites, with higher initial SOC stocks (12.8 and 14.3 g C/m<sup>2</sup>), SOC stocks in all treatments decreased during a 30-year period, ranging from 11 to 168 g C/m<sup>2</sup>/yr. The four-parameter model ICBM allowed us to describe SOC dynamics for the continuous forage rotation ('A') without parameter tuning: deviation between measured and predicted final SOC stocks were less than  $\pm$  5%. The adaption of parameters (yield/crop residue input, manure addition) that affected annual inputs and 'litter quality' explained a major part of the differences between treatments, and when we also took differences in cultivation into account we could satisfactorily describe all treatments. However, without separate measurements of cultivation effects ('How much carbon is actually lost due to cultivation effects only) we cannot separate cultivation effects from other components of  $r_e$ . To be able to actually refine and develop models we need more high-precision, unbiased field from adequately designed field experiment (see, e.g., Andrén et al. 2008).

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# Modelling N<sub>2</sub>O emissions from agroecosystems: the WNMM experience

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#### **Abstract**

Nitrous oxide  $(N_2O)$  is primarily produced by the microbially-mediated nitrification and denitrification processes in soils. It is influenced by a suite of climate and soil variables, interacting soil and plant nitrogen (N) transformations as well as land management practices. Numerous simulation models have been developed to predict  $N_2O$  emissions from agroecosystems. In this paper, we report on our experiences of simulating  $N_2O$  emissions from irrigated maize-wheat, irrigated wheat, rainfed wheat, irrigated pasture and sugarcane ecosystems by using the Water and Nitrogen Management Model (WNMM).

# **Key Words**

Nitrous oxide, agroecosystems, WNMM; simulations.

## Introduction

N<sub>2</sub>O is a potent and long-lived greenhouse gas, contributes a Radiative Forcing of +0.16±0.02 W m<sup>-2</sup> of the atmospheric greenhouse effect, and is very effective in absorbing infrared radiation, and its global warming potential is 310 times greater than carbon dioxide (CO<sub>2</sub>) for a 100-year time horizon. Anthropogenic activities contributing to N<sub>2</sub>O emissions include the application of N fertilizers, crop biological N fixation, tillage, irrigation, animal manure, aquifers, sewage, industry, automobiles, biomass burning, land clearing and trash incineration. More than 60% of N<sub>2</sub>O emissions come from soil-based processes (Prather et al. 1995). Globally, agricultural lands contribute about 35% of all N<sub>2</sub>O emissions (FAO/IFA 2001). The production of N<sub>2</sub>O from soils is primarily from the microbially-mediated nitrification and denitrification processes. N<sub>2</sub>O flux from soils, relatively small compared to other N fluxes, is dependent on soil temperature, soil water content, O<sub>2</sub> availability, N substrate availability (nitrate and ammonium), and organic C substrate availability (Davidson 1991). All these regulators are strongly influenced by climate, vegetation, soil properties (bulk density, organic matter, pH and clay content), and land-use management or agricultural practices. N<sub>2</sub>O production is also influenced by other complex interacting N processes in the plant-soil N cycle, such as plant N uptake, ammonia volatilisation and nitrate leaching. All these influencing variables and processes contribute to high spatial and temporal variability of N<sub>2</sub>O emissions. Computational models. which simulate N<sub>2</sub>O emissions from soils by integrating all the influencing variables and interacting processes, provide a useful means of assessing gas fluxes at field-to-regional scales (Chen et al. 2008). Since the first Focht's N<sub>2</sub>O simulation model, various models were constructed to predict N<sub>2</sub>O production from nitrification and denitrification in agroecosystems, such as NGAS (Mosier et al. 1983), DNDC (Li et al. 1992), NLOSS (Riley and Matson 2000), ecosys (Grant 2001), DAYCENT (Parton et al. 2001), WNMM (Li et al. 2005), FASSET (Chatskikh et al. 2005), CERES-NOE (Gabrielle et al. 2006) and so on. The WNMM has been applied to simulate N<sub>2</sub>O emissions from the intensively-irrigated maize-wheat system in the North China Plain (NCP), the irrigated wheat system in Mexico, the rainfed wheat, irrigated pasture and sugarcane systems in Australia.

### Methods

**WNMM** 

The WNMM (Li *et al.* 2007) is a spatially referenced (coupled with GIS) biophysical model developed to simulate dynamic soil water movement and soil-crop C and N cycling under agricultural management, for the purpose of identifying optimal strategies for managing water and fertilizer N under intensive cropping systems (mainly wheat-maize) and pasture system. It simulates the key processes of water and C and N dynamics in the surface and subsurface of soils, including evapotranspiration, canopy interception, water infiltration and redistribution, groundwater fluctuations, soil temperature, solute transport, crop and pasture growth, C and N cycling in soil-crop/pasture system, and agricultural management practices (crop rotation, irrigation, N fertilizer application, harvest, and tillage). It runs at the daily time step at a range of scales. Data required by WNMM are categorized as GIS layer information (soil type, land cover, and village administrative boundary); database-formatted source data (soil physical and chemical properties, land use

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types, and agricultural management practices); referenced data (climatic reference data and crop biological data); and control data (starting date, period of simulation, initial land surface and soil conditions). The detailed description of simulating soil water dynamics, solute transport and crop growth in WNMM is referred to Li *et al.* (2007).

The pasture growth component in WNMM is generally based on GrassGro (Moore *et al.* 1997). Three species of pastures, paspalum, ryegrass and white clover, are simulated, and their growths are controlled by temperature, radiation, water stress and nitrogen stress. The optimal N concentration of pastures (N<sub>o</sub>, kg N/kg DM) is described by using the equation:

$$N_o = N_{\text{max}} \cdot \left(\frac{\text{agDM}}{1000}\right)^{-0.32} \tag{1}$$

where  $N_{max}$  (kg N/kg DM) is the maximum N concentration in aboveground dry matter (kg DM/ha) of pastures, in this study, set to 0.02, 0.03 and 0.04 for paspalum, ryegrass and white clover, respectively.  $N_o$  is used for estimating the daily pasture N uptake demand. The actual pasture N uptake is computed based on the availability of mineral N contents in soil layers by considering the root density distribution in the soil profile. White clover is assumed to fixate  $N_2$  up to the remaining demand after N uptake. There is no animal production model, but during grazing pastures are removed by considering animal heads, grazing duration and intake rate. Of the grazed pastures, 20% is lost to the soil surface as animal trampling. In addition, an N load is applied to the soil surface as dung and urine.

WNMM simulates the transformations of several N species in agricultural soils, including mineralization of fresh crop residue N and soil organic N, formation of soil organic N, N immobilization to microbial biomass, nitrification, ammonia (NH<sub>3</sub>) volatilization, denitrification, and CO<sub>2</sub>, NO, N<sub>2</sub>O and N<sub>2</sub> emissions from the soil surface. It divides soil C into three pools: fresh residue C; microbial biomass C (living and dead), and humus C (active and passive). The flows between the different pools are calculated as first-order processes in terms of C, and the corresponding N flows depend on the C:N ratio of the receiving pools. The C:N ratios of the various pools are assumed to be constant in the simulation. Mineralization or immobilization is determined as the balance between the release of N during organic C decomposition and immobilization during microbial synthesis and humification. All the rate constants of first-order reactions for C and N transformations in the soil are modified by factors of pH, clay content, temperature, and water content in soil layers. Nitrification and denitrification are considered in WNMM as the only two microbially-mediated processes contributing to emissions of nitrogenous gases from soils. The WNMM simulation of N<sub>2</sub>O production from these two processes and emissions from the soil was described by Li *et al.* (2005).

## Results

# Irrigated maize-wheat system

The WNMM was applied to model  $N_2O$  emissions from two loam-textured arable soils grown the summer maize and winter wheat in the NCP, China, compared with 1- (1999-2000) and 2- (1998-2000) year round manual chamber observations (Li *et al.* 2005). The WNMM  $N_2O$  predictions for these two soils were highly correlated with the observations ( $R^2$ =0.45-0.54), with 2.1-3.4 kg N/ha/y of annual  $N_2O$  emissions. In addition, the nitrification-induced  $N_2O$  emissions estimated by WNMM accounted for 22-63% of annual emissions for the intensively-irrigated maize-wheat system in the NCP.

# Irrigated wheat system

Ahrens *et al.* (2009) used WNMM to simulate the irrigated wheat cropping system for 1994-1997 in Yaqui valley in Mexico with special focus on N<sub>2</sub>O and NO emissions. The N<sub>2</sub>O estimates by WNMM were fairly comparable with the chamber observations at various N forms, application rates, timing and methods.

# Rainfed wheat system

Li *et al.* (2008) applied WNMM to simulate  $N_2O$  emissions from a rain-fed wheat cropping system on a loam-textured soil for two treatments, conventional cultivation with residue burn (CC+BURN+N) and direct drill with residue retention (DD+RET+N) at Rutherglen in southeastern Australia from January 2004 to March 2005. Both treatments received the same amount of N fertilisers. The WNMM satisfactorily simulated the soil water content, mineral N contents and  $N_2O$  emissions from the soil, compared with the field observations in both treatments. The predicted annual  $N_2O$  emissions were low, 0.22-0.31 kg N/ha/y, and the site emission factor of 0.33% (no background emission correction) is much lower than the IPCC default value. The nitrification-induced  $N_2O$  emissions (simulated) accounted for 45% and 34% of total  $N_2O$  emissions for the treatments of CC+BURN+N and DD+RET+N, respectively. Then, the calibrated WNMM

was used to simulate  $N_2O$  emissions from this soil with historic daily weather data from 1968 to 2004 for seven scenarios of fertiliser N application. The correlation analysis found that the annual  $N_2O$  emissions for this rain-fed wheat cropping system were significantly correlated to the annual average of daily maximum air temperature (r=0.51 for CC+BURN+N and 0.56 for DD+RET+N), annual rainfall (r=-0.56 for CC+BURN+N and -0.59 for DD+RET+N) and fertiliser N application rate (r=0.43 for CC+BURN+N and 0.31 for DD+RET+N). Based on the 37-year historic simulations, multivariate regression models for estimating annual  $N_2O$  emissions were developed to account for climatic variation, and explained about 50% of variations of annual  $N_2O$  emissions estimated by WNMM.

Li *et al.* (2009) also applied WNMM to simulate  $N_2O$  emissions from a rain-fed and wheat-cropped system on a sandy duplex soil at Cunderdin, Western Australia, Australia from May 2005 to May 2007. WNMM satisfactorily simulated crop growth, soil water content and mineral N contents of 0-10 cm topsoil, soil temperatures at depths and  $N_2O$  emissions from the soil, compared with the field observations in two fertiliser treatments during calibration and validation. The annual  $N_2O$  emissions ranged from 0.09-0.18 kg N/ha/y, with an average emission factor of 0.1%. About 70% of total  $N_2O$  emissions were estimated as nitrification-induced, according to WNMM simulation for this semi-arid and wheat-cropped system. The uncertainty analysis by using 10000 Monte Carol simulations indicated that most of  $N_2O$  emission variations simulated by WNMM from the soil are contributed from variations of these soil properties of the 0-15 cm topsoil: pH, total N, organic matter, initial mineral N, bulk density and water content at field capacity, and of fertiliser N application rate.

# Irrigated pasture system

The dairy pasture system is a high input and high output agricultural production system, and is associated with intensive irrigation and N fertilizer applications. In the study of Chen et al. (2009), the daily and total chamber-measured N<sub>2</sub>O emissions from an intensively-irrigated pastoral clay loam-textured soil for the nonfertilizer (CK), urea and urine treatments at Kyabram in southeastern Australia from 1 Nov 2003 to 30 Jun 2005 (one year and eight months) were compared with the predictions by WNMM. The results suggested that WNMM was capable to estimate daily and annual N<sub>2</sub>O emissions from this intensively-irrigated pastoral clay loam-textured soil for the CK, UREA and URINE treatments, but with different levels of success during different seasons and at different temporal scales, based on the simple linear regression, sliding window correlation and summed correlation analysis of the chamber-observed and WNMM-predicted N<sub>2</sub>O emissions. The simulations and statistical analysis carried out in the study indicated that the WNMM performance in predicting the daily and monthly N<sub>2</sub>O emissions for three treatments is in this order; CK < UREA < URINE. The periodically-summed correlation analysis also showed that WNMM was more reliable to give the prediction of N<sub>2</sub>O emissions at the time scale of around 35 days from this intensively-irrigated dairy pasture system. The WNMM-estimated  $N_2O$  emission factor for this ecosystem was around 0.5%. The estimated annual N<sub>2</sub>O emissions ranged from 1.5-6.8 kg N/ha/y. The proportions of nitrification-induced N<sub>2</sub>O emissions in the simulated annual emissions were 12%, 21% and 45% for the CK, UREA and URINE treatments, respectively.

### Sugarcane system

An application of WNMM to predicting both the environmental drivers and the N<sub>2</sub>O emissions from a N-fertilized alluvial non-calcic brown soil with sugarcane cropping in a tropical region of eastern Australia was examined (Chen *et al.* 2008). The high soil moisture regimes, high soil temperatures and high levels of available C that characterise Australian sugarcane culture are expected to promote high evapotranspiration and intensify the normal processes of N cycling that lead to N<sub>2</sub>O production. Relevant predictions by WNMM were compared with field measurements made over 14 months: evapotranspiration by eddy covariance, soil water content and soil temperature by soil moisture probes and soil thermometers and N<sub>2</sub>O emissions by 6 automatic chambers. For the first growing season of 290 days, WNMM predicted the total N<sub>2</sub>O emissions reasonably well although there were lags between the predicted N<sub>2</sub>O emissions and observations after rainfall events. The observed N<sub>2</sub>O emissions over the same period showed a pronounced diurnal cycle and totalled 4.7 kg N/ha.

## Conclusion

Considering the strong spatial and temporal variability of  $N_2O$  emissions from soils, the WNMM was capable to estimate daily and seasonal/annual  $N_2O$  emissions from irrigated maize-wheat, irrigated wheat, rainfed wheat, irrigated pasture, and sugarcane ecosystems at the field scale. Upscaling is an essential

requirement, not only for more accurate regional and national inventories, but also for development of site-specific mitigation practices with the increased interest in full greenhouse gas accounting and emissions trading in the agricultural sector. Spatially-referenced and process-based models, such as WNMM, may increase in popularity with more testing.

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# Modelling of carbon flux in grassland ecosystems in Ukraine

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#### **Abstract**

For the better understanding of the dynamics of soil organic matter (SOM) in the natural grassland ecosystem, a simple process-based model is proposed and validated using the values of whole soil respiration (WR) and the microbial soil respiration (MR) measured in Chernozem and Kastanozem soils in Ukraine. Measured input values for the validation were light fraction C (LFC), clay content and plant biomass including shoot and root biomass, daily soil temperature and volumetric water content at 15 cm depth and daily air temperature and precipitation. As an influx of C to the soils, NPP was calculated by Chikugo model using annual temperature and precipitation. For the measured whole soil respiration rate, estimated WR value without root respiration showed close fitting under the drier conditions, probably because of the restricted root respiration. Under the wetter conditions, c.a. 50% of the WR would be attributed to root respiration. For the measured microbial respiration rate, the model estimation fitted well with measured values. These results suggested that the proposed model successfully simulated the decomposition processes in the natural grassland ecosystems.

# **Key Words**

Modelling, soil organic matter dynamics, soil respiration, natural grassland ecosystems.

#### Introduction

Soil respiration, i.e. carbon dioxide (CO<sub>2</sub>) emission from soils has been studied widely, as a major process of carbon dynamics between atmospheric carbon (780 Pg C) and soil organic carbon (1550 Pg C). In the Eurasian steppe, Chernozem and Kastanozem soils, which develop under short- or tall-grass steppe vegetation, spread out from areas near the Black Sea to northern Kazakhstan in a belt. These soils are important not only because of their high productivity of crops but also of their high accumulation of carbon. Though detailed studies on SOM dynamics are required in urgent, little is known about the relationship between in situ soil respiration, net primary productivity, soil temperature and moisture content, and soil properties in this region. So the objectives of this study are (i) to offer a process-based model to simulate the SOM dynamics using measurable soil properties, and (ii) to validate the model by in situ soil respiration rates measured in 2 grassland sites in Ukraine.

# Methods

Theory of Carbon Flux Model

According to the relationship between the potentially mineralizable OM and soil properties in Kadono *et al.* (2008), the following SOM dynamics model was proposed (Figure 1). In this model, all C fluxes are calculated in daily step. Since SOM is supplied by plant material, estimation of net primary productivity (NPP) is required for the model. NPP is the difference between whole plant photosynthesis (gross primary productivity; GPP) and plant respiration annually. In natural ecosystems, the annual NPP can be estimated by Chikugo model (Uchijima and Seino, 1985), using annual air temperature and precipitation. Daily NPP is estimated by the proportional distribution of the annual NPP to daily air temperature, if it is higher than 4 °C. The calculated daily NPP is allocated to shoot, root in 0-10 cm depth and root in 10-50 cm depth, referred to as NPP<sub>shoot</sub> ((1) in Figure 1, NPP<sub>root</sub> in 0-10 cm (2) and NPP<sub>root</sub> in 10-50 cm (3). Plants use the NPP for growth of the shoot and root biomass and exudates from root, such as mucilage, organic acid and polysaccharide. The NPP<sub>shoot</sub> and a portion of NPP<sub>root</sub> in 0-10 cm (NPP<sub>root</sub> – exudates in 0-10 cm) are added to the potentially mineralizable C (PMC) pool annually, corresponding to (1) and (5), respectively in Figure 1. In this model, the exudates are assumed to be decomposed immediately (6) (Luo *et al.* 2001).

The PMC is calculated by the regression equation obtained in Kadono *et al.* (2008), using light fraction carbon (LFC;  $< 1.60 \text{ g/cm}^3$ ) and clay content. This PMC pool is decomposed at the rate constant (k), which is dependent on soil temperature and moisture. The temperature dependency of the rate constant is assumed to follow the Arrhenius model, and usually set at  $Q_{10}$  (15-25 °C) of 2.0, or apparent activation energy of 49.5

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kJ/mol. The dependency of the rate constant on soil moisture is assumed to follow that in the Rothamsted Carbon model (Coleman and Jenkinson 1996). They calculated the moisture factor, which is multiplied to the rate constant and ranges from 0.2 to 1.0, according to the water deficiency. In this model, the moisture factor was calculated according to the proportional distribution between 1.0 at maximum volumetric water content (VWC) and 0.2 at minimum VWC recorded in the soil. Therefore, the daily rate constants are calculated by daily soil temperature and moisture data, and at the daily rate constant, PMC is decomposed in daily time step (4).

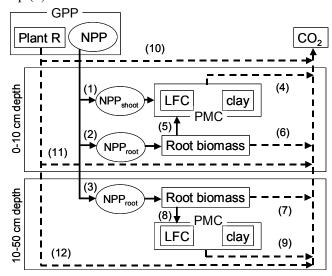


Figure 1. Soil organic matter dynamics model assumed. GPP: gross primary productivity, Plant R: plant autotrophic respiration, NPP: net primary productivity, NPP $_{shoot}$ : NPP allocated to shoot biomass, NPP $_{root}$ : NPP allocated to root biomass, LFC: light fraction (< 1.60 g/cm³) C, PMC: potentially mineralizable C. Arrows indicate flows of  $CO_2$  (broken line) and organic C (solid line). Numbers indicate the individual flows.

#### Experimental Sites

Two sites were selected to monitor CO<sub>2</sub> flux and soil temperature and moisture. The measurement of soil respiration was conducted from 2002 to 2004 in the natural grassland sites.

- (1) Grakovo Experimental Field (N49° 44', E36° 56', Alt: 154m) is located about 60 km southeast of Kharkov city, northern Ukraine. The meteorological data were assumed same as this city. Mean annual air temperature (MAT) and mean annual precipitation (MAP) were 6.9 °C and 536.6 mm, respectively. According to the U.S. Soil Taxonomy, this soil was classified into Pachic Haploxerolls (Soil Survey Staff, 1998). Soil organic carbon accumulation upper 1 m depth in this site is 315 Mg C/ha. Soil texture of the surface layer was classified as LiC.
- (2) Askania-Nova Biosphere Reserve (N46° 27', E33° 53', Alt: 27m) is located about 100 km east of Kherson city, southern Ukraine. MAT and MAP were 9.5 °C and 386.4 mm, respectively. The virgin fescue-feather grass steppe area has been reserved for more than 100 years. According to the U.S. Soil Taxonomy, this soil was classified into Calcic Haplustolls (Soil Survey Staff, 1998). Soil organic carbon accumulation upper 1 m depth in this site is 150 Mg C/ha. Soil texture of the surface layer was classified as LiC.

Measurement of in situ soil respiration rate for validation of output data of the model Soil respiration rate was measured several times during growing season by closed-chamber method (Anderson, 1982) using handy type Infra-red  $CO_2$  analyzer (Anagas CD98, Environmental Instruments, Leamington Spa, UK) or  $CO_2$  monitor (GH-250E, Sensonix Japan). The difference in the equipments did not affect the measurement of soil respiration. For the measurement of whole soil respiration (WR) rate, aboveground part of grasses were cut, chambers ( $\phi = 10.5$  cm, height = 20 cm) were inserted 5 cm into the soil, and increased  $CO_2$  concentration during 30 minutes were measured after the chamber was sealed. Though diameter and height of chambers used in 2002 were 20.8 cm and 12 cm, respectively, and the chambers were inserted 2 cm in the soils, no difference in WR was observed between the two types of chambers.

In addition to the whole soil respiration, measurement of microbial soil respiration (MR) rate using a trenching technique was conducted in 2002 to 2004 (Grakovo) and in 2003 to 2004 (Askania-Nova), as follows:

After aboveground part of grasses were cut, chambers were inserted 10 cm into the soil, the soils in the chambers were separated from the ground at the depth, and a plastic net was attached to retain the soil on the bottom of each chamber. This treatment was conducted on the first measurement each year. Just before the measurement of  $CO_2$  emission, the bottom of the chamber was covered by plastic bag to exclude  $CO_2$  diffusion from subsurface layers. Therefore, soil respiration emitted from this type of chamber is assumed to be microbial respiration, without plant root respiration and further addition of NPP into soil in each year.

# Soil properties and plant biomass

In Grakovo, soil samples were collected at the depth of 0-5, 10-15, 20-25, 30-35, 40-45 and 50-55 cm on May 11, 2003. In the grassland site in Askania-Nova, soils were sampled at the depths of 0-10, 20-30, 40-50, 70-80 and 100-110 cm on Apr. 29, 2004. All soil samples were air-dried and sieved to 2 mm for physicochemical analysis. Contents of light fraction (LF) were determined as follows. Briefly, 10 g aliquots of air-dried soil were dispersed in sodium iodide solution (1.60 g/cm³) and centrifuged at 2600 g (modified from Spycher *et al.* 1983). Material in the supernatant was considered to be LF (mostly partially decomposed plant residues), whereas that in the sediment was HF (more fully-decomposed residues and mineral material). Carbon contents in LF (LFC) were measured by dry combustion with an NC analyzer (Sumika, NC-800-13N). Contents of sand (2-0.02 mm), silt (0.02-0.002 mm) and clay (< 0.002 mm) were measured by sieving and the pipette method (Gee and Bauder, 1986) for surface (0-10) soil samples. Soil bulk density of 100 ml core samples taken at the depths of 0-5, 10-15 and 50-55 cm were measured in 3 replications for each site.

Since coarse (> 2 mm) plant materials are usually not included in the soils after sieving, one of the major differences between in situ soil respiration and in vitro C mineralization is the existence of the larger plant materials in the former measurement. In this study, aboveground (shoot) and belowground (root) biomass in a unit area (15 × 50 cm) was measured. Shoot biomass was collected and weighted after oven drying at 110 °C. Root biomass was collected with soils at certain depths, each soil was enclosed in a flexible mesh bag, and the roots were separated from soil by washing the mesh bag in water. After washing, roots and sand remained in the bag were dipped into another bucket of water, and they were separated by floatation of the roots. The roots were oven dried and weighted. This experiment was conducted in 3 and 2 replications in Grakovo and Askania-Nova, respectively, in the summer of 2003. Carbon content in the plant biomass was set at 45% (Kudeyarov and Kurganova, 1998) in this study.

# Results and discussion

Validation of the proposed model for whole soil respiration

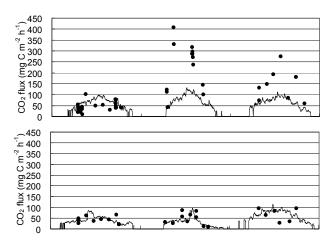
The estimated whole soil respiration rate without root respiration rate (WR-RR; (4)+(6)+(7) in Figure 1) and measured WR are shown in Figure 2. In Grakovo 2002 and in Askania-Nova, estimated values for WR-RR fitted the values of measured WR, while in Grakovo 2003 and 2004, measured WR was more than 2 times higher than the simulated WR-RR. This would be partly due to the large variation of plant respiration, probably caused by the annual precipitation as NPP. Hanson *et al.* (2000) reported root respiration usually accounts for c.a. 50% of whole soil respiration, it varied 10% to 90% among the previous studies.

# Validation of the proposed model for microbial soil respiration

The measured microbial soil respiration (MR) includes the  $CO_2$  flux of (4), and all the separated root biomass are assumed to be entered to PMC (Figure 1). The initial pool of PMC for each year was assumed to be 870 and 881 g C m<sup>-2</sup> in Grakovo and Askania-Nova, respectively. The estimated and measured MR are shown in Figure 3. Estimated annual MR for 2002, 2003 and 2004 was 318, 326 and 397 g C/m<sup>2</sup>/y, respectively in Grakovo, while in Askania-Nova 338, 351 and 375 g C/m<sup>2</sup>/y, respectively. Except for the 2 measured values in 2003, estimated MR values well simulated the measured MR in Grakovo.

### Conclusion

For the better understanding of SOM dynamics in the Eurasian steppe, a model using measurable soil properties was provided and validated for the whole soil respiration (WR) and the microbial soil respiration (MR) measured in Chernozem and Kastanozem soils under the natural grassland ecosystems. Measured input values for the validation were light fraction C (LFC), clay content and plant biomass including shoot and



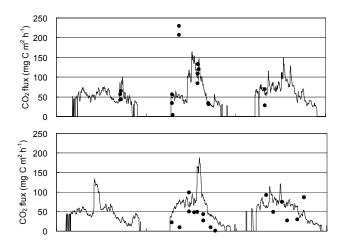


Figure 2. Measured in situ whole soil respiration (circle) and estimated whole soil respiration without root respiration (line) in Grakovo (upper) and in Askania-Nova (lower).

Figure 3. Measured in situ microbial soil respiration (circle) and estimated microbial soil respiration (line) in Grakovo (upper) and in Askania-Nova (lower).

root biomass, daily soil temperature and volumetric water content at 15 cm depth and daily air temperature and precipitation. As an influx of C to the soils, NPP was calculated by Chikugo model using annual temperature and precipitation. For the measured whole soil respiration rate, estimated WR value without root respiration showed close fitting under the drier conditions, probably because of the restricted root respiration. Under the wetter conditions, c.a. 50% of the WR would be attributed to root respiration. For the measured microbial respiration rate, the model estimation fitted well with measured values. These results suggested that the proposed model successfully simulated the decomposition processes of PMC as well as the distribution of NPP<sub>root</sub> to PMC and root exudates in natural grassland ecosystems.

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# N<sub>2</sub>O and CO<sub>2</sub> emissions following clover and cellulose incorporation into a New Zealand pastoral soil

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#### **Abstract**

Clover (*Trifolium repens* L.) and clover + different proportions of cellulose were incorporated into soil and the nitrous oxide ( $N_2O$ ) and carbon dioxide ( $CO_2$ ) emissions measured. Ground, dried clover shoots and cellulose were mixed to carbon: nitrogen (C: N) ratios of ~9 ('clover only'), 20, 30 and 40. Soil samples were incubated at water–filled pore space (WFPS) of 86% and 20°C. Over 42 d,  $N_2O$  emissions from the controls averaged 9 mg/kg soil (6 g total N/kg soil), indistinguishable from the 'clover only' (1.5 g N incorporated/kg soil) and 'C: N 20' treatments. Corresponding  $N_2O$  emissions from the 'C: N 30' and 'C: N 40' treatments averaged nearly 50% greater (P < 0.05) and these two treatment effects were indistinguishable. Over 42 d,  $CO_2$  emissions from the controls averaged 4 g/kg soil. There was a linear C (incorporation rate) 'dose effect' on  $CO_2$  emissions (0.15 g  $CO_2$ /g C,  $R^2 = 0.80$ ) with no difference between clover and clover + cellulose. Over 145 d,  $CO_2$  emissions from the controls averaged 17 g/kg soil and the C 'dose effect' was 0.38 g  $CO_2$ /g C ( $R^2 = 0.98$ ). Incorporating different plant materials into soil affected the  $N_2O$  and  $CO_2$  emissions differently.

# **Key Words**

'Dose effect', plant litter, C: N ratio, decomposition, nitrous oxide, carbon dioxide.

## Introduction

Plant litter is a complex C and N source, so its biochemical composition may affect mineralization rate. For example, plant litter of a lower C: N ratio may be more susceptible to decomposition and mineralization (Pal et al. 2010). Plant litter mainly contains soluble carbohydrates, cellulose, hemicellulose and lignin (in increasing order of recalcitrance) (Melillo et al. 1982), as well as N. Cellulose (C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>), an unbranched, β–(1,4)–linked, linear polymer of glucose, is a carbohydrate synthesized by plants and the most abundant organic polymer. Biodegradation of cellulose requires a distinct set of extracellular enzymes viz. cellulase, cellobiohydrolase and β–glucosidase, which act synergistically to hydrolyse the β–1,4 bonds of cellulose to glucose for further energy generation processes (Clarke 1997). Fungi including *Penicillium sp.* and *Aspergillus sp.* and bacteria such as *Streptomyces sp.* and *Pseudomonas sp.* aid in the extracellular cleavage of cellulose. The effect of cellulose in plant litter on N<sub>2</sub>O emissions has received little attention. A potent greenhouse gas, N<sub>2</sub>O has a global warming potential of 298 over 100 years and it is a precursor molecule involved in stratospheric ozone depletion (Forster et al. 2007). This paper reports the results of an experiment to measure N<sub>2</sub>O and CO<sub>2</sub> emissions following clover and cellulose incorporation into soil sampled beneath pasture grazed by dairy cattle near Lincoln, New Zealand.

# Methods

*Litter incorporation and measurements* 

Temuka silt loam soil was sampled at a grazed pasture site (0–10 cm) and sieved to  $\leq$  4 mm. Dried, ground clover shoots and cellulose (in different proportions) were incorporated into the soil to achieve C: N ratios of ~9, 20, 30 and 40 representing 'clover only', 'C: N 20', C: N 30' and C: N 40' treatments, respectively. After treatment, soil was packed into PVC containers (internal diameter 8.0 cm, total height 10 cm) to a depth of 4.5 cm with the bottom covered by fine nylon mesh. The soil was incubated at 86% water filled pore space (WFPS) and 20°C for 145 d. Emissions of N<sub>2</sub>O and CO<sub>2</sub> were measured using a chamber technique with gas chromatography and infrared gas analysis, respectively.

#### **Results and Discussion**

Soil and litter properties

The  $\theta_g$ ,  $\theta_v$ ,  $\rho_b$ , and  $\phi$  were 0.31 kg water/kg dry soil, 0.23 m<sup>3</sup> water/m<sup>3</sup> dry soil, 736 kg soil/m<sup>3</sup> soil and 0.72

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m<sup>3</sup> pores/m<sup>3</sup> soil. The pH was 5.7, and there was 64 g/kg total C and 6 g/kg total N. The clover shoots had 51 g N/kg, 430 g C/kg, a C: N ratio of 8.5, 155 g cellulose/kg, 37 g hemicellulose/kg, and 23 g lignin/kg.

# N<sub>2</sub>O emissions

The maximum  $N_2O$  emissions were 8 h after treatment at  $152.3 \pm 10.1$ ,  $97.6 \pm 12.9$ ,  $45.6 \pm 7.6$  and  $21.7 \pm 3.1$  ng  $N_2O/kg$  soil/s (mean  $\pm$  standard error of the mean, n = 5) for the 'C: N 40', 'C: N 30', 'C: N 20' and 'clover only' treatments, respectively (P < 0.05, Figure 1). Eleven hours later,  $N_2O$  emissions from the 'C: N 40' and 'C: N 30' treatments remained significantly greater than the 'C: N 20' and 'clover only' treatments, in turn greater than the controls. Over 42 d, when  $N_2O$  emissions measurements ceased, the cumulative emissions from the 'C: N 40', 'C: N 30', 'C: N 20', 'clover only' and the control were  $14.3 \pm 0.5$ ,  $12.4 \pm 1.2$ ,  $8.0 \pm 0.6$ ,  $8.7 \pm 1.2$  and  $9.1 \pm 0.9$  mg  $N_2O/kg$  soil, respectively. These emissions were in the order of control = 'clover only' = 'C: N 20' < 'C: N 30' < 'C: N 40' (P < 0.05). While, unexpectedly, cumulative  $N_2O$  emissions from the controls were indistinguishable from the 'clover only' and 'C: N 20' treatments, the time courses differed significantly with 90% of the corresponding totals completed in ~38, 7 and 9 d. Corresponding  $N_2O$  emissions from the 'C: N 30' and 'C: N 40' treatments included 90% of the total completed in ~9 d. Thus, clover incorporation produced the most rapid  $N_2O$  emissions' response and adding the largest quantities of cellulose significantly enhanced the  $N_2O$  emissions response to clover incorporation.

The dry, ground clover and cellulose incorporated into the soil evidently blocked the soil pores, reducing oxygen diffusion rate and contributing to the attainment of anaerobic conditions. Higher N<sub>2</sub>O emissions would be expected under more anaerobic conditions. The presence of available C can increase denitrification, directly, by increasing energy and electron supply to the denitrifiers, and indirectly, by enhanced microbial growth and metabolism, thereby stimulating higher O<sub>2</sub> consumption (Beauchamp *et al.* 1989; Gillam *et al.* 2008). The current results cannot delineate the N<sub>2</sub>O production mechanism but given the soil moisture content and the fact that cellulose was being utilised, and that the N<sub>2</sub>O emissions were lower than the control during 2.3–4.3 d; it is likely that the C substrate further enhanced denitrification and permitted the further reduction of N<sub>2</sub>O to N<sub>2</sub> (Firestone and Tiedje 1979).

# CO<sub>2</sub> emissions

Four hours after treatment the  $CO_2$  emissions were  $12.0 \pm 0.4 < 17.5 \pm 1.1 = 15.0 \pm 2.2 = 11.7 \pm 1.0 > 1.9 \pm 0.1 \,\mu g \, CO_2/kg \, soil/s \, from the 'C: N 40', 'C: N 30', 'C: N 20', 'clover only' and the control, respectively (Figure 2). The maximum <math>CO_2$  emissions occurred at 1.4 d with  $23.9 \pm 0.04 > 25.1 \pm 0.05 > 22.4 \pm 0.17 > 18.0 \pm 0.12 > 1.4 \pm 0.01 \,\mu g \, CO_2/kg/s \, from 'C: N 40', 'C: N 30', 'C: N 20', 'clover only' and the control, respectively. The relatively low <math>CO_2$  emissions from controls suggest disturbance was not responsible for the higher emissions of treated soil; rather, the soil microbial biomass may have switched from the recalcitrant soil organic matter to the incorporated substrate (Sparling *et al.* 1982; Cheng 1996). Moreover, these higher emissions can be accounted for the so called r–strategist activity of rapid catabolism of the fresh organic matter in soil (Fontaine *et al.* 2003).

The  $CO_2$  emissions steadily declined after 1.4 d but at 10.3-11.1 d, a further increase in  $CO_2$  emissions was observed (Figure 2) but this increase was very minor in the 'clover only' treatment. Furthermore the 'secondary peak' in those treatments with cellulose additions was dependant on the rate of cellulose applied (i.e. 'clover only' < 'C: N 20' < 'C: N 30' = 'C: N 40') which indicated cellulose utilisation as an energy source. The 'C: N 30' and 'C: N 40' emissions did not significantly differ at 1.4 d probably because of the abundant amount of added cellulose already present in the soil. A significant 'C dose effect' was observed over the entire incubation period since the 'clover only' and 'C: N 20' treatments reached the control levels at 112.2 d followed by 'C: N 30' at 145.3 d. The cumulative  $CO_2$  emissions over 145 d averaged  $98.5 \pm 3.0$ ,  $83.8 \pm 2.3$ ,  $66.4 \pm 0.9$ ,  $42.0 \pm 1.4$  and  $16.6 \pm 2.5$  g  $CO_2$ /kg soil from 'C: N 40', 'C: N 30', 'C: N 20', 'clover only' and the control, respectively and were significantly different from one another. There was a linear 'C dose effect' (incorporation rate) on  $CO_2$  emissions with no difference between the incorporation of clover and clover + cellulose into the soil (data not shown). Over 42 and 145 d,  $CO_2$  emissions from the controls averaged 4 and 17 g/kg soil and the 'C dose effect' was 0.15 and 0.38 g  $CO_2$ /g C, respectively. Over 42 d, on a  $CO_2$ -equivalent basis,  $CO_2$  emissions were  $\sim 90\%$  of ' $CO_2 + N_2O$ ' emissions following clover and cellulose incorporation into the soil.

Cellulose occurs naturally in plant tissues and forms the basis of plant cell walls. It requires more energy to catabolise/cleave the bound cellulose for use in energy generation processes. Moreover, lignin present in the

plant tissues physically protects, and therefore retards the catabolism of the bound cellulose but in the absence of lignin; it may aid the cellulose to decompose faster (Swift *et al.* 1979). We incorporated pure cellulose powder directly in the soil which although may be a recalcitrant form of C, was labile enough for the microbes as an energy source (as it was not required to be cleaved before use). Moreover, N availability can stimulate the decomposition rates (Carreiro *et al.* 2000; Geisseler and Horwath 2009). The labile–N originating from the plant litter in the present study may have stimulated the cellulose decomposition and hence caused higher  $CO_2$  generation with an additive effect with  $N_2O$  generation.

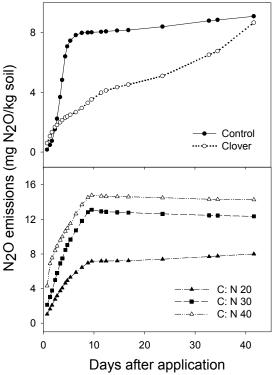


Figure 1. Cumulative N<sub>2</sub>O emissions from 'clover only', 'C: N 20', 'C: N 30' and 'C: N 40' treatments and controls during incubation (see Methods for details).

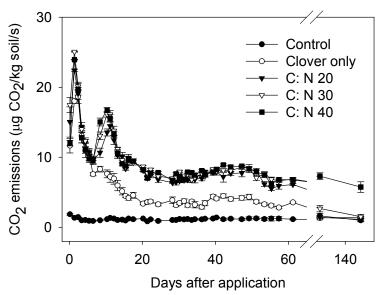


Figure 2. Soil CO<sub>2</sub> emissions from 'clover only', 'C: N 20', 'C: N 30' and 'C: N 40' treatments and controls during incubation. Data are means  $\pm$  SE (n = 5) (see Methods for details).

Cellulolytic microorganisms thrive well and are enhanced in anaerobic conditions (Clarke 1997). In the present study, the high moisture content of the soil (86% WFPS) could also have produced conditions that were conducive for the cellulolytic organisms thus causing higher CO<sub>2</sub> emissions due to better decomposition of the incorporated cellulose.

### Conclusion

Over 42 d, unexpectedly,  $N_2O$  emissions from the controls were indistinguishable from the 'clover only' and 'C: N 20' treatments. However, time courses of the  $N_2O$  emissions differed significantly; 90% of the total was completed in ~38, 7 and 9 d for controls, 'clover only' and 'C: N 20' treatments, respectively. Corresponding  $N_2O$  emissions from the 'C: N 30' and 'C: N 40' treatments averaged nearly 50% greater and 90% of the total was completed in ~9 d. Thus, clover incorporation produced the most rapid  $N_2O$  emissions response and adding the largest quantities of cellulose significantly enhanced the  $N_2O$  emissions response to clover incorporation. There was a linear C dose effect on  $CO_2$  emissions with no difference between the incorporation of clover and clover + cellulose into the soil. Over 42 and 145 d,  $CO_2$  emissions from the controls averaged 4 and 17 g/kg soil and the 'C dose effect' (incorporation rate) was 0.15 and 0.38 g  $CO_2$ /g C, respectively. Over 42 d, on a  $CO_2$ -equivalent basis,  $N_2O$  emissions were ~10% of ' $N_2O$  +  $CO_2$ ' emissions following clover and cellulose incorporation into the soil.

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# $N_2O$ emission in *Acacia mangium* stands with different ages, in Sumatra, Indonesia

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#### **Abstract**

We compared  $N_2O$  emissions at various-aged acacia plantation forests for 1 year in Sumatra, Indonesia. Three areas were prepared for this experiment, in each of which three acacia forests (1, 3, and 5 year-old, respectively) and one secondary forest were selected. The  $N_2O$  emission was high from November to March (rainy season) and low from May to November (relatively drier season). The average of  $N_2O$  emission was higher in the order of 1 year old acacia > 3 year old acacia > 5 years old acacia > secondary forest. Although our results suggest that plantations of leguminous trees possibly cause increased  $N_2O$  emission from soils, the emission may fluctuate along with the age of the stand due to the control of nitrogen availability for microorganisms in the soil.

# **Key Words**

Leguminous tree plantation, nitrous oxide, fast-growing wood plantation, humid tropical forest, global warming, nitrogen availability.

## Introduction

Nitrous oxide ( $N_2O$ ) is a strong greenhouse gas with a global warming potential 296 times as high as that of  $CO_2$ .  $N_2O$  emission from wet tropical forest is the largest natural ecosystem source of  $N_2O$  and is estimated to be 3.0 Tg N/y (Prather *et al.* 2001). Acacia is one of the most important leguminous trees for industrial plantations because of its fast growth and tolerance to acidic and nutrient-poor environments. These plantations are favoured in Asia, where 96% of the total global plantation area is located (FAO 2001). Recently, Arai *et al.* (2008) suggested that these acacia plantation soil is a possible "new" emission source of  $N_2O$  due to its nitrogen fixation ability. In their report, the  $N_2O$  emission had been enhanced 8 times higher compared to the control of secondary forest. But the experiment was carried out only at 7-year-old acacia forest, in which the growth rate of acacia gradually decreases from the period showing the highest growth rate (around 5 years old). However, the demand for nitrogen resource to the plant should change and the excess nitrogen available for microorganisms to stimulate  $N_2O$  emission from soils might also fluctuate with age. It is hypothesized that the stand age of acacia plantation, controlling nitrogen availability for microorganism in the soil, will affect  $N_2O$  emission rate. In this study, we are to clarify the stand-age effect to  $N_2O$  emission in acacia plantation forest. This result will contribute to the precise evaluation in the  $N_2O$  emission in a whole rotation period of such leguminous plantation.

## Methods

Site description

Field measurements were carried out in humid tropical forests in Muara Enim, South Sumatra Province, Indonesia (3°30′–4°05′S, 103°50′–104°10′E). Annual rainfall is 2750 mm and the annual average temperature is 27.3°C from 1991 to 2002 in Subanjeriji and Benakat (Arai *et al.* 2008). Although there is no apparent dry seasons, the rainfall is less from May to September. The soils are Acrisols derived from Tertiary sedimentary rocks. Three areas (Sodong, Gemawang, and Banding Anyar) were selected for flux measurements. In each area, we selected four types of forest, i.e., 1-year-old (SD1, GM1 and BA1), 3-year-old (SD3, GM3 and BA3), and 5-year-old (SD5, GM5 and BA5) acacia plantations, respectively, and secondary forest (SN, MB and AU). The soil texture was clay or sandy clay.

# Flux measurements

N<sub>2</sub>O flux measurements were carried out using a static chamber method (Arai *et al.* 2008). Gas sampling was performed every 45 days from September 2007 to August 2008. Six replicate chambers made of PVC tubes

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0.207 m in diameter and 0.15 m in length were inserted into the soil on one day before sampling day. After sealing the chambers with lids, which had sampling ports and air bags to equilibrate the inside pressure to atmospheric pressure, we took 40-mL gas samples using a syringe after 0, 15, and 30 min. We compressed the gas samples into 30-mL glass vials with butyl rubber stoppers that had been evacuated beforehand in the laboratory. The temperature inside the chamber and in the soil at a depth of 5 cm was measured using a temperature sensor. The glass vials were brought to the laboratory, and  $N_2O$  concentrations were analysed using a gas chromatograph (Shimadzu GC-14B) with an electron capture detector. We calculated fluxes using the slope of a linear regression, substituting the data at 0, 15, and 30 min elapsed time.

# Soil sampling and analysis

Soil samples for chemical and biochemical analysis were taken from 0–5 cm depth, in September and December in 2007 and March and June in 2008. In each plot, a composite soil sample was obtained by mixing six 200-mL samples taken approximately 2 m from each chamber using three 100-mL cylinders (5.1 cm in diameter and 5 cm in height). These soils were passed through a 2-mm-mesh sieve and stored at 4°C. Soil pH (H<sub>2</sub>O) was measured using a glass electrode with a well-mixed solution of 10 g soil and 25 mL deionized water. Total carbon and nitrogen contents were determined using an NC analyzer (JM1000CN, J-SCIENCE LAB Co., Ltd., Kyoto, Japan) for air-dried samples. Inorganic ammonium (NH<sub>4</sub><sup>+</sup>-N) and nitrate (NO<sub>3</sub><sup>-</sup>-N) were extracted by shaking a mixture of 5 g fresh soil and 50 mL 2M KCl for 1 h within 1 day of sampling. Ammonium and nitrate concentrations in the extracted solution were determined using a flow-injection analyzer (AQUA LAB Co., Ltd., Tokyo, Japan). Bulk density was determined using six core samples in each site collected in September 2008. We also took soil samples every 45 days at depths of 0–5 cm to measure soil water content.

### **Results and discussion**

The average soil pH ranged from 4.4 to 5.0 (Table 1). The average ammonium and nitrate contents in the soil were the highest in 1-year-old acacia plantation and the lowest in secondary forest. This suggests that the excess nitrogen, not absorbed by plant, is abundant in 1-year-old acacia forest.

Table 1. Statistics of soil properties in each stand age and secondary forest

Vegetation	pН		Bulk D	ensity		2	N	1	NH	4-N	NO	3-N
type	$(H_2O)$		Mg	$m^3$	mg	g/g	mg	g/g	μgl	N/g	μgN	√g
	ave.	std.	ave.	std.	ave.	std.	ave.	std.	ave.	std.	ave.	std.
acacia 1yr	4.46	0.17	0.99	0.12	0.38	0.05	0.026	0.003	20.4	10.4	20.8	5.4
acacia 3yr	4.62	0.22	0.88	0.15	0.46	0.09	0.031	0.005	9.7	6.5	6.1	4.0
acacia 5yr	4.66	0.11	0.93	0.01	0.37	0.05	0.027	0.003	10.4	0.1	5.5	0.7
Secondary	4.94	0.51	0.86	0.12	0.38	0.04	0.027	0.001	8.8	5.5	3.6	1.5

The  $N_2O$  flux was high in the wet season and low in the drier season (Figure 1). The exceptionally high flux in drier season on June was due to the heavy rain just before the sampling day. The order of average  $N_2O$  flux was: 1 year old acacia > 3 year old acacia > 5 years old acacia > secondary forest.

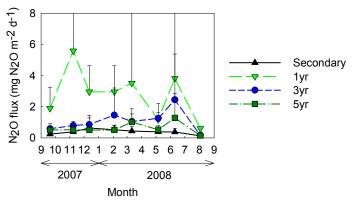


Figure 1. The seasonal fluctuation in  $N_2O$  flux in each forest. The vertical bar means the standard deviation in three site.

The  $N_2O$  flux highly correlated with nitrate content in the soil ( $R^2$ =0.9558), indicating that the nitrogen availability for microorganisms is the key role for  $N_2O$  emission from soils. Because the nitrogen availability for microorganisms might be trade-off between plant uptake rates of nitrogen, the differences in  $N_2O$  emission rate in the different-aged acacia forests might reflect the difference in plant uptake rates of nitrogen.

### Conclusion

The  $N_2O$  flux in acacia forests differed among the sites with different age. This indicates that the evaluation of  $N_2O$  emission in these land-use have to account the whole rotation cycle of these plantation. This result will contribute to the precise evaluation in the  $N_2O$  emission in such leguminous plantation at temporally and spatially expanded scales.

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# N<sub>2</sub>O emissions from a tea field in subtropical China

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### **Abstract**

Nitrous oxide  $(N_2O)$  is one of the potent greenhouse gases, and accurate estimation of  $N_2O$  emissions from fertilized arable lands is vital for the national greenhouse gas inventory and the development of emission mitigation strategies. It is well-known that acidic soils are characterised with low pH, high acidification and high  $N_2O$  production and emissions due to chemo-denitrification, compared with other cropped soils. In this paper, we report on our experiment to measure  $N_2O$  emissions from a tea field soil using the closed chamber method in subtropical China.

### **Key Words**

Nitrous oxide, tea field subtropical China.

### Introduction

N<sub>2</sub>O is a potent and long-lived greenhouse gas, and contributes a radiative forcing of +0.16±0.02 W m<sup>-2</sup> of the atmospheric greenhouse effect, with a global warming potential 310 times greater than carbon dioxide (CO<sub>2</sub>) for a 100-year time horizon (IPCC 2007). Arable soils to which nitrogen fertilizers applied are considered to be one of the main sources of N<sub>2</sub>O emissions (Mosier 1994). N<sub>2</sub>O emissions in arable fields exhibit high spatial variability due to many driving factors, such as crop rotations, soil properties, application method for nitrogen fertilizer, topography, and climatic conditions as well. In order to gain high tea yields in subtropical China, more and more nitrogen fertilizers are applied to the tea fields. The large amount of nitrogen fertilizers not only improves the quality of tea leaves, but also causes adverse impacts on the environment at the same time, such as nitrogen leaching and N<sub>2</sub>O emissions. It was observed that more nitrogen infiltrates through soil root zones and percolates into the ground water, causing severe ground water contamination (Kihou and Yuita 1991). Heavy application of nitrogen fertilizers also induces soil acidification, and therefore lowers soil pH in the tea fields. Nakasone et al. (2000) reported that in 21 Japanese tea fields, soil pH was observed ranging from 2.96-6.26, and even soil micro-organisms was not able to be detected in some fields with the lowest pH value. It is widely established that the low soil pH limits soil biological activities. Hayatsu (1993) indicated that the lowest limit of pH value for soil nitrification in the tea field was around 2.9. It is evidenced that the low pH in the soil is strongly associated with a large leakage of N<sub>2</sub>O from the soil nitrification process (Venterea and Rolston 2000). When the amount of nitrogen fertilizer exceeded 1,000 kg N/ha/y, the N<sub>2</sub>O production of tea field soil increased with the decreasing of the soil pH value (Tokuda and Hayatsu 2001). It suggested that the nitrogen fertilization and soil acidification may have effects on the nitrogen cycle and N<sub>2</sub>O emissions in the tea field soils. Given the booming and intensifying of tea industries in subtropical China, we therefore continuously monitor N<sub>2</sub>O emissions from a tea field under three different agricultural managements over a three-year period, and try to analyse the relationship between N<sub>2</sub>O emissions and its controlling factors. We also investigate the temporal and spatial variability of N<sub>2</sub>O emissions in tea fields.

# Material and method

Site

The experiment is carried out in a tea field in the Jinjing experimental base of Institute of Subtropical Agriculture, The Chinese Academy of Sciences (113°20'E, 28°35'N, elevation of 105 m). It is located at 50 km south of Changsha, the capital city of Hunan Province, China. The soil is the Alisols (FAO-UNESCO classification) developed from the granite parent materials. Normally, the tea production seasons are from May to September; and the fertilizers are applied in between tea rows in the fields from March to May and in October. The typical tea yield for this region is 4000-6000 kg/ha/y.

# Closed chamber method

N<sub>2</sub>O fluxes are measured using the static closed chamber method. Measurements take place between 9 AM and 11 AM when fluxes are expected to close to the mean of the daily fluxes (Benasher *et al.* 1994). There are three different treatments in the tea field, including the conventional treatment (CON, the amount of N

fertilizers applied is the same as the standard application rate for the tea cultivar-specified recommendation, 450 kg N/ha/v with three even splits: two in March-May using urea and one in October using oil seed trashes), the rice straw mulching treatment (SM, the nitrogen fertilizer application rate refers to the CON treatment), and the non-fertilizer treatment (CK, 0 kg N/ha/y). Each treatment has three replicates distanced by 10-20 meters. In addition, we also monitor N<sub>2</sub>O emissions from the close-by paddy field, vegetable field and masson pine wood land for comparison purpose. The closed chamber is made of two parts, the base and the chamber which covers the former when in the operation. During the installation of closed chambers, the soil and vegetation within the base are not disturbed. Each chamber covers an area of 100 cm<sup>2</sup>, and stands a height of 120 cm for the tea field, and 65×65×50 cm<sup>3</sup> for the paddy field, vegetable field and masson pine wood land. The base is made of stainless steel, and the chamber is made of polyvinyl chloride. In sampling, each gas sample is taken from the headspace of the chamber using a 100 ml syringe equipped with three-way cocks and a rubber septum at 0, 10, 20 and 30 min and stored in pre-evacuated 12-ml vials fitted with rubber septum. Gas samples are then brought back to the laboratory for the gas concentration determination by using a gas chromatograph with a 63 Ni electron capture detector. N<sub>2</sub>O fluxes (g N ha<sup>-2</sup>/d) were calculated using the gas concentration gradient with the time as the gas accumulates inside the chamber. The flux measurements will be conducted from January 2010 to December 2012 at either a 1-2 days interval for rainfall and fertilization events or a 1-2 weeks interval for plain seasons.

# Environmental factors

Soil temperatures and moistures at depths of 10, 20, 50 and 100 cm are measured by the ECH<sub>2</sub>O system (www.decagon.com). Soil pH is measured in a soil/water suspension (1:2.5, dry weight basis) with a glass electrode. Soil solutions at depths of 0-10, 10-20, 20-50 and 50-100 cm are extracted by using the suction cup method, and the inorganic nitrogen contents (nitrate and ammonium) in them are measured by the NP Autoanalyzer. Such measurements are carried out for all replicates of all treatments.

#### Results

The measurements start from January 2010. So far we have had only two sampling on 21 and 25 January 2010, respectively. With each sampling, we observe that N<sub>2</sub>O concentrations in chambers show a significantly positive linear correlation with the time. Furthermore, the increasing rates of the  $N_2O$ concentration in chambers vary among treatments and land uses. On 21 January 2010, the N<sub>2</sub>O fluxes from three treatments in the tea field are 29.4, 43.1 and 10.8 g N/ha/d, respectively, while on 25 January 2010, they are 27.5, 33.6 and 6.4 g N/ha/d, respectively. We consider the variation of N<sub>2</sub>O emissions among treatments is caused by the strong spatial variability of N<sub>2</sub>O emissions from soils since the treatment management has not commenced yet. Because the fertilization and mulching will take place in February 2010, we consider the N<sub>2</sub>O fluxes from treatments in the tea field as one value and compare with N<sub>2</sub>O fluxes from other close-by land uses we are observing. Although the measurements are carried out in the cold winter time (5-10°C), we observe quite large N<sub>2</sub>O fluxes from the fields. The average values of our observed N<sub>2</sub>O fluxes from the tea field, paddy field, vegetable field and masson pine wood land are 25.1, 24.8, 243.9, and -2.9 g N/ha/d, respectively. The N<sub>2</sub>O flux from the vegetable land is the highest, whilst the N<sub>2</sub>O flux from the masson pine wood land is the lowest, -2.9 g N/ha/d, not emitting but absorbing N<sub>2</sub>O. The discrepancy of N<sub>2</sub>O emissions between the tea and paddy fields in these two sampling is very small as both fields are not in the productive stage.

# Conclusion

Our preliminary result from few observations of  $N_2O$  fluxes even in the winter time indicates that the tea field may be a high spot for  $N_2O$  emissions, which is now neglected from the national greenhouse gas emission inventory. In August when the  $19^{th}$  WCSS commences, we will have more data to present in the event.

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# Monitoring nitrous oxide emissions from manure-fertilized alfalfa and corn cropland in the Northeastern US

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## **Abstract**

Elevated nitrogen (N) loadings in modern agriculture have led to enhanced denitrification losses and resultant increases of atmospheric nitrous oxide (N<sub>2</sub>O). Continuous monitoring of N<sub>2</sub>O emissions from corn (*Zea mays*) and alfalfa (*Medicago sativa*) fields fertilized with dairy manure was carried out with an eddy covariance (EC) system from 2006 to 2008, with a short comparative chamber campaign in the summer of 2008. Manure N loading was the most important factor controlling N<sub>2</sub>O emissions, with fluxes reaching maxima during or immediately following manure spreading. Emissions peaks during the growing season were promoted by strong rainfall and warmer temperatures, whereas winter/early spring peaks followed snowpack thaw events. Cumulative emissions were 3.2 kg N<sub>2</sub>O-N/ha (alfalfa 2006 growing season), 9.7 kg N<sub>2</sub>O-N/ha (corn 2007), and 3.6 kg N<sub>2</sub>O-N/ha (split alfalfa/corn field 2008). Emission factors ranged from 0.62 to 1.1% of applied manure N, the greatest factor resulting from summer 2006 manure spreading on alfalfa. The EC system was run concurrently with a 4-day campaign of 28 chambers placed in a transect across the split corn/alfalfa field in 2008. Both EC and chamber methods revealed similar mean emissions and day-to-day trends, showing that concurrent field-scale EC and small-scale chamber measurements can cross-validate emission determinations.

# **Key Words**

N<sub>2</sub>O, emission factor, micrometeorology, dairy manure, soil chambers.

# Introduction

Agricultural practices related to N fertilization and manure management are believed to be the greatest anthropogenic contributor to the steady increase in atmospheric N<sub>2</sub>O (Kroeze *et al.* 1999) which is of concern given its persistence, its role in ozone depletion and its high CO<sub>2</sub> equivalence (310 CO<sub>2</sub> eq.). The dairy industry is the largest agricultural activity in the Northeast US, and significant levels of regional feed N importation can resulted in high rates of manure N fertilization of croplands, creating potential for elevated environmental losses. Boyer *et al.* (2002) found that riverine exports represent only a fraction of net N imports for 16 major watersheds in the Northeast US, implying large gaseous emissions. Whereas the majority of manure N losses occur as ammonia volatilization, there is a potential for significant denitrification and N<sub>2</sub>O formation, since many soils in the region are underlain by dense glacial tills that promote shallow seasonal perched water tables and elevated soil moisture contents that promote denitrification (Singurindy *et al.* 2009).

Researchers report large variability and uncertainty of N<sub>2</sub>O fluxes for crops commonly associated with dairy farming, with literature values of annual N<sub>2</sub>O emissions of 0.6–8.7 kg N<sub>2</sub>O-N/ha for corn and 0.7–6.3 kg N<sub>2</sub>O-N/ha for alfalfa; manure applications substantially increased the level of N<sub>2</sub>O emissions from any crops. Difficulties in quantification of N<sub>2</sub>O fluxes from agricultural soils and the detection of any regular emission patterns arise from both the large diversity of combined climatic and land conditions affecting flux formation as well as the highly variable and instantaneous 'spike-like' nature of N<sub>2</sub>O fluxes. Most N<sub>2</sub>O flux responses to environmental changes or anthropogenic factors can occur on the time scales of several hours to several days (Teepe *et al.* 2001), making continuous long-term monitoring of N<sub>2</sub>O field emissions an important component of understanding temporal emission patterns. However, long-term field scale monitoring offers little insight into spatial variability of flux generation due to soil heterogeneity, including in-field moisture soil gradients. Since chambers are the only tool currently available for estimating spatial variability of N<sub>2</sub>O emissions at the field scale, parallel measurements with both techniques can be a useful tool to cross-validate both methods and identify the local sources of N<sub>2</sub>O emissions, especially where heterogeneities of crops, soil conditions and/or other treatments may be present in the contributing area (Pattey *et al.* 2007). This paper presents a brief overview of our work (Molodovskaya *et al.* 2009ab, Singurindy *et al.* 2009) to date.

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### Methods

Test fields

N<sub>2</sub>O flux observations were carried out on two fields at Cornell University's Animal Science Teaching and Research (T&R) Center in Harford, NY, USA (42°26'N, 76°15'W). With over 500 ha of cropland in corn and alfalfa and ~750 head of dairy cattle, the T&R Center represents a large dairy farm with typical regional cropping practices. Monitored fields (selected to ensure a minimum 100:1 fetch:sampling height ratio) were slightly rolling to level at an elevation of 375-380 m, on well-drained Howard gravelly loam (loamy-skeletal, mixed, active, mesic Glossic Hapludalfs). The first was an existing alfalfa stand monitored during growing season of 2006. In 2007, the experimental system was moved to the second field prior to corn planting. Monitoring continued at the same site in 2008, when approximately a half of the field area was rotated to alfalfa whereas the balance remained in corn. Fields were moldboard (corn) or chisel plowed (alfalfa) followed by disc harrowing before planting in early spring. Fields received fresh semi-solid and/or liquid dairy manure annually, with application determined by farm manure management needs (which, due to lack of on-farm storage led to widely-varying application patterns and rates, sometimes exceeding crop needs; Table 1). Manure was surface broadcasted for up to 12 weeks each year without immediate incorporation.

Table 1. Monitored field areas and manure loading summary.

Monitored site	Field	Observation period	Manure application period	Total N applied	NH <sub>3</sub> -N applied
	(ha)			(kg/ha)	(kg/ha)
Alfalfa-2006	25	20-Apr – 10-Oct-06	09-Jun-06 – 30-Sep-06	291	147
Corn-2007	30	1-Dec-06 – 31-Dec-07	22-Dec-06 – 15-Mar-07	1296	585
Split -2008 alfalfa	14	1-Jan-08 – 31-Dec-08	18-Jan-08 – 10-Apr-08	750	340
corn	16	1-Jan-08 $- 31$ -Dec-08	30-Apr-08 – 14-May-08	125	70

## Equipment

The micrometeorological EC system described in detail by Molodovskaya *et al.* (2009a) consisted of a 3-D sonic anemometer (CSAT3) and TDLAS trace gas analyzer (TGA100A; both Campbell Scientific, Inc.) to measure wind speed and  $N_2O$  concentration, respectively. High-frequency (10Hz)  $N_2O$  concentration and wind data was collected using a model CR5000 data logger. Quality control was performed on the half-hour data prior to the covariance calculations. Covariances were rotated to a natural coordinate system. Data with friction wind velocity  $\leq 0.1$  m/s and horizontal wind speed  $\leq 1.5$  m/s were discarded to exclude periods when turbulent mixing was not sufficient. To remove potential disturbances to the wind, data associated with wind directions  $\geq 120^{\circ}$  and  $\leq -120^{\circ}$  from the sonic anemometer pointing axis were also discarded. Fluxes were averaged over half-hour and daily periods. Source area contribution to the integrated flux was estimated as described by Schuepp *et al.* (1990) and Laville *et al.* (1999); footprint analysis showed that 40% of the flux originated within 75m of the system mast, and 75% of the flux originated within 150m of the mast. Other measurements included volumetric soil moisture content (two CS616 Water Content Reflectometer sensors installed 10 cm below the surface), soil temperature (4 replicated thermocouples 10cm deep), air temperature and humidity (Vaisala HMP45A/D), and precipitation (tipping bucket gauge).

The 4-day comparative chamber campaign (Molodovskaya *et al.* 2009b) was conducted June 30-July 3, 2008, with three deployments per day using 28 static closed chambers installed in replicate pairs on a transect (10m spacings) across the split alfalfa/corn fields. Chambers (0.07 m² coverage area, 0.017 m³ enclosed volume) consisted of a cylindrical collar installed in the soil, and a removable cover fitted with sampling and vent ports, installed on the collars only during 30 min sampling runs to minimize potential artifacts. Air samples were withdrawn by syringe and placed in evacuated vials for analysis (Agilent 6890N GC/ECD). The N<sub>2</sub>O flux measured by static chambers was calculated from rate of change of N<sub>2</sub>O concentration during 30 min cover deployment (Rochette and Bertrand 2007). Daily mean fluxes were calculated for each chamber from three deployments per day. EC and chamber fluxes were tested for normality with the K-S test (P=0.05), and corn/alfalfa and chamber/EC differences were analyzed with parametric unpaired t-test or non-parametric Mann-Whitney rank sum test. Descriptive statistical parameters for EC and chamber fluxes were calculated and compared for the chamber campaign.

# Results

Long-term EC system monitoring

Growing season (April-October) rainfall in 2006 was 700 mm, in contrast to 481 mm (895 mm annual) in

2007 and 438 mm (833 mm annual) in 2008. Average growing season temperatures for the research site were 16.7 (2006), 14.3 (2007) and 13.9°C (2008), compared to the area 10-year average (15.0°C). Despite elevated manure N loadings (typical N loading rates being  $\leq$ 200 kg N/ha), fluxes observed by the EC system (Figure 1) were comparable to other literature EC flux measurements, which generally exceed those of chamber studies due in part to the continuity of sampling which diminishes the risk of missing peaks that can account up to 50% of annual emissions. Average monthly N<sub>2</sub>O-N fluxes for all three years of monitoring ranged from -0.4 to 108.4 g N<sub>2</sub>O-N/ha/d.

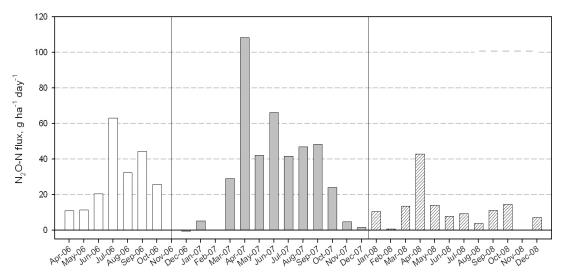


Figure 1. Mean monthly emissions from alfalfa (2006), corn (2007) and split corn/alfalfa (2008) fields.

Cumulative measured emissions were 3.2 kg  $N_2O$ -N/ha from alfalfa (growing season only) in 2006; 9.7  $N_2O$ -N/ha for corn in 2007 (9.1 kg/ha for growing season); and 3.6 kg  $N_2O$ -N/ha the split field in 2008 (2.3 kg/ha for growing season). Source area analysis for the 2008 split alfalfa/corn field (based on wind direction calculations) showed that cumulative  $N_2O$ -N emissions from the alfalfa field were 3.0 kg/ha vs. only 0.6 kg/ha from corn. The alfalfa field also produced 89% of total daily fluxes over 100 g/ha/d. Daily means varied widely, with coefficients of variance (CV) of 160% (2006), 238% (2007) and 328% (2008).  $N_2O$ -N fluxes reached maxima during or immediately after manure fertilization events combined with seasonal weather changes. For both 2007 and 2008, winter manure applications were followed by spring thaws that resulted in emission peaks in April of each year. The magnitude of each annual maximum (63 g  $N_2O$ -N/ha/d in July 2006 (alfalfa), 108 g/ha/d in April 2007 (corn), and 43 g/ha/d in April 2008 for alfalfa/corn) exceeded the next highest monthly average of any given year by at least 30%. Emission factors (EF) for all three years of observations were calculated using the updated IPCC methodology which includes manure N and crop N residue inputs. Emission factors were 1.11% (2006), 0.75% (2007) and 0.62% (2008), as compared to the IPCC default factor of 1% for non-organic soils.

# Comparative study

Daily mean EC and chamber  $N_2O$  fluxes are shown in Figure 2. Chamber fluxes from both alfalfa and corn transects were normally distributed, with the overall mean flux from the alfalfa field almost twofold of that from the corn field, again reflecting the greater N loadings. Chamber  $N_2O$  fluxes were -1.1 to +5.6  $\mu$ g  $N_2O$ -N/m²/min (alfalfa) and -2.4 to +6.1  $\mu$ g  $N_2O$ -N/m²/min (corn), reflecting heterogeneity of soil  $N_2O$  formation including, in places, net  $N_2O$  consumption. Concurrent EC fluxes varied from -10.5 to +40.0  $\mu$ g  $N_2O$ -N/m²/min and strongly depended on contributing footprint. The wind direction and footprint analysis showed that approximately 75% of the integrated daily EC flux was primarily constituted by emissions from the area under alfalfa treatment, which was confirmed by the similar daily EC and alfalfa chamber means. Corn chamber data were more variable than alfalfa, both spatially and temporally. Overall chamber and EC fluxes showed a continuous decrease for the period over four days of observations both on alfalfa and corn sites, which was likely related to the steadily diminishing soil moisture content. The four-day mean EC flux was approximately four times greater than corn and two times greater than alfalfa overall chamber means. However daily chamber fluxes along the transect between the two fields were not significantly different from the daily mean EC flux, likely due to the high variability of the data.

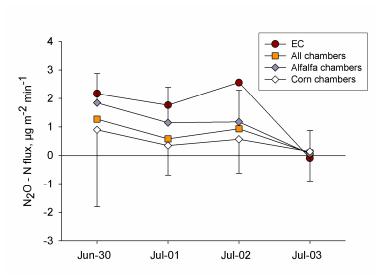


Figure 2. Comparative results of 4-day EC system and chamber campaign (Molodovskaya et al. 2009b).

#### Conclusion

Despite widely ranging loadings, emission factors determined by continuous EC monitoring ranged from 0.62 to 1.1% of applied manure N. Concurrent field-scale EC and small-scale chamber measurements can cross-validate emission determinations.

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# Nitrogen fertiliser increases nitrous oxide emissions from a semi arid Vertosol

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#### **Abstract**

Nitrous oxide  $(N_2O)$  has 300 times more climate warming effect than carbon dioxide so the accurate measurement of  $N_2O$  emissions from agricultural soils is important for the verifiable accounting of greenhouse gas emissions. Studies of wheat production systems in semi arid regions of Australia have so far indicated low emissions of  $N_2O$  by international standards, however the studies are limited. We examined the emissions from a typical rainfed Vertosol growing winter wheat in south-eastern Australia. Continuous gaseous measurements using an automated enclosure chamber system were combined with the simultaneous monitoring of soil water, temperature, mineral nitrogen (N) and weather parameters. The agronomic treatments were winter wheat grown without N fertiliser, following either a grain legume crop (fieldpeas) or a legume pasture (medic), or wheat grown with N fertiliser following a crop of canola. In a relatively dry year, the  $N_2O$  emissions were similar in scale to other Australian studies from semiarid climates. The application of N fertiliser at sowing increased  $N_2O$  emissions for approximately two months. The use of previous legume crops to supply N for following wheat crops may reduce  $N_2O$  emissions from this cropping system.

# **Key Words**

Greenhouse gas, wheat, N<sub>2</sub>O, emissions factor, south eastern Australia.

### Introduction

Australian agriculture was responsible for an estimated 16% of the net national greenhouse gas emissions in 2006, and contributed 84% of the nitrous oxide (N<sub>2</sub>O) emissions, 75% of which resulted from the nitrogen (N) enrichment of agricultural soils (Department of Climate Change 2008). The sources of N enrichment include synthetic fertiliser. The Intergovernmental Panel on Climate Change (IPCC) has estimated that 1.25% of all N fertiliser applied to soil in the northern hemisphere is lost as N<sub>2</sub>O. However, N<sub>2</sub>O emissions from N fertiliser applied to Australian crops have been found to be much less (Barker-Reid *et al.* 2005), reflecting the drier nature of Australian agro-ecosystems and low N application rates by international standards. Although only a few comprehensive studies have been made of N<sub>2</sub>O emissions from rained-fed crops in semi-arid climates (Barton *et al.* 2008), the fertiliser emissions factor for rain-fed cropping in Australia has been reduced to 0.3% (Department of Climate Change 2008). Our objectives in this study were to measure gaseous emissions and establish the fertiliser emissions factor of wheat in a typical south east Australian rainfed cropping environment on alkaline soils. Measurements of gaseous N<sub>2</sub>O emissions were made 24 hours a day and combined with measurements of soil water, temperature, plant available N and weather parameters.

# Methods

The study site was near Horsham, on the Plant Breeding Centre farm (36°45'S; 142°8'E), in the Wimmera region of Victoria. The Wimmera has a temperate climate with mediterranean style hot, dry summers, and cool to mild winters that are relatively wet (Cawood *et al.* 1996). The soil type was a Kalkee Clay, which is an alkaline expanding-clay Grey Vertosol (Martin *et al.* 1996; Isbell 2002). The trial was a randomised block design consisting of three treatments replicated three times. Winter wheat (*Triticum aestivum* cv. Carra) was grown in three treatments; (1) Rain-fed wheat with no nitrogen fertiliser following a crop of medic (*Medicago truncatula* Gaetn. cv. Mogul), (2) Rain-fed wheat with no nitrogen fertiliser following a crop of fieldpeas (*Pism sativum* cv. Kaspa), (3) Rain-fed wheat with 50 kg N/ha urea fertiliser side-banded at sowing, following a crop of canola (*Brassica napus* cv. Beacon). Gas collection commenced on 8 March 2008 and ended on 7 April 2009. The growing season was relatively dry (195 mm compared to the long-term average of 268 mm for June to Nov) and supplementary irrigation was applied on the 3<sup>rd</sup> (14 mm) and 15th - 16th (30 mm) of October. The cultivation (minimum tillage) and fertiliser rates were otherwise representative of farming practices in the region.

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Measurements of N<sub>2</sub>O were made using automated gas collection chambers. The collection chambers consisted of moveable boxes (0.8 m x 0.8 m x 0.5 m high) constructed from stainless steel and polycarbonate, which were clipped to an open stainless steel base unit (0.8 m x 0.8 m x 150 mm depth) that was pressed approximately 100 mm into the soil. Two base units (0.5 m apart) were installed in each plot so that the position of the chambers could be alternated weekly. As the crop grew an extension box of similar construction was fitted to each chamber to double its height. The nine automated gas collection chambers were located at one end of the agronomic plots (plot size 7 m x 15 m) and were programmed to measure N<sub>2</sub>O flux in a closed chamber 16 times a day. The lids of the three chambers within a replicate group closed simultaneously for 30 minutes, and the air from each chamber of the group was then sampled sequentially for 30 seconds every three minutes. Gas samples were distributed through a pressure controlled manifold and driers, to a tuneable diode laser trace gas analyser (Campbell Scientific Inc.), which measured N<sub>2</sub>O adsorption in continuous comparison to a standard concentration N<sub>2</sub>O gas. During each cycle, instrument grade air was also sampled as a working standard gas to correct for offset errors, as well as the ambient air. Flux was determined by calculating the rate of change in N<sub>2</sub>O concentration (corrected to density) from ten measurements over the 30 minute period (Barton et al. 2008). The chambers vented automatically during the closure time if the temperature in the chambers exceeded 50°C, or if the site received 0.51 mm rain in 5 min.

Soils were characterised using standard methods (Rayment and Higginson 1992) prior to plot establishment in 2008 for bulk density, pH (1:5 CaCl<sub>2</sub>), electrical conductivity (EC) in 1:5 w/v solution, exchangeable sodium percentage (ESP), total nitrogen (Leco FP2000, MI, USA) and plant available N (air dry soil<2mm, 2M KCl extraction). Permanent wilting point (PWP) and field capacity (FC) were determined by pressure plate method at -1500 and -30 kPa respectively (Klute 1986). Potentially mineralisable nitrate (AMN) was determined from samples collected in July 2008, as the difference in KCl extractable N between post-incubated and non-incubated extracts (Sparling and Searle 1993). Soil water content in the surface soil (0-60 mm depth) was monitored in each chamber base using thetaprobes (Theta-Probe MK2x, Delta-T Devices Ltd).

# Results and discussion

Daily  $N_2O$  emissions ranged from -0.37 to 9.3 g  $N_2O$ -N/ha/day over the trial period for the three treatments. The mean daily emission was 0.45 g  $N_2O$ -N/ha/day, although the data set was highly skewed and so the median rate of emission was 0.11 g  $N_2O$ -N/ha/day. Prior to sowing, the autumn season of 2008 (March to May) was relatively dry and soil moisture in the top 50 mm was below PWP until the "break" rainfall event on the  $16^{th}$  of May (Table 1). The  $N_2O$  emissions were relatively small (Figure 1) throughout this period. The average rates of emission until sowing were  $0.18\pm0.22$  g  $N_2O$ -N/ha/day for medic stubble,  $0.1\pm0.16$  g  $N_2O$ -N/ha/dayfrom pea stubble, and  $0.09\pm0.09$  g  $N_2O$ -N/ha from the canola stubble treatment.

The wheat was sown in the plots on 6 June 2008. Seasonal conditions improved during winter, with 151 mm rain falling from June to August. The soil moisture reached field capacity in the topsoil on the  $8^{th}$  of July (Figure 1). Emissions from the fertilised plots increased in comparison to the other treatments, but only between 10 June and 16 August 2008. In this period, the wheat + N fertiliser treatment released  $152 \pm 31$  g  $N_2O-N/ha/day$ , compared to  $65\pm17$  g  $N_2O-N/ha/day$  from wheat sown in medic stubble and  $52\pm28$  g  $N_2O-N/ha/day$  from wheat sown in pea stubble. When the entire June to December cropping period was considered, the soil under wheat + N had a significantly greater rate of emission compared to soil under wheat that was sown in pea stubble with no N fertiliser (P<0.05).

Table 1. Soil properties in a Vertosol in the Wimmera region of Victoria, under summer fallow in February 2008 following crops of either medic, field peas or canola, including soil bulk density (BD), permanent wilting point (PWP), field capacity (FC), electrical conductivity (EC), Exchangeable Sodium percentage (ESP) and plant available N (Mineral N).

Depth	BD	PWP	FC	pН	EC	ESP	Total N	Mineral	$N (\mu g N / \mu g)$	g soil)
m	g/cm <sup>3</sup>	%V/V	$% \frac{1}{2} \left( \frac{1}{2} \right) = $	CaCl <sub>2</sub>	1:05	%	%	Canola	Medic	Pea
0.0-0.1	1.12	23.1	41.2	7.9	0.25	3.9	0.08	16.5	36	27.2
0.1-0.2	1.23	26.8	46	8.1	0.25	5	0.04	7.7	14.2	12.6
0.2 - 0.4	1.26	26.7	45.7	8.2	0.36	6.5	0.03	9.5	9.8	12.2
0.4-0.6	1.32	31.3	52.7	8.4	0.5	8.9	0.02	5.7	12.3	7.4
0.6 - 0.8	1.34	33.4	59.5	8.6	0.74	11.7	0.01	7.2	5	6.3
0.8-1.0	1.39	36.3	62.6	8.6	1.08	13.8	0.01	5.7	4.6	4.2
1.0-1.2	1.37	35.9	64.1	8.7	0.99	15.2	0.01	6.9	5.7	5.2

The amount of background N in this soil is relatively low (Table 1) and a sodic subsoil restricts the root depth in these very alkaline soils (Hazelton and Murphy 2007) so that the available N can be manipulated by the crop rotation. The objective of the pre-treatments was to reduce plant available N in the canola plots, so that the amount of N would be similar across the treatments when the ex-canola plots were fertilised at sowing. We confirmed that soil mineral N (nitrate plus ammonium) in the summer fallow stage in February 2008 had been reduced in the canola stubble plots, compared to the plots in medic and pea stubble (Table 1). There was approximately 57 kg/ha more mineral N in the top 600 mm of the medic plots, and 38 kg/ha more mineral N in the pea stubble plots, compared to the soil under canola stubble. Subsequent analysis of the potentially mineralisable N (AMN) in July 2008 also found that there was less mineralisable N in the top 100 mm of the canola stubble plots ( $50\pm17~\mu gN/g$  soil compared to  $67\pm15~\mu gN/g$  soil for ex medic and  $60\pm22~\mu gN/g$  soil for ex peas). The medic stubble plots therefore contained an estimated 72 kg potentially mineralisable AMN-N/ha in the top 10 cm, while the pea stubble contained 66~kg AMN/ha, compared to 52~kg N/ha in the canola plots. The increased emissions from the fertilised plots therefore may have been caused by a difference in the form of N in the soil (nitrate, ammonium or organic) rather than a difference in the quantity of N.

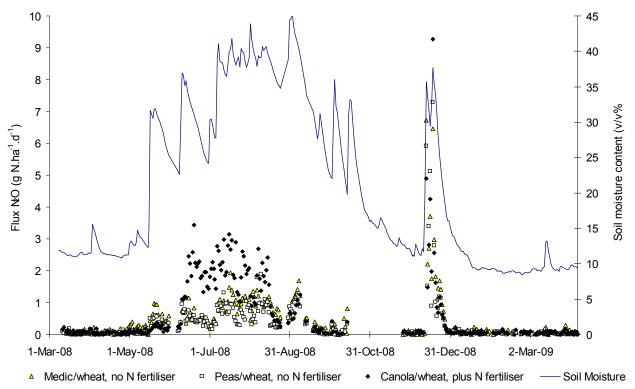


Figure 1. Soil emissions of nitrous oxide and changes in soil moisture, from wheat in the Wimmera region, Victoria.

The amount of winter rainfall was close to the long term mean but only 44 mm rain fell from September to November, which was a third of the long term expected rainfall for spring. Despite supplementary irrigation on 3<sup>rd</sup>, 15<sup>th</sup> and 16<sup>th</sup> of October, the soil moisture levels declined and had returned to PWP (crop lower limit) by late October. Equipment breakdowns between 15<sup>th</sup> October and 24<sup>th</sup> November caused an unfortunate gap in the data but only 11.4 mm of rain fell during this period, so the emissions are expected to have been minimal.

The initial wheat establishment was uneven and subsequent growth was poor, resulting in very low grain yields (mean 0.67 t/ha) and no significant differences between the agronomic treatments. Conditions after harvest remained very dry until 72 mm rain fell between the 9<sup>th</sup> and 17<sup>th</sup> December. There was a resulting peak in emissions for a short period (Figure 1), before rapidly declining as the soil moisture returned to PWP. Subsequently, only 15 mm rain fell, so conditions remained dry and emissions were minimal until the experiment was terminated in early April 2009.

The  $N_2O$  emissions from this study in 2008–09 were similar to those recorded from a wheat crop growing in a temperate climate on acid soils in Rutherglen, Victoria (Barker-Reid *et al.* 2005), and in a semi-arid climate on acid sandy soils in Cunderdin, Western Australia (Barton *et al.* 2008). A fertiliser emissions factor was calculated for the Wimmera site, based on the annual difference between the  $N_2O$ -N emitted by the fertilised soil under canola stubble and the average of the unfertilised treatments, divided by the amount of fertiliser applied (50 kg/ha N). The average fertiliser emissions factor for the whole monitoring period was 0.16%, confirming that a reduced emissions factor is appropriate for N fertiliser applied to semiarid rainfed grain crops in Australia.

### **Conclusions**

The growing season rainfall (April to October) for 2008 was only decile 1 in the Wimmera (Price and Sounness 2008). In this year, the  $N_2O$  emissions from wheat cropping soils, and the fertiliser emissions factor, were both similar to two other studies made in Australian wheat crops. Despite the dry conditions in 2008, there was a clear flux response to the application of N fertiliser, which caused a threefold increase in  $N_2O$  emissions that lasted for 68 days. The use of legumes, instead of fertiliser, as a source of N for wheat crops may reduce  $N_2O$  emissions from cropping soils.

# Acknowledgments

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# Nitrogen fertilizer rate management as a nitrous oxide mitigation strategy: Development of a nitrous oxide emission reduction protocol (NERP)

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## **Abstract**

Nitrous oxide ( $N_2O$ ) is a potent agricultural greenhouse gas (GHG). More than 50% of the global anthropogenic  $N_2O$  flux is attributable to emissions from soil, primarily due to large fertilizer nitrogen (N) applications to corn and other non-leguminous crops. Quantification of the trade–offs between  $N_2O$  emissions, fertilizer N rate, and crop yield is an essential requirement for informing management strategies aiming to reduce the agricultural sector GHG burden, without compromising productivity and producer livelihood. There is currently great interest in developing and implementing agricultural GHG reduction offset projects for inclusion within carbon offset markets. Nitrous oxide, with a global warming potential (GWP) of 298, is a major target for these endeavours due to the high payback associated with its emission prevention. In this paper we use robust quantitative relationships between fertilizer N rate and  $N_2O$  emissions, along with a recently developed approach for determining economically profitable N rates for optimized crop yield, to propose a simple, transparent, and robust  $N_2O$  emission reduction protocol (NERP) for generating agricultural GHG emission reduction credits. This NERP has the advantage of providing an economic and environmental incentive for producers and other stakeholders, necessary requirements in the implementation of agricultural offset projects.

# **Key Words**

Agriculture, cap and trade, N<sub>2</sub>O mitigation.

### Introduction

The rate at which reactive N enters into the biosphere each year has increased dramatically through the intensification of anthropogenic pathways. Global synthetic fertilizer N consumption has increased from  $\sim 10$  Tg N in the late 1950s to  $\sim 100$  Tg N in 2008 (Robertson and Vitousek 2009). The need to feed and provide energy for a growing population drives this increase in demand for fixed N, but also results in increased emissions of  $N_2O$ . Human induced emissions of  $N_2O$  are increasing by  $\sim 150$  Tg N/y, with the current global atmospheric concentration of  $N_2O \sim 322$  ppbv, compared with a pre–industrial concentration of  $\sim 270$  (Forster et al. 2007). Annual agricultural emissions of  $N_2O$  are estimated at  $\sim 2.8$  Gt  $CO_2$  equivalents ( $CO_2$ e) (Smith et al. 2007), the vast majority attributable to field crop management activities (EPA 2009). As  $N_2O$  in agricultural soil is produced predominantly through microbial transformations of inorganic N, the potential to produce and emit  $N_2O$  increases with increasing N availability. With the strong influence of available N on  $N_2O$  emissions, some emissions of  $N_2O$  are an unavoidable consequence of maintaining highly productive cropland. However, management technologies that lower N input or reduce N availability without compromising crop productivity have great potential for reducing emissions of  $N_2O$  (e.g., Follett et al. 2005).

Manipulating N input, is a readily accessible management tool for altering crop N availability, with fertilizer N rate a crucial parameter for estimating both crop yield and  $N_2O$  emissions. Quantification of the trade–offs between  $N_2O$  emissions, crop yield and fertilizer N rate is essential for proposing strategies which optimize productivity at economically and environmentally favorable N inputs. Increasing fertilizer N rate typically increases  $N_2O$  emissions. As a result of extensive reviews and meta–analyses (e.g., Bouwman *et al.* 2002), anthropogenic N addition is used in IPCC Tier 1 methodologies as the primary controlling factor for estimating country–wide emissions of  $N_2O$  from managed land (IPCC 2006).

Our paper focuses on using fertilizer N rate as a quantitative proxy to calculate reductions in  $N_2O$  emissions from cropland. This narrowed focus is important in establishing protocol transparency for all stakeholders and is cognizant of the practical undertakings necessary to allow for ease of use in the validation, monitoring, and verification process required for a NERP. The benefits of utilizing a simple, scientifically robust N management practice as a  $N_2O$  mitigation surrogate will far outweigh the cost of adoption if the practice gains producer confidence and is initiated with minimal associated financial or social expense.

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IPCC Tier 1 methodology relies on a linear relationship between fertilizer N rate and  $N_2O$  emissions, i.e., the  $N_2O$  emission factor (EF) is constant (1.0%) irrespective of fertilizer N rate. This linear approach however, may be too conservative. Evidence from high resolution N fertilizer gradient studies in the US Midwest (McSwiney and Robertson 2005; Hoben *et al.* 2010; Millar *et al.* 2010a) suggest that  $N_2O$  emissions can increase exponentially with increasing fertilizer N rate, particularly at rates which exceed ecosystem (crop + soil) N uptake capacity. In these studies,  $N_2O$  emissions were substantially increased at fertilizer N rates above where crop yield was optimized when compared to emissions at rates that were insufficient for optimization. This non–linearity translates into an increasing EF value as N rate increases. Consequently, identical reductions in fertilizer N rate occurring above the threshold fertilizer N rate for optimized productivity result in very different calculated reductions in  $N_2O$  emissions, dependant on the form of the relationship. This has significant environmental and economic implications regarding the generation of  $N_2O$  emission reduction credits and the incentives for adopting reduced fertilizer N rate strategies.

## **Protocol development**

We developed our N<sub>2</sub>O reduction protocol (NERP) for calculating reductions in direct N<sub>2</sub>O emissions from row–crop agricultural systems in the US Midwest (Midwest). We compared the IPCC Tier 1 linear methodology (constant EF) with our Tier 2 regional non–linear calculation (variable EF) and coupled these with a recently developed approach for determining economically profitable N rates for optimized crop yield to construct a simple, robust NERP for generating agricultural GHG emission reduction credits resulting from fertilizer N rate reduction (Millar *et al.* 2010b). For our purposes, the Midwest comprises the states of Iowa, Illinois, Indiana, Michigan, Minnesota, Ohio and Wisconsin. The region is characterized by extensive crop cultivation and is the major US producer of corn, soybean, and wheat. The corn–soybean rotation is the representative agricultural ecosystem in the Midwest, as well as in eastern and central North America generally.

# Fertilizer N rate recommendations

Recently, the yield–based approach for crop N rate recommendations has been questioned, primarily due to the poor relationship between the recommendations and the economic optimum N rate (EONR). This has lead to a newly developed Midwest approach to optimize crop yield (Sawyer *et al.* 2006), which utilizes current N rate research data from field trials in corn–soybean rotations and continuous corn in the seven Midwest states to determine economically profitable N inputs. These inputs are expressed as a range of N rate around the maximum return to N (MRTN) at different N and corn prices, defined to be at or within  $\pm$  \$1.00 acre<sup>-1</sup> of the MRTN (i.e., + or - \$1.00 acre<sup>-1</sup> is the *high* or *low* N rate, respectively).

# Baseline and credit

Any reduction in fertilizer N rate below a previous baseline (common practice) level can be considered to generate emission reduction credits, due to the concomitant decrease in  $N_2O$  emissions. For our purposes these credits are provided by the reduction in N from the *high* to the *low* profitable MRTN rate (Figure 1; Table 1), i.e., we assume that producers who, given the choice of an N rate to apply within an economically profitable input range, would choose to apply the highest rate within this range in order to hedge against a perceived inadequate N supply.

#### Equations

Emission reductions of N<sub>2</sub>O from a reduction in fertilizer N rate can be calculated from:

$$N_2O_R = N_2O_{+N(B)} - N_2O_{+N(A)}$$
 (1)

Where:

N<sub>2</sub>O<sub>R</sub> Reduction in N<sub>2</sub>O emissions brought about by fertilizer N rate reduction,

Mg CO<sub>2</sub>e/ha/y;

N<sub>2</sub>O<sub>+N (B)</sub> Direct N<sub>2</sub>O emissions following N fertilizer input before fertilizer N rate reduction,

kg CO<sub>2</sub>e/ha/y;

 $N_2O_{+N(A)}$  Direct  $N_2O$  emissions following N fertilizer input after fertilizer N rate

reduction, kg CO<sub>2</sub>e/ha/y;

The subscripts  $_{\rm B}$  and  $_{\rm A}$  represent the scenario before and after the fertilizer N rate reduction, respectively. Emissions of N<sub>2</sub>O under these scenarios can be calculated from:

$$N_{2}O_{+N (B/A)} = [((F_{SN} + F_{ON})_{(B/A)} \times EF_{n}) + N_{2}O_{0N (B/A)}] \times N_{2}O_{MW} \times N_{2}O_{GWP}$$
(2)

Where:  $N_2O_{+N\;(B\;/\;A)}$ Direct N<sub>2</sub>O emissions following N fertilizer input, kg CO<sub>2</sub>e/ha/v: Direct N<sub>2</sub>O emissions following zero fertilizer N input, kg N<sub>2</sub>O–N/ha/y;  $N_2O_{0N(B/A)}$  $F_{SN\,(B\,/A)}$ Mass of N applied from synthetic fertilizer, kg N/ha/v; Mass of N applied from organic fertilizer, kg N/ha/y;  $F_{ON(B/A)}$ Emission factor for N<sub>2</sub>O emissions from N inputs, kg N<sub>2</sub>O-N (kg N input)<sup>-1</sup>  $EF_n$ (n = 1 or 2 for Tier 1 or Tier 2 approaches, respectively); Ratio of molecular weight of N<sub>2</sub>O to N (44/28), kg N<sub>2</sub>O (kg N)<sup>-1</sup>;  $N_2O_{MW}$ Global Warming Potential for N<sub>2</sub>O (298), kg CO<sub>2</sub>e (kg N<sub>2</sub>O)<sup>-1</sup>;  $N_2O_{GWP}$ 

EF<sub>1</sub>: The IPCC Tier 1 default emission factor (EF<sub>1</sub>) has a value of 0.01 or 1.0% (IPCC 2006), and is insensitive to fertilizer N rate.

EF<sub>2</sub>: The value of the regional Tier 2 emission factor (EF<sub>2</sub>) determined from the N fertility gradient field sites in the Midwest (Figure 1; Hoben *et al.* 2010) is sensitive to N rate and can be expressed as:

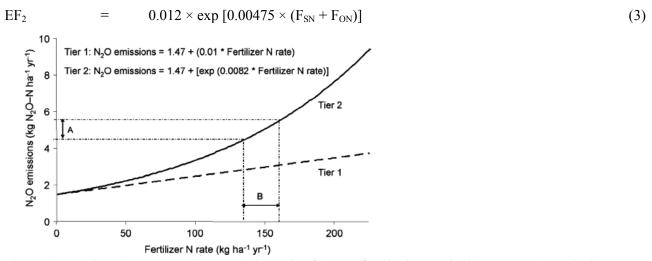


Figure 1. Relationship between direct emissions of  $N_2O$  (kg  $N_2O-N/ha/y$ ) and fertilizer N rate (kg N/ha/y) determined from a linear (Tier 1, dashed line) and non–linear (Tier 2, solid line) approach. The Midwest background emission value (1.47 kg  $N_2O-N/ha/y$ ) determined from the N gradient sites is included in Tier 1 and Tier 2 approaches. The  $N_2O$  emission reduction A ( $\sim$  1.1 kg  $N_2O-N/ha/y$ ), results from an N rate reduction B (160 to 135 kg N/ha/y) using the Tier 2 approach (dash—dot lines). The equivalent reduction using the Tier 1 approach (not shown for clarity) is  $\sim$  0.3 kg  $N_2O-N/ha/y$ .

Table 1. Annual reductions in  $N_2O$  emissions ( $CO_2e$ ; Mg  $CO_2/ha/y$ ) in Midwest states (selected data) under two cropping systems (continuous corn (C-C) and corn-soybean (C-S)) resulting from reductions in fertilizer N rate, calculated using the IPCC linear (Tier 1) and the regional non-linear (Tier 2) approach. The fertilizer N to corn price ratio used is 0.10, expressed as \$ per pound of applied N divided by \$ per bushel of corn yield.

		PNRR low†	PNRR high†	Linear (Tier 1)	Non linear (Tier 2)	
State	System	N rate (kg N/ha)		CO <sub>2</sub> e reductions ‡ (Mg CO <sub>2</sub> /ha/y)	CO <sub>2</sub> e reductions ‡ (Mg CO <sub>2</sub> /ha/y)	
Iowa	С-С	184	212	0.13	0.78	
Illinois#	C-C	185	217	0.15	0.93	
Indiana	C-S	180	207	0.13	0.73	
Michigan	C-S	135	160	0.12	0.50	
Minnesota	C-C	152	173	0.09	0.44	
Ohio	C-C	206	237	0.14	1.00	
Wisconsin ¤	С-С	145	166	0.10	0.44	

<sup>†</sup> The Profitable Nitrogen Rate Range (PNRR) is the N rate values at a \$1.00 / acre (\$0.40 / ha) net return range (*low* and *high*) around the maximum return to N (MRTN). ‡  $CO_2e$  reductions calculated using equations 1 and 2 above. # Data for Central region of Illinois.  $\square$  Data for high to very high yield potential (6.3-13.8 Mg/ha) soils in Wisconsin.

From equations 1 and 2 we calculate an  $N_2O$  emission reduction of 0.5 Mg  $CO_2e/ha/y$  for the corn component of a corn-soybean rotation in Michigan (using  $EF_2$ ) as a result of reducing fertilizer N rate from the *high* (160 kg N/ha) to the *low* (135 kg N/ha) N rate of the profitable range (Figure 1). However, many

producers are currently still fertilizing at N rates based on yield goal recommendations that can significantly exceed 160 kg N/ha. For example, a reduction from a starting N rate of 200 kg N/ha to 135 kg N/ha would yield an emission reduction credit of 1.5 metric tons CO<sub>2</sub>e/ha/y.

# **Summary**

In developing the NERP we have deliberately focused on fertilizer N rate. Other management and environmental factors influence  $N_2O$  emissions, however as an unambiguous proxy, fertilizer N rate can be viewed as a transparent, tangible, and readily manageable commodity within a future  $N_2O$  credit framework. We believe that utilizing the Midwest field based MRTN approach introduces the necessary economic component to the protocol framework and promotes producer confidence in the process. Although row crop agriculture in the Midwest is highlighted, this protocol could be applicable to other agricultural regions globally. For these reasons, we believe our protocol has merit and potential to be utilized in future agricultural offset projects developed for the carbon offset markets.

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# Nitrous oxide emissions from a clay soil depend on timing of autumn mouldboard ploughing

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### **Abstract**

Soil tillage under wet conditions can have negative consequences on the soil structure, especially on clay soils. This may result in decreases in crop growth and thereby nitrogen (N) uptake causing increased levels of soil mineral N during periods with no crop N uptake. A more dense soil structure as well as increase amounts of nitrate could give increased losses of N by leaching or by gaseous emissions. Declining grain yields during almost ten years of mouldboard ploughing in late autumn (November) under wet conditions compared with ploughing in September when the soil still is dry raised the question if deteriorated soil structure increases nitrous oxide ( $N_2O$ ) emissions. Data on  $N_2O$  emissions measured by manual chambers from a Swedish long-term field experiment with early and late mouldboard ploughing compared with tine cultivation as primary tillage will be presented as well as data from micrometeorological measurements.

# **Key Words**

Clay soil, N<sub>2</sub>O emissions, mouldboard ploughing, timing.

## Introduction

Agriculture is the largest anthropogenic source of nitrous oxide (N<sub>2</sub>O), accounting for 65% to 80% (Crutzen et al. 2008, IPCC 2006). Nitrous oxide is 298 times more potent as green house gas compared to carbon dioxide (on a 100 year basis) and has a long half time in the atmosphere (114 years). Thus, there is a need for measurement of fluxes and identifying the driving variables causing the emission. By identifying critical occasions in the crop rotation, changed management options may be developed from the results. Knowledge is needed on emission of N<sub>2</sub>O from Swedish clay soils, and on possible ways to mitigate these emissions by altered farming practice. It is well known today that the risk for nitrogen (N) leaching from sandy soils in Sweden is high during the winter season if the soil is ploughed early in autumn compared to delayed tillage operations (Stenberg et al. 1999; Aronsson 2000; Aronsson et al. 2003). The N leaching from clay soils have been reported to be lower (Torstensson 2003; Ulén et al. 2005; Lundström 2004). However, Wetterlind et al. (2005) found differences in mineral N accumulation in the soil profile 0-90 cm during autumn in wet years compared with dry years with higher accumulations dry years. Wet years, there was little accumulation of mineral N. This could indicate gaseous N losses from the soil wet years rather than leaching losses. Stenberg et al. (2005) found that grain yields during an eight-year period declined in the late ploughed treatments compared with the early ploughed. This indicates a deteriorated soil structure, negatively affecting yields, due to ploughing during wet conditions in late autumn. Here, early autumn ploughing was compared with late ploughing as well as tine cultivation in respect of emissions of N<sub>2</sub>O, soil mineral N dynamics and grain yields.

## Methods

Lanna experimental farm is situated in south-west Sweden (lat. 58 21 N, long. 13 08 E) on a large agricultural plain. The soil was classified as an Uderic Haploboroll (USDA) with two diagnostic horizons, a Mollic epipedon and a Cambic horizon (Bergström *et al.* 1994). The clay content increases with depth, 45.1% in 0-30 cm, 57.2% in 60-90 cm and 58.4% in the 60-90 cm layer. Top soil pH (H<sub>2</sub>O) is 6.8 and subsoil pH 7.0-7.2. Organic carbon content is 3.4% in the top-soil and 0.6% and 0.0% in the sub-soil layers. The soil structure has been described as strong coarse subangular blocky in the top-soil and strong fine to medium angular blocky and strong coarse angular blocky in the sub-soil layers. The 1961-1990 average annual precipitation was 560 mm and annual temperature 6.1°C (Alexandersson and Eggertsson Karlström 2001). Normally the soil is frozen during parts of the winter. The drains normally flow from November to April and for longer in some years (Larsson and Jarvis, 1999). The soil is normally unsaturated to a depth of 2.2 m and this zone is characterized by numerous cracks and biotic macropores. Cereal crops as winter

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wheat, spring barley and spring oats, and oil seed rape (winter or spring) are common crops in the area. Lanna research station is representative for several areas of Swedish clay soils.

Micrometeorological measurements (MT) are conducted over six plots of 1 ha size (Figures 1 and 2). The MT emission is calculated from the difference in the N2O concentrations at 0.5 and 1m height measured with a Tunable Laser system, at the same time as the air movement between the different intakes is measured. Chamber measurements of  $N_2O$  emission is carried out in a long-term soil tillage field experiment (Figures 1 and 2 and Table 1) where early ploughing (A) is compared with late ploughing (C) and tine cultivation (J) described by Stenberg *et al.* (2005).

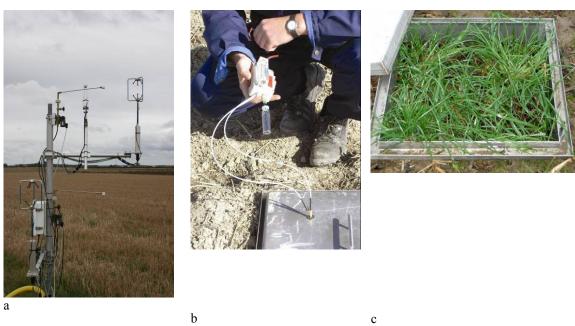


Figure 1. Micrometeorological equipment at Lanna (a), and chambers (b and c) used for gas sampling in the long-term experiment.

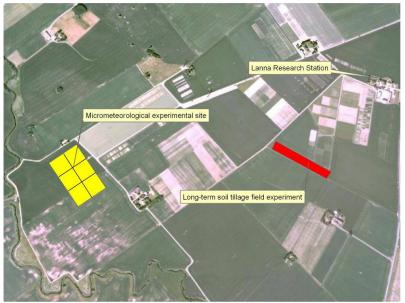


Figure 2. The experimental sites on a clay soil at Lanna research station in south-west Sweden.

Table 1. Treatments in the long	term field experiment at	Lanna research station.
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I an	ie 1. Treatments in the long term nera experiment at Lanna research station.
Α	Early mouldboard ploughing/Straw incorporation/No catch crop
В	Early mouldboard ploughing//Straw removal/No catch crop
С	Late mouldboard ploughing/Straw incorporation/No catch crop
D	Late mouldboard ploughing//Straw removal/No catch crop
Е	Carrier-cultivation to 5 cm early spring/No catch crop
F	Carrier-cultivation to 5 cm early spring with perennial ryegrass as a catch crop
G	Stubble cultivation 10 cm 1 Sept., straw incorporation/No catch crop
Н	Stubble cultivation 10 cm 20-25 Oct., straw incorporation/No catch crop
I	Carrier-cultivation to 5 cm 1 och 25 sept, straw incorporation/No catch crop

Early and late stubble cultivation/Straw incorporation/No catch crop

### Results

Measurements of  $N_2O$  emissions in the long-term filed experiment started in September 2009. Emission data from early and late autumn ploughing will be presented at the conference, as well as grain yields and soil mineral nitrogen concentrations from de measurement period.

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# Nitrous oxide emissions from irrigated cotton soils of northern Australia

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### **Abstract**

An automated gas sampling methodology has been used to estimate nitrous oxide ( $N_2O$ ) emissions from heavy black clay soil in northern Australia where split applications of urea were applied to furrow irrigated cotton. Nitrous oxide emissions from the beds were 643 g N/ha over the 188 day measurement period (after planting), whilst the  $N_2O$  emissions from the furrows were significantly higher at 967 g N/ha. The DNDC model was used to develop a full season simulation of  $N_2O$  and  $N_2$  emissions. Seasonal  $N_2O$  emissions were equivalent to 0.83% of applied N, with total gaseous N losses (excluding NH<sub>3</sub>) estimated to be 16% of the applied N.

# **Key Words**

Nitrous oxide, cotton, DNDC, nitrogen.

## Introduction

Cotton is one of many agricultural industries heavily reliant on nitrogenous fertilizers and water storages to maintain high levels of production. Irrigated cotton farming systems have been labelled as potentially highrisk agricultural systems with respect to gaseous losses of nitrogen to the atmosphere with the inefficient use of fertiliser applied N also reducing profitability. Irrigated cotton grown on alkaline grey clay soils often use nitrogen fertilizer inefficiently, due largely to nitrogen loss (commonly 50 - 100 kg N/ha) through denitrification. These and the heavier black clays (Vertisols) are the dominant soils in the cotton growing region of Australia and with their high water holding capacity are ideal environments for denitrification and associated losses of nitrous oxide (N<sub>2</sub>O) and N<sub>2</sub>. The nitrogen gases emitted also include ammonia, but it is N<sub>2</sub>O, a potent greenhouse gas with a Global Warming Potential (GWP) approximately 300 times that of carbon dioxide (CO<sub>2</sub>), which has fuelled debate. Rochester (2003) has estimated that just over 1% of applied N is emitted as N<sub>2</sub>O from alkaline grey clay soils in a cotton system. There is much speculation about the actual contribution of cotton cropping systems to global warming, a secondary objective of this study. The Intergovernmental Panel for Climate Change (IPCC, 2006) prescribe 1% of applied fertilizer N as a general figure to estimate direct N<sub>2</sub>O emissions from fertiliser application. The only reported direct measurements of N<sub>2</sub>O emissions from cotton soils in Australia were obtained from a 10 weeks during the 2002-03 season by Grace et al. (2003) using a simple manual chamber technique and these ranged from 0.2-1.53% of applied N. This study details both field experimentation and simulations to derive more reliable estimates of nitrogen losses, specifically N<sub>2</sub>O emissions from N fertilizer applied to cotton growing soils, with the potential for identifying management strategies for reducing total N losses, increasing nitrogen use efficiency and profitability.

## Methods

Site management

The furrow irrigated cotton field was located on the Crothers farm near Dalby, Queensland. The field had been under continuous cotton (with winter fallow) for 10 years. The block has a long history of conventional tillage, with a spraying regime typical for cotton production in this area. Bollgard varieties are typically used. The black clay (clay 68%) is typical of the region with an average soil organic carbon content in the top 10 cm of 1.0% and a pH of 8.5. Urea was banded on 10 and 30 August, 2005, at 92 and 70 kg N/ha, respectively. Cotton was sown on 2 November, with 30 kg N/ha NH<sub>3</sub> applied with irrigation water on 26 January, 2006, and an additional 15 kg N/ha water run urea applied on 24 February. A total of 207 kg N/ha was applied during the season, with post-sowing irrigation events restricted to a single occasion (24 February, 2006) due to fact the farm received exceptional rainfall during the season.

# Equipment

Soil emissions of carbon dioxide ( $CO_2$ ), methane ( $CH_4$ ) and  $N_2O$  during the 2005/06 (August-March) growing season were estimated using a fully automated gas sampling and analysis system. The automated system used in this project is a modified design of closed chamber technique originally described by Butterbach-Bahl *et al.* (1997) and allows for data collection and analysis on a two hour cycle. Briefly, the measuring system consists of a gas chromatograph (SRI GC8610) equipped with a 63Ni electron capture detector (ECD) for  $N_2O$  analysis and flame ionization detector (FID) for  $CH_4$  analysis, a LICOR Infrared gas analyzer (IRGA) for  $CO_2$ , a gas sampling system, a compressor, six measuring chambers and computer for operating software and data storage.

To meet the demand for portability, the system is entirely contained in two steel boxes. The square aluminium chambers have transparent acrylic panes, and cover 2500 cm². The chambers have an internal temperature sensor, with 55°C set as the threshold for opening to avoid any heat damage to plants. Transparent extensions can be fitted to increase the height of the chambers to 75 cm and 100 cm, to accommodate actively growing plants. Three chambers were assigned to a single bed and placed five metres apart, and three to an adjacent furrow after skipping two rows. Gas sampling was confined to the period 9 October, 2005 to 23 March, 2006. Soil samples (0-10 cm) were periodically removed for nitrate analysis. Yield samples were also taken at harvest.

## Simulation

The DNDC model version 8.9 (Li *et al.* 1996) was used to test the viability of a simulation approach to mimic N<sub>2</sub>O emissions from irrigated cotton soils of northern Australia and to estimate emissions at the beginning of season as N fertiliser had been applied in early August, well before planting and deployment of the automatic chambers. The crop production aspect of the model had been calibrated with data collected the previous year before at Narrabri, NSW. The only difference was the use of location specific input variables for soil properties, climate and crop management for the Crothers farm. The internal parameters of the model relating to soil carbon, nitrogen and water cycles remained the same as distributed with the model.

## Results

The daily emissions of  $N_2O$  from 69-257 days after the initial fertiliser application are presented in Figure 1. Note the incidence of rainfall and irrigation events (arrowed) which resulted in the surface soil being saturated, and the corresponding increase in emissions at 108, 144 and 170 days after fertiliser (DAF) application. Soil nitrate (0-10 cm) declined from 77 to 27 kg N/ha from 83 to 153 DAF.

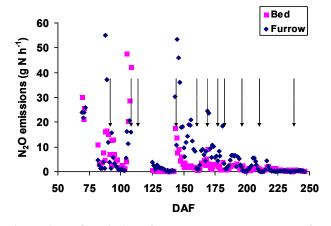


Figure 1.  $N_2O$  emissions from a black clay at Dalby, Queensland (2005/06) fertilised with a split application of 207 kg N (DAF – Days after fertiliser applied; arrows indicate rainfall and irrigation events which have restored the surface soil to saturation).

Nitrous oxide emissions from the beds were 643 g N/ha during the measurement period of 188 days (with 14 days lost as downtime) whilst the  $N_2O$  emissions from the furrows were significantly higher at 967 g N/ha. This observation confirms the leakage of nitrate from beds to furrows and the higher potential for emissions where soils were saturated for longer periods for time. The observed values for  $N_2O$  emissions depicted in Figure 2 are the mean value of the observations for the bed and furrow chambers.

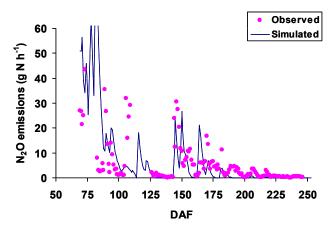


Figure 2. Simulated and observed N<sub>2</sub>O emissions from a black clay at Dalby, Queensland (2005/06) fertilised with a split application of 207 kg N (DAF – Days After Fertiliser applied).

The reliability of DNDC to accurately simulate the observed  $N_2O$  emissions from the Dalby site confirms the models potential as a potentially feasible means of simulating the emissions for the entire season. Simulated daily  $N_2O$  and  $N_2$  losses for the full season at Dalby in 2005/06 are presented in Figure 3. Note the increase in all emissions during mid season when the soils were moist for long periods of time and soil temperate was also elevated.

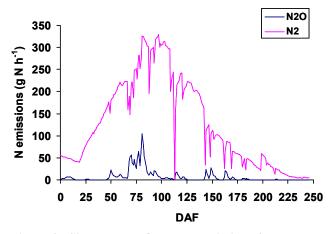


Figure 3. Simulated  $N_2O$  and  $N_2$  emissions from a black clay at Dalby, Queensland (2005/06) fertilised with a split application of 207 kg N (DAF – Days after Fertiliser applied).

Total simulated emissions of  $N_2O$  and  $N_2$  for the 2005/06 season were 1.7 and 30.7 kg N/ha, respectively. The 1.7 kg N/ha for  $N_2O$  is equivalent to 0.83% of the fertiliser applied during the season, and significantly below the default value of 1% suggested by the IPCC for N applications. The fact that the 207 kg N/ha was a split application over many months has played a large part in the low % emission of  $N_2O$ . The total N emission ( $N_2 + N_2O$ ) is equivalent to 16% of the N application for the season, and the  $N_2/N_2O$  ratio is 18/1.

# Conclusion

Typical on-farm  $N_2O$  emissions from irrigated black clays where split applications of N are applied to cotton are 0.83% of applied N, with total gaseous N losses (excluding NH<sub>3</sub>) being estimated (through simulation) as 16% of the applied N. The practice of split applications is increasing across the cotton industry and its positive impact on reducing emissions is obvious, however more work on the  $N_2$  component of N loss is required before a final total N loss figure can be confirmed. Substantial leakage of nitrate from beds to furrows has been experimentally confirmed in the on-farm component of this project and is a significant source of N loss and  $N_2O$  emissions. This is an area of concern, considering the majority of growers currently use furrow irrigation.

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# Nitrous oxide emissions from nitrogen-enriched cattle manure compost pellets applied to Andosols

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## **Abstract**

High levels of nitrous oxide ( $N_2O$ ) are emitted when manure compost pellets are applied to soil. In order to find ways to decrease this emission, we studied the  $N_2O$  emissions for nitrogen-enriched manure compost pellets; preliminary incubation tests showed that these pellets produced lower  $N_2O$  emissions than the commonly used manure compost pellets. In the field experiments, 4 types of manure—nitrogen-enriched manure compost pellets (N + MCP), manure compost pellets (N + MCP), nitrogen-enriched manure compost (N + MCP), non-pelletized)—were applied to a forage corn field in autumn 2008 and summer 2009, and the  $N_2O$  emissions during each treatment were measured. The total  $N_2O$  emission rates (kg N/ha) in the 2 cultivation periods were 2.519 (MCP treatment), 0.755 (N + MCP treatment), 0.441 (MC treatment), 0.287 (N + MC treatment), and 0.150 (control treatment). The emission rate during the N + MCP treatment was slightly higher than that during the non-pelletized manure treatment (MC and N + MC treatment) but significantly lower than that during the MCP treatment. These results indicate that the use of nitrogen-enriched manure compost pellets resulted in a decrease in the  $N_2O$  emissions from manure compost pellets applied to the soil.

## **Key Words**

Mitigation of GHG emissions, organic material, agriculture.

### Introduction

Manure compost pellets have gained attention for their excellent handling properties in agricultural practices and their contribution to the improvement in the balance of manure distribution in agricultural areas. However, it was reported that compared to the ordinary manure compost (non-pelletized) or chemical fertilizers, the application of manure compost pellets leads to most of the nitrous oxide ( $N_2O$ ) emissions (Inoue and Shibukawa 2008; Hayakawa *et al.* 2009; Yamane and Yamada 2009). Nitrous oxide ( $N_2O$ ) is one of the most important greenhouse gases and relates to the depletion of stratospheric ozone. To increase the use of manure compost pellets, it is important to develop techniques for decreasing  $N_2O$  emissions from the pellets. We have conducted incubation experiments based on the reduction of  $N_2O$  emission; the results showed that the  $N_2O$  emissions from nitrogen-enriched manure compost pellets mixed with soil were lower than those from ordinary manure compost pellets (data not shown). The nitrogen-enriched manure compost is a side product of the systems for deodorizing offensive odors from animal wastes and is created as a result of aeration and absorption of the odor by well-matured manure composts; its nitrogen content is higher than that of ordinary manure composts because the odor contains a high amount of ammonia. Our objective is to verify the  $N_2O$ -decreasing effect of nitrogen-enriched manure compost pellets in fields.

# Methods

Study site and experimental design

The experiments were conducted in a field located in the National Agricultural Research Center for Kyushu Okinawa Region (KONARC, 32°52' N, 130°44' E) during 2 cultivation periods (autumn 2008 and summer 2009). Forage corn (*Zea mays* L.) was grown in this field. The soil in the field belonged to Andosols. In the field experiment, a total of 5 treatments, comprising 4 types of manure-application treatments and a control treatment, were performed. The treatments were as follows (1) nitrogen-enriched manure compost pellet treatment (N + MCP), (2) manure compost pellet treatment (MCP), (3) nitrogen-enriched manure compost treatment (N + MC, non-pelletized), (4) manure compost treatment (MC, non-pelletized), and (5) control treatment (no nitrogen). The physical and chemical properties of the manures and the application rates of the manure and nitrogen in each treatment are shown in Table 1. The application rates of the manures were adjusted to the carbon rate when the MC was applied at the rate of 10 Mg DM/ha. The inorganic nitrogen applied during each treatment was 246.8 kg N/ha; this was the value in the N + MCP treatment. If the inorganic nitrogen was insufficient in the other treatments, it was complemented with chemical fertilizer

(urea). Manure compost pellets (N + MCP and MCP) in a columnar shape (5 mm, diameter; 8 mm, length) were prepared using a disc pelletizer. Each treatment was carried out in 2 plots (18 m² each) and plots were arranged randomly.

# Field measurements

N<sub>2</sub>O flux was measured by the closed-chamber method (Ralston 1986) using an acrylic chamber (20 cm × 30 cm × 30 cm). Three chambers were prepared for each treatment (1 chamber in 1 plot and 2 chambers in the other plot). In each chamber, 500 mL of the air was sampled with a pump at 0 min, 15 min, and 30 min after the chamber was set. The N<sub>2</sub>O concentration of the sampled gas was determined using a gas chromatograph (GC-2014, SHIMADZU Co. Ltd., Kyoto, Japan) equipped with an electron capture detector. N<sub>2</sub>O gas flux was calculated from the difference in the N<sub>2</sub>O concentration at different sampling times. Manure was applied on September 3, 2008 (for autumn 2008) and April 16, 2009 (for summer 2009). The N<sub>2</sub>O fluxes were measured from August 31 to November 22 in 2008 (for autumn 2008) and from April 12 to August 20 in 2009 (for summer 2009). The gas was sampled 4–7 times/week, immediately after manure application; once a week, 7–30 days after application; and 2–3 times a month, from 30 days after the application to the end of the experiment. The N<sub>2</sub>O emission rates were calculated using the linear trapezoidal method. Soil moisture was represented by the water-filled pore space (WFPS). WFPS was calculated with the following formula: WFPF (%) =  $[(gravimetric water content \times soil bulk density)/total soil porosity]$ , where soil porosity = [1 -(soil bulk density/particle density)]. Temperatures in the soil (at a depth of 5 cm) and chamber were recorded by a thermo-recorder (ONDOTORI; T&D Co. Ltd., Nagano, Japan) with 2 channels. Climatic data were collected from the Kikuchi automated weather station (32°56.8' N, 130°46.9' E; autumn 2008) and an observatory in KONARC (summer 2009).

Table 1. Physical and chemical properties of the manures used in the field experiments and the application rates of the manures and nitrogen in each treatment. Abbreviations: N + MCP, nitrogen-enriched manure compost pellet; MCP, manure compost pellet; N + MC, nitrogen-enriched manure compost; MC, manure compost. The values in parentheses in the inorganic nitrogen values column indicate the amount of inorganic nitrogen added as a chemical fertilizer (urea).

Treatments	Manure	Con	Components in manure		Manure rates	Nitrogen rates		
	compost		compost		$\operatorname{compost}$		applied	(kg N/ha)
	moisture		(g/kg DM)		(g/kg DM)		(Mg DM/ha)	
	(kg/kg)	T-C	T-N	Inorganic N		T-N Inorganic N		
N + MCP	0.12	324.9	36.5	21.7	11.37	415.1 246.8 ( - )		
MCP	0.11	352.9	20.4	1.1	10.47	448.9 246.8		
						(235.3)		
N + MC	0.18	361.0	38.7	20.6	10.24	432.1 246.8 ( 35.9)		
MC	0.15	369.5	20.2	1.1	10.00	437.8 246.8		
						(235.8)		

## Results

 $N_2O$  flux and emission rate in autumn 2008

In autumn 2008, the mean air temperature was  $19.0^{\circ}$ C, and the total rainfall was 408.5 mm at the time of measurement. The  $N_2O$  flux in autumn 2008 is shown in Fig.1A.  $N_2O$  emissions in all the treatments except the control treatment peaked at 1-3 days after the application. The peak  $N_2O$  emission in the MCP treatment  $(2460.2~\mu g~N_2O-N/m^2/hr)$  was notably (48-94~times) higher than that in the other treatments  $(26.1-51.3~\mu g~N_2O-N/m^2/hr)$ . The peak  $N_2O$  emission decreased 13-31 days after the application. Following this, lower levels of  $N_2O$  emissions ( $<10~\mu g~N_2O-N/m^2/hr$ ) were observed in all the treatments. In autumn 2008 (Table 2), the emission rates for the MCP treatment were the highest (1.658~kg~N/ha), followed by those for the N+MCP treatment (0.157~kg~N/ha), MC treatment (0.130~kg~N/ha), N+MC treatment (0.096~kg~N/ha), and control treatment (0.056~kg~N/ha). The  $N_2O$  emission rate for the MCP treatment was significantly higher (p <0.05; Tukey test) than those in the other treatments. The percentages of  $N_2O-N$  to total-N applied  $[(N_2O)$  emission rate in the treatment -  $N_2O$  emission in the control treatment)/(total nitrogen rate applied in the treatment) were 0.357% for the MCP treatment, 0.024% for the N+MCP treatment, 0.017% for the MC treatment, and 0.009% for the N+MC treatment.

# $N_2O$ flux and $N_2O$ emission rate in summer 2009

In summer 2009, the mean air temperature was  $22.4^{\circ}$ C, and the total rainfall was 880.5 mm at the time of measurement. The  $N_2$ O flux in summer 2009 is shown in Fig.1B. Except for the control treatment,  $N_2$ O

emissions in all the treatments peaked 5–10 days after the application. Similar to autumn 2008, the peak  $N_2O$  emission was the highest for the MCP treatment (342.4  $\mu$ g  $N_2O$ -N/m²/hr) and was approximately 5–15 times higher than that for the other treatments (23.4–65.9  $\mu$ g  $N_2O$ -N/m²/hr). However, in summer 2009, the peak  $N_2O$  emission for the MCP treatment decreased to approximately one-seventh that of autumn 2008. Once  $N_2O$  emissions settled 14–30 days after the application in all the treatments,  $N_2O$  emissions ranged 5–45  $\mu$ g  $N_2O$ -N/m²/hr had been observed mainly in the treatments applied manure compost pellets (MCP and N + MCP treatment) from 37 days after the application to the end of the experiment. The  $N_2O$  emission rates in autumn 2009 (Table 2), were similar to those in autumn 2008; the emission rate in the MCP treatment was the highest (0.860 kg N/ha), followed by that in the N + MCP treatment (0.599 kg N/ha), MC treatment (0.311 kg N/ha), N + MC treatment (0.190 kg N/ha), and control treatment (0.093 kg N/ha). However, the difference between the  $N_2O$  emission rates during the MCP treatment and those during the other treatments was smaller in summer 2009 than in autumn 2008; in summer 2009, no significant difference was observed between the  $N_2O$  emission rates of the MCP and N + MCP treatments (p = 0.05; Tukey test). Percentages of  $N_2O$ -N for total-N applied were 0.171% in the MCP treatment, 0.122% in the N + MCP treatment, 0.050% in the MC treatment, and 0.022% in the N + MC treatment.

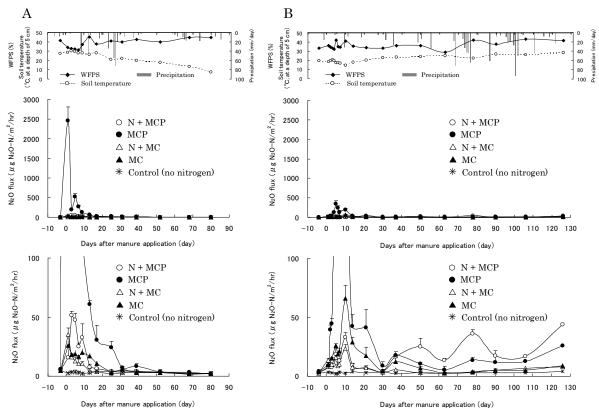


Figure 1. Nitrous oxide  $(N_2O)$  fluxes, soil temperature (at a depth of 5 cm), soil moisture (WFPS), and precipitation in the field experiments. The figures on the left (A) show the results for autumn 2008, and the figures on the right (B) show the results for summer 2009. Refer to Table 1 for the abbreviations used for the treatments. The lower 2 figures are enlarged versions of the upper ones. Manure was applied on September 3, 2008 (autumn 2008) and on April 16, 2009 (summer 2009).

# Conclusion

The total  $N_2O$  emission rates in the 2 cultivation periods are shown in Table 2. The  $N_2O$  emission rate in the MCP treatment (2.519 kg N/ha) was the highest, followed by that in the N + MCP treatment (0.755 kg N/ha), MC treatment (0.441 kg N/ha), N + MC treatment (0.287 kg N/ha), and the control treatment (0.150 kg N/ha). While the emission rate in the N + MCP treatment was a little higher than that in the non-pelletized manure treatments (MC and N + MC treatment), it was significantly lower than that in the MCP treatment. These results suggest that the use of nitrogen-enriched manure compost pellets is an effective option for decreasing the level of  $N_2O$  emissions from manure compost pellets applied to the soil; it is important to elucidate the mechanism of decrease of  $N_2O$  emission with the use of these nitrogen-enriched pellets.

Table 2.  $N_2O$  emission rates and percentage of  $N_2O$ -N to total-N applied in the field experiments. Refer to Table 1 for the abbreviations used for the treatments. The different letters seen in the columns indicate a significant difference among  $N_2O$  emission rates (p < 0.05; Tukey test). Percentage of  $N_2O$ -N to total-N applied (%) = [( $N_2O$  emission rate in the treatment -  $N_2O$  emission rate in the control treatment)/(total nitrogen rate applied in the treatment) × 1001.

<u> </u>	200].						
Treatments	Aut	umn 2008	Sum	mer 2009	Total		
	N <sub>2</sub> O Percentage of		N <sub>2</sub> O	Percentage of	N <sub>2</sub> O	Percentage of	
	emission rate $N_2O-N$ to total-N		emission rate	N <sub>2</sub> O-N to total-N	emission rate	N <sub>2</sub> O-N to total-N	
	(kg N/ha)	applied (%)	(kg N/ha)	applied (%)	(kg N/ha)	applied (%)	
N + MCP	0.157 b	0.024	0.599 a	0.122	0.755 b	0.073	
MCP	1.658 a	0.357	0.860 a	0.171	2.519 a	0.264	
N + MC	0.096 b	0.009	0.190 b	0.022	0.287 c	0.016	
MC	0.130 b	0.017	0.311 b	0.050	0.441 bc	0.033	
Control	0.056 b	-	0.093 b	-	0.150 c	-	

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# Nitrous oxide emissions from soils in Australian sugarcane production systems

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## **Abstract**

Use of nitrogen fertiliser is a major cause for increased emissions of nitrous oxide ( $N_2O$ ) from soils, which are the biggest source of greenhouse gas emission from sugarcane production. To reduce greenhouse gas emissions from sugarcane production, and increase the crop's attractiveness as a sustainable biofuel, we will need a better understanding of  $N_2O$  emissions from soils and how they can be managed. To investigate both the management and consequences of management of these emissions, we simulated whole-of-crop  $N_2O$  emissions over a range of environments and management practices in Australia. Predictions of  $N_2O$  emissions were consistent with the few measurements made previously, and support conclusions from these measurements that  $N_2O$  emissions from sugarcane soils are greater than expected from experience in other crops. We also predict that emissions in other sugarcane areas will be as high, or higher than those measured. The ability to mechanistically simulate emissions of similar magnitude to those measured give added confidence in the measurements. We provide an example of the degree to which higher nitrogen fertiliser prices might reduce both  $N_2O$  emissions and sugarcane production, and show that the economic value of the mitigated emissions may be substantially lower than the value of lost productivity.

## **Key Words**

Denitrification, greenhouse gas, mitigation, APSIM, irrigation, trash.

# Introduction

Use of nitrogen (N) fertiliser is a major cause of increased emissions of N<sub>2</sub>O, a potent greenhouse gas, from soils. Commercial sugarcane production requires substantial applications of N fertilisers, which may result in N<sub>2</sub>O emissions from soils being the biggest greenhouse gas emitted from sugarcane production (Thorburn et al. 2009). Yet there are relatively few measurements of N<sub>2</sub>O emissions from sugarcane, and most of those have been made in Australia (e.g. Weier et al. 1996, 1998; Weier 1999; Denmead et al. 2008; Wang et al. 2008; Macdonald et al. 2009). Emissions are higher than expected compared with other cropping systems and N fertiliser use (Galbally et al. 2005). While emissions are of general concern because of their high impact on global warming, they are of particular concern for sugarcane production because of the wide interest in the crop for biofuel production. Additional information on N<sub>2</sub>O emissions from sugarcane soils will help identify management practices to reduce them, and the likely consequence of implementing these practices. Simulation models are increasingly being employed, in addition to experiments, to gain information on N<sub>2</sub>O emissions from cropping systems (e.g. Del Grosso et al. 2009). APSIM is a farming systems simulator (Keating et al. 2003) with a well developed capacity to simulate N dynamics in sugarcane systems (Thorburn et al. 2005). Recently, the denitrification processes in APSIM have been tested and the capability added for partitioning denitrified N into the different gasses produced by the process, N<sub>2</sub>O and dinitrogen (Thorburn et al. 2010a). Thus, APSIM is now a useful tool for exploring potential N<sub>2</sub>O emissions from sugarcane production systems in areas and/or for issues where measurements are unavailable. In this paper, we use APSIM to investigate N<sub>2</sub>O emissions from a range of conditions found in sugarcane production in Australia, both in regions where emissions have been previously measured and where there is no information. We also explore some options for reducing N<sub>2</sub>O emissions and the economic impacts they may have.

# Methods

Contrasting sugarcane production systems were analysed using long term (40-60 years) simulations to investigate how N<sub>2</sub>O emissions from soils varied (full details are given by Thorburn *et al.* 2010a). The systems were based on soils, climate and crop management information from previous studies of sugarcane production in four regions. These spanned a wide range of environments, including the super-humid tropics (Tully; ~17.9S, 145.9E), dry tropics (Burdekin River Irrigation Area; ~19.8S, 147.2E), humid tropics (Mackay, two soils; ~21.2S, 149.0E) and dry sub-tropics (Maryborough; ~25.5S, 152.7E). N<sub>2</sub>O emissions have previously been measured in the Mackay region, at Eton (Weier *et al.* 1998) and Te Kowai (Denmead *et al.* 2008; Macdonald *et al.* 2009), allowing verification of the predicted emissions.

A range of management practices and soils were represented in the simulations. Irrigation management varied, with sugarcane fully irrigated in the Burdekin simulations, grown under supplementary irrigation in Maryborough simulations and not irrigated in the other environments. Simulations for the two soils in Mackay each had two different crop residue managements (retention and removal). The amount of N applied in the simulations reflected common practice in the regions, ranging from over 200 kg/ha (averaged across all crops and fallows) in the Burdekin region to less than 130 kg/ha in the Tully and Maryborough regions (Figure 1). Soils ranged from clays in the Burdekin and the Eton site in Mackay, to sandy-clay-loams at the Te Kowai site in Mackay. Average cane yields in the simulations ranged from 74 t/ha (averaged across all crops), at Maryborough, to 80-84 t/ha for the loamy soils at Tully and Mackay (Te Kowai), to 87-91 t/ha in the clay soils of Mackay (Eton) and the Burdekin.

For the Te Kowai site in Mackay, cane yield,  $N_2O$  emissions and the profitability of sugarcane production were also predicted for a wide range of N application rates (35-200 kg/ha), keeping all other management factors the same as in the previous simulations. Profitability was represented by the partial gross margin (PGM) to farmers, calculated from the income from sugarcane (assuming a sugar price of AU\$400/t and CCS of 13.5) less the cost of N fertiliser. The N application rate corresponding to the highest PGM was identified over a range of N prices to explore the sensitivity of  $N_2O$  emissions, which are a function of N rate, to N price, assuming N application rates were those that gave the highest profitability.

## Results and discussion

# Magnitude of emissions

Nitrous oxide emissions from soils were equivalent to 2-5% of N fertiliser applied (Figure 1) in the simulations. The simulated emissions from the Mackay-TeKowai site were consistent with independent measurements of emissions (Denmead *et al.* 2008; Macdonald *et al.* 2009). The results also support the conclusions from these and other experiments (Weier *et al.* 1996, 1998; Weier 1999; Allen *et al.* 2008; Wang *et al.* 2008) that N<sub>2</sub>O emissions from soils in Australian sugarcane crops are substantially greater than expected for the level of N fertiliser use and experience in other crops (Galbally *et al.* 2005). The ability to mechanistically simulate emissions of similar magnitude to those measured give added confidence in the measurements. Additionally, we provide the first estimates of emissions for fully irrigated production (Burdekin) and partly irrigated production (Maryborough), and rainfed production in the wet tropics (Tully), and predict them to be similar or higher than emissions in other regions. While very high emissions (~20% N fertiliser) have been measured from sugarcane growing in highly acidic soils with shallow water tables (Denmead *et al.* 2008; Wang *et al.* 2008), these areas are relatively small in Australia and are unlikely to represent the common situation.

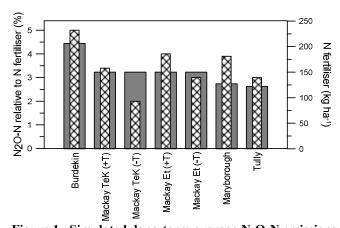


Figure 1. Simulated, long-term average  $N_2O$ -N emissions from soils (hatched bars) and N fertiliser applications (grey bars) at five sites. For Mackay, sites were at Te Kowai (TeK) and Eton (Et) and either had crop residues retained (+T) or removed (-T) in the simulations.

If our predictions prove generally correct, global warming potential of world-wide sugarcane production may be equivalent to 29-48 Mt  $\rm CO_2$ -e year<sup>-1</sup>. This is 2-3 % of the global warming potential attributed to  $\rm N_2O$  emissions from all fertilised croplands (Stehfest and Bouwman 2006). We suggest that reducing  $\rm N_2O$  from soils growing sugarcane is likely to be a higher priority than may have been previously thought for increasing the sustainability of sugarcane production, both in Australia and globally.

The variations in emissions between regions were consistent with the processes known to drive  $N_2O$  emissions. At the Mackay sites for example, predicted emissions were higher from the clay soil at Eton than the more loamy soil at Te Kowai. Also, retaining crop residues on these soils increased simulated denitrification and  $N_2O$  emissions, as expected from experimental results (Weier *et al.* 1998). Emissions were simulated to be high at the Burdekin site, reflecting the heavy textured soils combined with the fully irrigated nature of cane production in Burdekin River Irrigation Area. Our results therefore indicate that the cause of the high  $N_2O$  emissions from sugarcane is the relatively warm and moist climate and the availability of carbon in the soils.

# Managing emissions

Reducing N fertiliser applications will reduce  $N_2O$  emissions from soils (Stehfest and Bouwman 2006). But what might the cost be, in terms of lost production, relative to the benefit? Improved N recommendations have shown there is considerable scope for reducing N rates in Australian sugarcane production without significantly reducing productivity (Thorburn *et al.* 2010b). Thus at Te Kowai for example (Figure 2a), reducing N application from 170 kg/ha (the recent average in that region) to 120 kg/ha would reduce  $N_2O$  emissions by  $\sim$ 40% with little or no loss of production and a consequent increase in profitability.

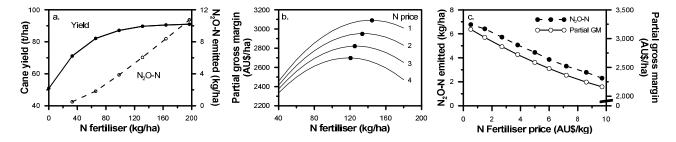


Figure 2. Simulated, long-term average response of (a) cane yields and soil  $N_2O$ -N emissions to increasing application of N fertiliser, (b) maximum partial gross margins at different N fertiliser prices, and (c) the change in  $N_2O$  emissions and maximum partial gross margin with increasing N fertiliser price (assuming N fertiliser is applied at the rate corresponding to the maximum partial gross margin shown in b) for the Te Kowai site.

However, N applications may also be reduced if the price of N fertiliser increases, a likely event if emissions trading schemes are introduced. As N fertiliser prices increase, maximum profitability occurs at lower N application rates (Figure 2b). So farmers may respond to price increases by reducing N applications, which would result in lower N<sub>2</sub>O emissions. However, with increased N price, not only is the N rate at which maximum profitability reduced, the maximum profit itself also decreases. Thus, higher N prices could result in both lower N<sub>2</sub>O emissions and lower farm profitability if farmers respond by reducing N applications. In the simulations for Te Kowai, the trade off between N<sub>2</sub>O emissions and farm profitability can be illustrated for varying N prices by taking the N rate at which maximum PGM occurs (i.e. the dots on the curves in Figure 2b) and calculating the corresponding N<sub>2</sub>O emissions and PGM values over a range of N prices (Figure 2c). In this example, N<sub>2</sub>O emissions decrease by ~0.46 kg N<sub>2</sub>O-N/ha for each unit (i.e. AU\$1) increase in N price. If the price of carbon is AU\$20/t CO<sub>2</sub>-e the value of the reduced N<sub>2</sub>O emissions is ~AU\$4.25. The corresponding decrease in PGM is ~AU\$98 per unit increase in N price, or more than 20 times the value of N<sub>2</sub>O emissions. The economic impact of increased N prices will be even greater if price increases are such that they drive N applications low enough so that cane yields and sucrose concentrations are reduced. In this situation, the reduced cane and sugar supply would potentially reduce mill profitability. This analysis illustrates the point that decreases in N fertiliser application rates, below recommended rates, as a response to higher N prices could have substantial negative net economic effects.

Nitrous oxide emissions from soils are enhanced by high concentrations of nitrate and carbon in the soils and anaerobic soil conditions. Thus, as well as reducing N fertiliser applications, other management practices affect N<sub>2</sub>O emissions. In our simulations, as expected, the highest relative emissions occurred in the two irrigated production systems, Burdekin and Maryborough (Figure 1). In irrigated production systems, minimising water logging following irrigation will help reduce N<sub>2</sub>O emissions. Also as expected, retaining crop residues also increased emissions (Figure 1). Given the advantages of this widely-adopted practice in Australian sugarcane production, other methods to reduce emissions will need to be employed. Practices such as splitting N fertiliser applications may help (Weier 1999; Allen *et al.* 2008), as might slow release fertilisers or nitrification inhibitors (Wang *et al.* 2008), although the benefits of these practices have not been consistent.

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# Nitrous oxide production in soil: Microbial source partitioning to inform management options for mitigation

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### **Abstract**

Terrestrial systems are major sources of atmospheric  $N_2O$ , which accounts for ~6% of the current greenhouse effect. Production of  $N_2O$  in soil is predominantly biological, and produced during several microbial processes, which may occur simultaneously within different micro-sites of the same soil. Here we explore the biogeochemical pathways in which these microbes can produce and reduce  $N_2O$ , consider the approaches available for determining the predominant  $N_2O$ -producing process under certain conditions, highlight any current uncertainties in microbial sources of  $N_2O$  to direct future research, and examine how understanding the  $N_2O$  source can aid us in managing terrestrial systems to lower emissions of this greenhouse gas. Such source partitioning of  $N_2O$  is inherently challenging, but is vital to close the  $N_2O$  budget and to better understand controls on the different processes, with a view to developing appropriate management practices for mitigation of  $N_2O$ .

# **Key Words**

Nitrous oxide, stable isotopes, rhizosphere, denitrification, ammonia oxidation.

# Introduction

Soil microbial  $N_2O$  production occurs via nitrification (ammonia oxidation) and nitrate dissimilation (denitrification and nitrate ammonification) pathways (Figure 1). The different processes involved in  $N_2O$  production respond differently to environmental parameters or imposed management, and the enzymatic systems of each process are regulated differently. This means that the down-regulation of  $N_2O$  production in one process as a result of management practice or change in environmental conditions may well lead to the up-regulation of  $N_2O$  production in another. Thus appropriate management for one process, may not be appropriate for another, and may well need to be flexible depending on the system, the prevailing environmental conditions, and the management options available. Unless the controls on enzyme regulation associated with these processes, and associated molar ratios of products are determined, then it will not be possible to target mitigation strategies. Here we give examples of stable isotope approaches that have provided advances in our understanding of the processes producing  $N_2O$  in soil, the conditions under which each process predominates, and suggest how this information can be used to develop more targeted management options to lower emissions.

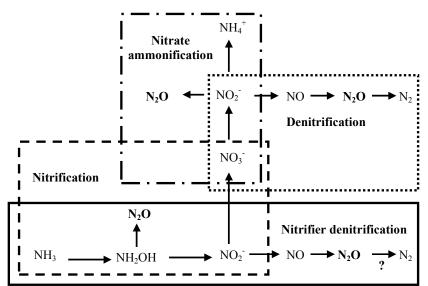


Figure 1. Microbial sources of  $N_2O$  in soil. Source Baggs (2008) showing  $N_2O$  production from all microbial processes, including nitrate ammonification.

# Approaches for distinguishing microbial sources of N<sub>2</sub>O

Stable isotope enrichment

These studies have mostly focused on distinguishing between nitrification (ammonia oxidation or nitrifier denitrification) and denitrification following application of <sup>15</sup>N-labelled fertiliser. Application of <sup>15</sup>N-NH<sub>4</sub> and/or <sup>15</sup>N-NO<sub>3</sub> to soil and attribution of the <sup>15</sup>N-N<sub>2</sub>O fluxes to nitrification or denitrification depending on the <sup>15</sup>N source applied negates the need for C<sub>2</sub>H<sub>2</sub> inhibition, thereby overcoming the problems associated with application of C<sub>2</sub>H<sub>2</sub> to soil (Baggs et al. 2003; Bateman and Baggs 2005). For example, using this approach Bateman and Baggs (2005) demonstrated denitrification to be the sole source of N<sub>2</sub>O emissions in a silt loam soil at 70% water-filled pore space (WFPS), the predominance of nitrification between 35-60% WFPS, but, surprisingly, the dominance of denitrification in the 20% WFPS soil (Figure 2). Unfortunately, this approach is unable to distinguish denitrification from nitrate ammonification or nitrifier denitrification. A combined <sup>15</sup>N-, <sup>18</sup>O-enrichment approach has been proposed by Wrage *et al.* (2005) involving application of <sup>18</sup>O-labelled water to estimate N<sub>2</sub>O production during nitrifier denitrification. Using this approach we have demonstrated the proportional contribution of ammonia oxidation but not nitrifier denitrification to vary with availability of different C amendments, and have also shown nitrifier denitrification to be proportionally a more significant N<sub>2</sub>O source in soils amended with 5 g N/m<sup>2</sup> than those amended with 40 g N/m<sup>2</sup>, where ammonia oxidation was more important (Figure 3). Unfortunately, quantification of nitrate ammonification N<sub>2</sub>O by enrichment approach remains elusive.

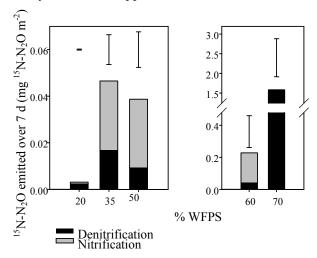


Figure 2. The contribution of nitrification and denitrification to <sup>15</sup>N-N<sub>2</sub>O emissions after fertiliser application to a silt loam soil at different soil water-filled pore space (WFPS). Source: Baggs (2008).

# Natural abundance approaches

These approaches have been applied to the determination of the microbial source of  $N_2O$  in a range of ecosystems and controlled environment experiments, and are most advantageous in natural or unfertilised systems (e.g. Webster and Hopkins, 1996; Wrage *et al.* 2004; Perez *et al.* 2006). Natural abundance approaches rely on the biological fractionation against  $^{15}N$  and  $^{18}O$ . Fractionation during nitrification is generally higher than for denitrification, so that  $N_2O$  produced during nitrification is more depleted (more negative  $\delta$ ) in  $^{15}N$  and  $^{18}O$  relative to substrates than that produced during denitrification (Wahlen and Yoshinari 1985; Yoshida 1988), but unfortunately the fractionation during nitrate ammonification has yet to be determined.

The isotopomer site preference of  $^{15}N$  in  $N_2O$  has recently been proposed as a means to determine the microbial source of  $N_2O$  (Bol *et al.* 2003; Well *et al.* 2006).  $N_2O$  is a linear molecule, N-N-O, and the  $^{14}N/^{15}N$  ratios of the central and outer N atom can naturally vary. Site preference (SP) is termed as the difference in  $\delta^{15}N$  between the central and outer N atoms in  $N_2O$ , with different microbial processes and functional groups thought to exhibit distinct  $^{15}N$ -SPs (Bol *et al.* 2003; Sutka *et al.* 2003; 2004). This technique is in its infancy and in our presentation we will critically assess the feasibility of this approach for estimating contribution of a wider range of processes than possible with  $^{15}N$ -enrichment or  $\delta^{15}N$ ,  $^{18}O$  fractionation.

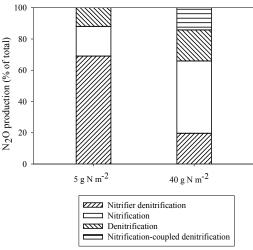


Figure 3. Proportional contributions of different microbial processes to <sup>15</sup>N-N<sub>2</sub>O production following application of 5 and 40 g N/m<sup>2</sup> as NH<sub>4</sub>NO<sub>3</sub> (10 atom % excess <sup>15</sup>N; 1 atom % excess <sup>18</sup>O in water) to soils.

# Source partitioning across different scales

Source partitioning for  $N_2O$  has mostly been undertaken at plot or microcosm scales, these scales in part dictated by the technology available, but we currently do not have appropriate tools for verifying microbial sources at larger as well as smaller scales. Herrmann *et al.* (2007) have demonstrated the potential for detecting  $^{15}N$ -enriched bacterial cells within a soil matrix using nano-scale secondary ion mass spectrometry (NanoSIMS) which can image and quantify isotopic enrichment down to a 50nm spatial resolution. In our presentation we suggest how such an approach could be coupled with stable isotope methods for source partitioning, offering the potential to understand controls on regulation at a scale relevant to the microbiology, and to determine the spatial location of different processes within a heterogeneous soil matrix. At the other end of the scale spectrum we need the tools to validate source partitioning at the catchment, landscape or even national scale and to unite the source partitioning with modeling approaches.

## **Opportunities for mitigation**

Data on the environmental regulation of  $N_2O$  production during the different microbial processes is scarce, particularly for nitrifier denitrification and nitrate ammonification. Lowering application loads of inorganic N fertilizers has traditionally been considered as the most successful option for lowering net emission of  $N_2O$ . However, our source partitioning (Figure 3) adopting a  $^{15}N_{-}$ ,  $^{18}O_{-}$  enrichment approach suggests that nitrifier denitrification may be increased under low N conditions and therefore lower N application may not necessarily be the most appropriate strategy in all systems. Other options lie in manipulating inputs into the plant rhizosphere, thereby changing the composition of plant-derived carbon flow or nitrogen uptake demand, or through crop spacing, tillage or integrated inorganic fertiliser, residue and soil organic matter (SOM) management, but their effects on  $N_2O_{-}$  genic microbial processes are currently unknown. Richardson *et al.* (2009) argue that it is unlikely that it will ever be possible to develop practices that completely eliminate  $N_2O_{-}$  emission from agriculture. They propose that a more reliable approach to mitigating  $N_2O_{-}$  emissions lies in the understanding the regulation of the denitrifier  $N_2O_{-}$  reductase, which will inform the development of management options to lower net  $N_2O_{-}$  emissions by enhancing its reduction to  $N_2$ , rather than to trying to eliminate denitrification. In our presentation we explore how this may be possible in the rhizosphere environment.

## Conclusion

Our ability to determine the microbial source of  $N_2O$  in terrestrial systems, and to quantify the contribution from each source, is improving with the advent and development of new techniques outlined here. This offers us exciting opportunities for targeted management options to optimise mitigation potential, but we still have some way to go before this can become a reality. To be able to determine the microbial source of  $N_2O$  with any degree of accuracy in natural, unfertilised, or fragile ecosystems we need to refine methodologies, or combine established and new methodologies, moving us away from reliance on application of  $^{15}N$ -labelled substrates, which may artificially favour one process over others. Any mitigation approach should be grounded in predictions of future emissions from different management scenarios under a continuing changing climate. To achieve this, models require further development to encompass all microbial sources of

N<sub>2</sub>O. This will be facilitated by advances in techniques to unite source partitioning with upscaling of emissions from the microplot. It is also essential to ensure that any management option imposed to lower emissions has no adverse effect on the diversity and functioning of the microbial community.

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# Physical and chemical manipulation of urea fertiliser for reducing the emission of gaseous nitrogen species

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## **Abstract**

Concerning environmental consequences, technological attempts to decrease reactive N species emitted by the application of urea fertiliser to agricultural soils are being continued. To find suitable mitigation options, urea size and placement depths as well as new inhibitors of various chemical origins were tested in loess soil cropped to spring wheat under greenhouse conditions. Relatively a larger urea granule (USG;  $\leq$ 0.7 g) inhibited nitrification up to 7 weeks and reduced both NH<sub>3</sub> and NO<sub>x</sub> emissions up to 94%. Under cropped conditions, the USG point-placed at 7.5 cm depth showed similar response to urea prills on N<sub>2</sub>O emissions (0.20-0.21% of the added N) though increased to 0.53% at relatively higher soil moisture content. Urease inhibitor (substituted phosphoric acid triamide) decreased NH<sub>3</sub> losses substantially (60%), and also N<sub>2</sub>O (47%) when mixed into soil. Nitrification inhibitor (Dicyanamide plus triazole)-amended urea inhibited nitrification up to 5 weeks and reduced N<sub>2</sub>O emission from 20 to 60%. A combination of urease and nitrification inhibitors-included urea decreased both NH<sub>3</sub> (60%) and N<sub>2</sub>O (25-52%) losses. Results imply that both approaches could mitigate substantially the urea-induced emissions of reactive N species.

## **Key Words**

Nitrogen fertiliser, trace gases, mitigations, cambisol, arable crop.

## Introduction

Reactive N species viz. N<sub>2</sub>O, NH<sub>3</sub> and NO<sub>x</sub> have large potentials for global warming, stratospheric ozone layer depletion and acid deposition. Technological attempts are being continued to reduce their emission from agricultural soils where urea, as the cheapest and mostly used N fertiliser globally (>50%; IFA, 2010), seems to take a major share. As an alkaline-hydrolyzing N fertilizer, urea (prills/small granules) influences nitrification through a transient rise in pH with subsequent denitrification leading to the formation and release of large volumes of N<sub>2</sub>O (Mulvaney *et al.* 1997; Khalil *et al.* 2002) as well as NH<sub>3</sub> and NO<sub>x</sub> when broadcast (Khalil *et al.* 2006; 2009a). In the placement zone of USG, high localized urea/NH<sub>4</sub><sup>+</sup> and NO<sub>2</sub><sup>-</sup> levels and soil pHs develop through enzyme-catalysed urea hydrolysis and diffuse slowly outward under aerobic conditions. This results in either little or no immobilization initially and inhibits both urease and nitrifier activity (Shah and Wolfe 2003) and thus reduces gaseous N emissions (Khalil *et al.* 2006; 2009 a,b).

Numerous urease and nitrification inhibitors or their combination of different chemical origins found to be effective in reducing NH<sub>3</sub> volatilization and N<sub>2</sub>O emissions from agricultural soils. Nitrification inhibitor dicyandiamide (DCD)-amended urea can reduce N<sub>2</sub>O emission largely but its affectivity in limiting NH<sub>4</sub><sup>+</sup> oxidation was short-term compared to 3,4-dimethypyrazole phosphate (DMPP) (Linzmeier *et al.* 2001; Majumdar *et al.* 2002). The lower efficacy and higher volatility, instability and decomposition rate of a sole compound lead to apply larger dosage but the combination of two would enhance nitrification inhibition efficiency and allow to reduce the dosage. Besides, a combination of urease and nitrification inhibitors amended with urea can be useful to reduce both NH<sub>3</sub> and N<sub>2</sub>O losses (Boeckx *et al.* 2005; Schraml *et al.* 2005). A combination of urease (P204/98) and nitrification (DCD/TZ) inhibitor, which is larger (2-3 mm) than urea prills, could reduce NH<sub>3</sub> loss (Schraml *et al.* 2005) and N<sub>2</sub>O emission by inhibiting nitrification (Khalil *et al.* 2009c). This paper deals with a comparison between the above-mentioned physical and chemical manipulation of urea fertilizer in reducing the reactive N species.

# Materials and methods

The soil used for experiments done in Germany was a loess silt loam (20% sand, 60% silt and 20% clay; Cambisol). It had a pH<sub>H2O</sub> of 6.4, a CEC of 17.6 cmol<sub>c</sub> (+)/kg soil and a C/N ratio of 9.5 (0.17% N and 1.61% organic C). Under aerobic conditions, several laboratory and greenhouse investigations were carried out with urea granule sizes, placement depths, soil types (sandy loam, silt loam and clay loam), and urease and nitrification inhibitors and their combination with or without spring wheat (Khalil *et al.* 2006; 2009 a,c).

Under greenhouse conditions, polyvinyl boxes (110 cm x 70 cm x 40 cm) were filled with 5 cm of sand on the bottom, followed by 20 cm and 15 cm of subsurface and surface soils, respectively. Here, the following experiments are illustrated but comparisons with others done are also made in the results and discussion.

# *Urea super granules on* $N_2O$ , $NH_3$ *and* $NO_x$ *emissions*

The treatments of this experiment to measure  $N_2O$  emissions were  $N_0$  - unfertilised control, PU - prilled urea (<1 mm) mixed homogenously with the soil, and USG<sub>7.5</sub>- urea super granule (dia. 10.1 mm; wt. ~0.69 g/USG) point-placed at 7.5 cm depth. The PU labeled with  $^{15}N$  (2.9 atom %) and USG, which was prepared from the former using a mechanical press, were applied at 88.15 kg N/ha. The cumulative amount of water added was 320 L over 116 days of wheat growth period. Another experiment was conducted to measure  $N_2O$ ,  $NH_3$  and  $NO_x$  emissions during a 70-day growth period with treatments: unfertilised control ( $N_0$ ), USG point-placed at 2.5 (USG<sub>2.5</sub>), 5 (USG<sub>5.0</sub>) and 7.5 cm (USG<sub>7.5</sub>) soil depths. Urea-N labeled with  $^{15}N$  (5.1 atom%) was applied at 91.74 kg N/ha. Water depletion was slower, with the total amount of water added being 120 L in 70 days, presumably due to initial stunted plant growth and lower evaporative demands associated with this experiment being performed in the winter.

# *Inhibitors-amended urea and granular size for* $N_2O$ *emissions*

The treatments of this experiment were unfertilized control, PU, urea granule (GU), USG, urease inhibitor (UI), and the combination of urease and nitrification inhibitors (UNI). The nitrification inhibitor (NI) treatment was not included as the response was similar to the UNI under laboratory conditions (Khalil *et al.* 2009c). The USGs were point-placed at 5 cm depth, and soil was mixed down to a 5 cm depth for the other treatments and urea was applied at 88.2 kg N/ha. The cumulative amount of water added was 170 L over 70 days. Spring wheat experienced all natural weather conditions except rainfall.

# Gas samplings, measurement and statistics

Gas for N<sub>2</sub>O was collected using a closed chamber method and measured using an automated gas chromatography (Varian Star 3400, USA) equipped with electron capture and its <sup>15</sup>N abundance was measured using GC-IRMS. NH<sub>3</sub> and NO<sub>x</sub> were measured simultaneously by flowing the sample air to a two-channel chemiluminescence NO-Analyser (CLD 700AL, Fa. EcoPhysics, Gürnten, CH). Statistical analyses were performed using the computer package JMP v4.0.2 of SAS Inc. Total gaseous emissions were calculated by integrating the area of the daily fluxes. Relative and actual N<sub>2</sub>O losses of the added N were calculated based on its total fluxes from the control.

## Results and discussion

The USG, in general, delayed N<sub>2</sub>O emissions for 2-3 weeks, emitting almost similar amount (relative losses of 0.20-0.21% or 0.01% of the added <sup>15</sup>N) with the USG placed at 7.5 cm soil depth to PU under controlled soil water conditions (Khalil *et al.* 2009a). In the experiment with various USG placement depths, higher water content somewhat enhanced N<sub>2</sub>O emission (0.50-0.73%), in line with Khalil *et al.* (2009b), following fertilization to wheat (Table 1). Overall, N<sub>2</sub>O emissions somewhat increased with increasing USG placement depths (Tenuta and Beauchamp 2000; Khalil *et al.* 2006; 2009b). The contribution of added <sup>15</sup>N to N<sub>2</sub>O emissions decreased over time and was small (0.02-0.15%), indicating soil N as the major source (Linzmeier *et al.* 2001). However, the emission factors were much lower than the IPCC default (1.25%), signifying the large potential of USG in reducing N<sub>2</sub>O emission. This is in agreement with Khalil *et al.* (2006) but with the exact effect being soil-specific as fine-textured soil may exacerbate N<sub>2</sub>O emission.

Table 1. Total N<sub>2</sub>O over 70 days, and NH<sub>3</sub> and NO<sub>x</sub> emissions over 43 days growth period of spring wheat, and their relative losses of added N as influenced by placement depths of urea super granules.

Treatments	N <sub>2</sub> O emission		NH <sub>3</sub> volati	lisation	NO <sub>x</sub> emission		
	Total emission Relative loss		Total volatilized	Relative loss	Total flux	Relative loss	
	(g N/ha)	(%)	(g N/ha)	(%)	(g N/ha)	(%)	
USG-2.5	737.0	0.67	1071.8	1.22	1409.4	1.60	
USG-5.0	787.3	0.73	230.2	0.26	1116.5	1.27	
USG-7.5	607.4	0.53	61.9	0.07	178.8	0.20	
$LSD_{0.05}$	242.0	ns	-	-	-	-	

USG-2.5, 5.0 and 7.5 = urea super granule point-placed at 2.5, 5.0 and 7.5 cm soil depths; LSD = least significant difference at 5% level (after Khalil *et al.* 2009a)

The maximum NH<sub>3</sub> volatilization was detected within 8-15 day after fertilisation (DAF) and declined with increasing USG placement depths, ranged from 0.07 to 1.22%, and the deeper placement decreased it by 79-94% over the shallower placement. This larger NH<sub>3</sub> emission seems to be associated with shallower placement of USG under aerobic conditions. This finding is in agreement with others (Bouwmeester *et al.* 1985; Khalil *et al.* 2006), apparently relating to vapour diffusion from USG-induced high NH<sub>4</sub><sup>+</sup> concentration that was placed next to the soil surface. The mixing of PU deeper into the soil might reduce NH<sub>3</sub> volatilization greatly as for USG point-placed and/or banding of urea at a certain depth into consideration (Sommer *et al.* 2004; Khalil *et al.* 2006, 2009b). Soils having high H<sup>+</sup> buffering capacities might prevail over the high concentration gradients of NH<sub>4</sub><sup>+</sup> and pH, which occurs in the placement zone only (Khalil *et al.* 2006; 2009b), leading to the fixation of NH<sub>3</sub> vapour within the upper soil.

The trends for  $NO_x$  emission, peaked after 23 DAF, were similar to  $NH_3$  volatilization (Khalil *et al.* 2009a), as they are interactively favoured by similar soil and environmental conditions (Khalil *et al.* 2006). The deeper USG placements reduced total  $NO_x$  emission by 23 and 88% over the shallower placement. Hou and Tsuruta (2003) reported similar results through band placement of urea at a 12-cm depth. The presence of comparatively more  $NH_4^+$  for subsequent nitrification in the surface than the sub-surface layers could possibly influence  $NO_x$  emission (Khalil *et al.* 2006). The point-placed USG decreased  $NH_3$  and  $NO_x$  losses by placing in deeper soil layers and also the total gaseous  $N(N_2O + NH_3 + NO_x)$  losses.

Experiments with inhibitors versus USG under cropped conditions showed that the PU emitted smaller  $N_2O$  than the GU or USG but varied insignificantly (Table 2). This was probably linked to faster immobilization upon fertilisation and thereby the presence of mineral N at a lower amount. Khalil *et al.* (2006) also reported that  $N_2O$  emission increases with increasing urea granule size. The soil mixed UI could reduce  $N_2O$  emission by two-fold over the GU, presumably due to the delayed hydrolysis and thus restricted nitrification in the beginning, in agreement with Boeckx *et al.* (2005) who used hydroquinone (HQ). However, the broadcast UI limiting  $NH_3$  volatilization might exacerbate  $N_2O$  emission by 47% (Khalil *et al.* 2009c).

Table 2. Total N<sub>2</sub>O fluxes and the relative N<sub>2</sub>O loss of added N from a loess soil at varying urea size, UI and UNI under greenhouse conditions with spring wheat.

Treatments		Control	PU	GU	USG	UI	UNI	$LSD_{0.05}$
			(<1 mm)	(2-3  mm)	(~10 mm)	(as GU)	(as UI+NI)	
Total N <sub>2</sub> O flux	45 day	130.3	254.6	338.7	314.2	202.8	146.0	135.7
(g N/ha)	70 day	186.3	325.0	386.7	424.5	294.6	284.1	ns
Relative loss	45 day		0.14	0.24	0.21	0.08	0.02	0.20
of added N (%)	70 day		0.16	0.23	0.27	0.12	0.11	ns

Control = No N applied, PU = prills, GU = granule, USG = super granule, UI = urease inhibitor, UNI = combined urease plus nitrification inhibitors. LSD<sub>0.05</sub> = least significance difference at 5% level (after Khalil *et al.* 2009b)

Under laboratory conditions, the relative loss of N<sub>2</sub>O from either urea granule size amended with the NI and UNI (a new combined inhibitor) was small (0.08-0.14%) (Khalil et al. 2009c). They also found that the soil mixed NI and UNI reduced N<sub>2</sub>O by 13-20% over broadcasting method, relating either to delayed nitrification resulting in immobilization or to enhanced NH<sub>3</sub> volatilization in presence of NI. The NI alone either as DCD or DMPP variably decreased N<sub>2</sub>O emission, ranging from 20-53% under wheat and barley (Linzmeier et al. 2001; Mojumdar et al. 2002; Boeckx et al. 2005), and even up to 60% reduction with the DCD/TZ (Weber et al. 2004). However, application of NI was omitted under cropped conditions due to similar response as to UNI observed. Overall, the soil mixed UI and UNI reduced N<sub>2</sub>O emission by 23-31% over the PU and by 47-52% over the same granule size. Though smaller compared to ours, a reduction of  $N_2O$  with the DCD + HQamended urea by 25.1% (Boeckx et al. 2005) was in evidence. The USG retained more mineral N than the urea amended with inhibitors (Tenuta and Beauchamp 2000; Khalil et al. 2006), more (7 weeks) than the inhibitors (5 weeks) but effective, as observed with the NI by Weber et al. (2004). Its affectivity could last even up to 4-8 weeks using DCD or DMPP (Linzmeier et al. 2001; Majumdar et al. 2002). The difference in this research was probably due to the higher mobility of inhibitors, the type of N fertilizer, and the temperature differences in particular. Under cropped conditions, N<sub>2</sub>O emission was small particularly with the UNI, attributing to the controlled soil water conditions and the low N rate and the contribution of nitrification more, following degradation of DCD + TZ, than denitrification.

## **Conclusions**

The relatively larger urea granule (USG) appeared to be more practical and efficient in reducing  $NH_3$  and  $NO_x$  losses and delayed nitrification more as compared with the mixing of PU and urease inhibitor. The USG approach could increase somewhat  $N_2O$  emissions but the reduction potential is more than double over the IPCC default emission factor. Importantly, this can secure N supply at a later plant growth by delaying nitrification and gaseous N losses, similar to urease and nitrification inhibitors, over the PU. Surface application of UI could enhance  $N_2O$  emission more than the soil mixing approach. Though the NI responded similarly to reduce  $N_2O$  emissions, the UNI could reduce urea-induced  $NH_3$ ,  $NO_x$  and  $N_2O$  losses following either mixing or broadcasting methods but adjustment of timing for fertilisation would be required.

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# Quantifying N<sub>2</sub>O and CO<sub>2</sub> emissions from a subtropical pasture

David Rowlings<sup>A</sup>, Peter Grace<sup>A</sup>, Ralf Kiese<sup>B</sup> and Clemens Scheer<sup>A</sup>

## **Abstract**

Greenhouse gas emissions from a well established, unfertilized tropical grass-legume pasture were monitored over two consecutive years using high resolution automatic sampling. Nitrous oxide emissions were highest during the summer months and were highly episodic, related more to the size and distribution of rain events than WFPS alone. Mean annual emissions were significantly higher during 2008 (5.7  $\pm$  1.0 g N<sub>2</sub>O-N/ha/day) than 2007 (3.9  $\pm$  0.4 and g N<sub>2</sub>O-N/ha/day) despite receiving nearly 500 mm less rain. Mean CO<sub>2</sub> (28.2  $\pm$  1.5 kg CO<sub>2</sub> C/ha/day) was not significantly different (P < 0.01) between measurement years, emissions being highly dependent on temperature. A negative correlation between CO<sub>2</sub> and WFPS at >70% indicated a threshold for soil conditions favouring denitrification. The use of automatic chambers for high resolution greenhouse gas sampling can greatly reduce emission estimation errors associated with temperature and WFPS changes.

## Introduction

Increases in the concentrations of the greenhouse gases carbon dioxide ( $CO_2$ ), methane ( $CH_4$ ), and nitrous oxide ( $N_2O$ ) in the atmosphere due to human activities have long been linked to climate change. Greenhouse gas (GHG) emissions from agriculture are estimated to be about 16% of Australia's total GHG budget. This is expected to increase with intensification of agriculture over the coming decades. For these reasons full greenhouse accounting to comprehensively assess the impact of land management strategies has continued to gain momentum in recent years, aimed at ultimately developing mitigation strategies to reduce GHG emissions. Little comprehensive data exists for the processes related to GHG emissions from tropical soils and land management systems, the majority of work being associated with temperate climates or in laboratory conditions. During this experiment, GHG emissions were examined and compared between three landuses on a Haplic, Brown Dermosol as part of a larger study aimed at reducing uncertainties in GHG estimates from subtropical landscapes. In this paper  $N_2O$  and  $CO_2$  emissions from pastures will be examined.

# Methods

The study site was situated in the wet subtropical region of the Mooloolah valley; approximately 100km north of Brisbane, Queensland. Three landuses were examined; a grazed and mown tropical pasture dominated by *Setaria sphacelata*, Silverleaf Desmodium (*Desmodium uncinatum*) and White Clover (*Trifolia repens*), remnant Gallery rainforest (notophyll vine forest) and a 20 year old Lychee orchard. The greenhouse gases N<sub>2</sub>O, CO<sub>2</sub> and CH<sub>4</sub> were measured for two full years commencing the 1<sup>st</sup> of March 2007 and finishing on the 28 February 2009. Emissions were measured from three landuses; (three chambers per plot) using an automated gas sampling system described by (Breuer *et al.* 2000) and (Kiese 2002). Briefly the system consisted of nine automated measuring chambers linked to an automated sampling control system, computer and a gas chromatograph (SRI 8610C,) housed in a weatherproof trailer at a central position on the field site. Chambers from each plot were closed for 48 minutes and open for 96 minutes, allowing for 10 individual flux measurement periods per day while minimizing any impact on the soil environment. Auxiliary sub-daily soil temperature and moisture data was collected from each landuse and a weather station was situated on the site.

## **Results**

A total of 1928 mm rain fell at the site during the March 2007 to February 2008 measurement season, significantly (P <0.05) higher than the 1432 mm in the 2008/09 season and above the long term average of 1709 mm. Frequent heavy rainfall resulted in large and rapid changes in soil moisture content (amplitude of WFPS: 28-90%). Though rainfall was higher in the summer months no distinct wet/dayry pattern was observed, though seasonal patterns did persist over the 2 year measurement period. Temperatures ranged from a mean daily minimum of 9.0 °C during the winter to a daily maximum of 27.9 °C in the summer. The minimum hourly air temperature was -0.6 °C recorded in July 2007, while the maximum hourly temperature (38.2 °C) was recorded in February 2008.

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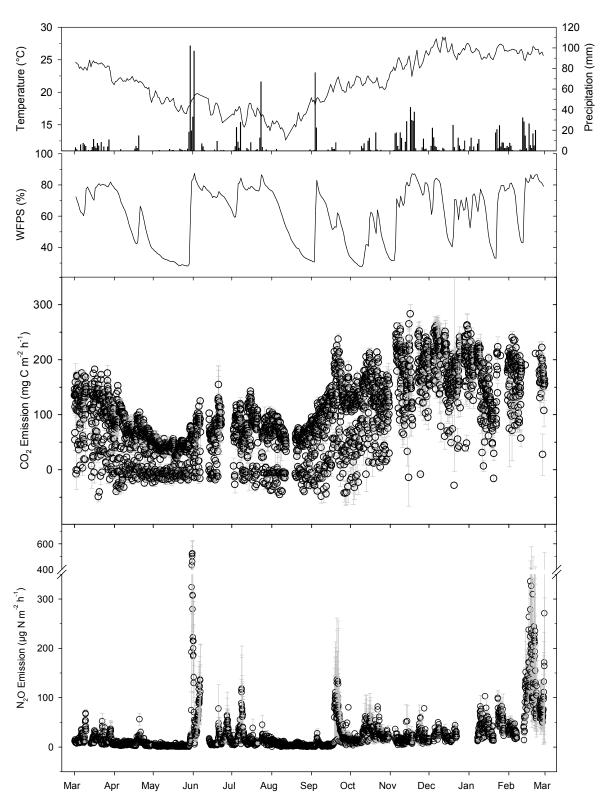


Figure 1. Hourly means of soil temperature (5 cm), water-filled pore space (WFPS), mean  $CO_2$ - emission rates (N = 3),  $N_2O$ -emission rates (N = 3) and daily precipitation for pasture (March 2008 February 2009).

# $N_2O$ and $CO_2$ emissions from soils

Despite data loss from leaks due to livestock and rodent activity, issues with the gas chromatograph due to high humidity and even the inundation of the chambers during a flood event, over 70 000, individual, real time gas concentration measurements were taken for each gas over the duration of the experiment. The use of the automatic chambers allowed for the high temporal variability of fluxes to be fully accounted (Fig.1). Emissions varied on a daily, seasonal and yearly basis driven chiefly by changes in WFPS and

temperature. Nitrous oxide fluxes were highly episodic with 48% of emissions occurring in just 16% of measurement days. Mean N<sub>2</sub>O fluxes for 2008 were  $5.7 \pm 1.0$  g N<sub>2</sub>O-N/ha/day, significantly (P < 0.01) higher than 2007 ( $3.9 \pm 0.4$  g N<sub>2</sub>O-N/ha/day). Emissions were highest during the summer with the highest daily flux of 94.2 g N<sub>2</sub>O-N/ha/day occurring on the  $18^{th}$  February 2009. The highest individual chamber flux also occurred on this day (197.8 g N<sub>2</sub>O-N/ha/day). Lowest emissions were recorded during the spring and winter. Detailed correlation analysis revealed a close relationship between WFPS and magnitude of N<sub>2</sub>O emissions for autumn (r = 0.52, P < 0.01), winter (r = 0.65, P < 0.01) and summer (r = 0.39, P < 0.01). Mean nightly CO<sub>2</sub> fluxes ( $28.2 \pm 1.5$  kg CO<sub>2</sub>- C/ha/day) were not significantly different (P < 0.01) between measurement years. Emission were highly significantly correlated (r = 0.73, P < 0.01) with temperature; highest fluxes (58.1 kg CO<sub>2</sub>-C/ha/day) occurring in late spring and early summer when maximum temperatures occurred. CO<sub>2</sub> and WFPS were less correlated (r = 0.33, P < 0.01) and in spring and summer negative correlations (r = -0.25, P < 0.01 and r = -0.37, P < 0.01 respectively) occurred as increasing WFPS (> 70%) inhibited O<sub>2</sub> availability in the soil.

Table 1. Mean annual emissions for CO<sub>2</sub> (t C/ha/y) and N<sub>2</sub>O (g N/ha/y).

Gas	2007			2008		
	Mean	N	CV%	Mean	N	CV%
$CO_2$	$11.2 \pm 0.4$	3	5.7	$10.7 \pm 0.4$	3	6.3
$N_2O$	$1504.7 \pm 126.7$	3	14.3	$2148.6 \pm 273.1$	3	22.0

## **Discussion**

Nitrous oxide emissions measured over the study period were twice as high as maximum values generally quoted in the literature (Dalal 2003; Denmead *et al.* 2000), and were highly episodic; responding more to individual rain events than to general trends in WFPS. Rainfall and subsequent WFPS, though playing a critical role; was less an influencing factor than the distribution and length of individual rainfall events. This was highlighted by emissions from 2007 being significantly lower than 2008, despite receiving almost 500 mm more rainfall. Carbon dioxide dynamics provide a good representation of microbial activity in the soil. Emissions continued at WFPS values well below 40% indicating microbial processes such as mineralization were less affected by low moisture. At values greater than 70% WFPS CO<sub>2</sub> emissions were inhibited by lack of available O<sub>2</sub>, creating soil conditions that favour denitrification. High moisture and legume component (which can fix up to 200 kg N/ha/y as stated by Peoples and Baldock, 2001) and a fine textured soil contributed to the comparably higher emissions on this site. In addition, traditional manual sampling is generally carried out on a weekly or fortnightly basis, leaving the potential to completely miss these large temporal events subsequently underestimation of annual totals.

## Conclusion

When considering the cost in equipment and time resources required to attain even one tenth of measured samples manually; the benefits of the automated system are clear. The combination of a fine textured soil, high soil moistures and temperatures and readily available N from legumes contributed to substantial  $N_2O$  emissions in the tropical pasture-legume system. The use of automatic chambers for high resolution greenhouse gas sampling can greatly reduce emission estimation errors associated with temperature and WFPS changes. However as legume content and distribution in long term pastures can change with time of year, rainfall, frost and grazing pressures,  $N_2O$  fluxes related to legume residues are likely to be just as variable in space as time.

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# Quantity and fate of root derived soil carbon produced after a growing season of canola, lentil, pea and wheat in Canadian prairies

Louis-Pierre Comeau<sup>A</sup> and Angela Bedard-Haughn<sup>B</sup>

### **Abstract**

Soil carbon (C) sequestration mitigates climate change and improves lands productivity. Root derived soil C during a growing season is the first step toward C sequestration. The goal of this work was to evaluate the quantity and fate of newly produced soil organic carbon (SOC) captured at the end of a single growing season of canola, lentil, pea and wheat in Canadian Prairie soils. This study was conducted using intact soil cores from two Agriculture and Agri-food Canada Research Stations (Scott and Swift Current). The crop rotations selected at Scott were pea-wheat, canola-wheat and continuous wheat and at Swift Current were lentil-wheat and continuous wheat. Using hermetic plexiglass chambers in a greenhouse, the plants of the first rotation phase were labelled with <sup>13</sup>CO<sub>2</sub> weekly for two hours over eight weeks. At the end of the growing season, the cores were broken and the amount of <sup>13</sup>C present in the dissolved organic matter (DOM), the light organic matter fraction, and heavy organic matter fraction was evaluated.

# **Key Words**

Root derived soil carbon, canola, lentil, pea, wheat, soil organic matter fraction, <sup>13</sup>C labelling, Chernozem.

## Introduction

Estimates have shown that since the nineteenth century, 40 to 50 Pg (10<sup>15</sup> g) of carbon (C) has been lost from soil and every year it is estimated that an additional 0.8 Pg C is released due to agriculture (Schlesinger 1995; Desjardins 2008). A recent Canadian study reports that since cultivation of croplands began, 15 to 30 percent of the C originally present in the surface soil layer has been lost, estimated as 1.1 Pg of C. Most of this C had been released into the atmosphere as CO<sub>2</sub>. However, an important part of the C that has been lost from these soils can potentially be regained by restocking this C (Boehm *et al.* 2004; Hengeveld 2008). Among the 45.5 million hectares of farmland in Canada, 86% (39.1 million hectares) are located in the four western provinces. Therefore, the Canadian prairies have a great potential to mitigate CO<sub>2</sub> emission by increasing soil C storage (Hengeveld 2008). Accumulation of SOC begins with root derived C yet little is known about how much C plant roots are capturing in a single growing season. The aim of this study was to evaluate the quantity and destiny of newly produced soil organic carbon (SOC) captured at the end of a single growing season of canola (*Brassica napus*), lentil (*Lens culinaris*), pea (*Pisum sativum*) and wheat (*Triticum aestivum*) in Canadian prairies soils.

## Materials and methods

Study sites and soil collection

This greenhouse study was carried out with intact soil cores (39cm by 20.3cm i.d.) from Agriculture and Agri-Food Canada Research Stations at Scott (AAFC-Scott) and at Swift Current (AAFC-Swift) (Figure 1). The AAFC-Scott station is located in the Moist Mixed Grassland Ecoregion of Saskatchewan Canada where the dominant soils are loamy textured Dark Brown Chernozems. The AAFC-Swift station is located in the Mixed Grassland Ecoregion, where the climate is considerably drier and the dominant soils are sandy loam textured Brown Chernozems (Acton and Ellis 1978; Ayres *et al.* 1985). At AAFC-Scott soil cores were collected from continuous wheat, pea-wheat and pea-canola rotations. At AAFC-Swift soil cores were collected from continuous wheat and lentil-wheat rotations. All rotations had completed a wheat phase of the rotation the previous year.

## Plant labelling

Pea, lentil, canola and wheat (from AAFC-Scott and AAFC-Swift) were grown (in its respective soil core) to maturity and pulse labelled with isotopic carbon 13 (<sup>13</sup>C) under controlled greenhouse conditions. Three plots were selected for each crop rotation, two replicas were made for each plot and a control (no labelling) was made for each replica (Table 1). Four plants were grown in each soil core. Plants were watered to field capacity every second day. In order to prevent soil biota and soil organic matter (SOM) dynamic alterations

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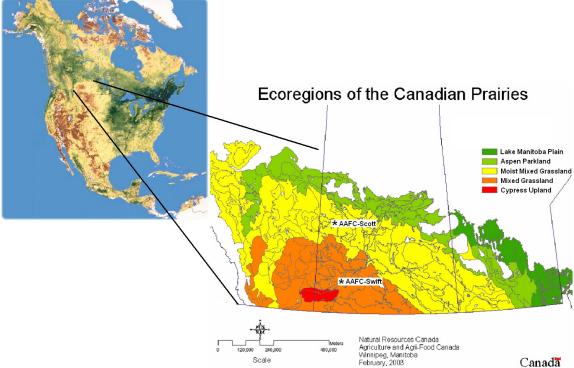


Figure 1. Map of Ecoregions of the Canadian Prairies. Natural Resources Canada, Agriculture and Agri-Food Canada.

no agrochemical were used during the experiment. Labelling was accomplished in polymethyl methacrylate chambers (Figure 2) from Sangster (2009 unpublished). Labelling was done weekly for 2 h starting 20 days after germination and continuing to the end of embryogenesis (8 label sessions). The soil surface was isolated from the enriched atmosphere during labelling. The atmospheric enrichment during the labelling session was 33 atom%  $^{13}CO_2$  and the total  $CO_2$  concentration was maintained around the current atmospheric concentration (380-430 ppm; IPCC 2007). The  $CO_2$  was devolved into the chamber by injecting a saturated solution of NaHCO<sub>3</sub> (33%  $^{13}C$ ) into a beaker with 12M HCl. Total  $CO_2$  concentration was monitored with an infrared gas analyzer (IRGA) (S151 Infrared CO2 Analyzer, Qubit Systems, Kingston, Ontario).

# Soil <sup>13</sup>C analyses

At harvest, soil samples (0-15, 15-30 cm) were collected from each soil core. Soil organic matter (SOM) was fractionated into dissolved organic matter (DOM), light fraction (LF) (0-1.7 g/cm³), and heavy fraction (HF) (>1.7 g/cm³) (Bird 2002; Chantigny 2007). For every SOM fraction, <sup>13</sup>C was analysed by isotope ratio mass spectrometer (Bird 2003). Natural abundance of <sup>13</sup>C in each SOM fraction was determined from the control soil cores. The comparative amount of newly produced SOC captured by the different plants was analysed with a general linear model (GLM) using the statistical program R (Foundation for Statistical Computing version 2.8.1) (Helbig 2008).

# Anticipated Significance

The results of this work will allow a better understanding of the biotic processes that control the carbon cycle, will aid to elaborate models of  $CO_2$  fluxes, and will improve the understanding of the crop-specific dynamics of SOC, which play a role in greenhouse gas emissions and mitigation.

Table 1. Number of field plot and replica for each crop rotation.

Site	Crop rotation	Number of field	Number of	Number of	Number of soil
		plot	replica by plot	control by plot	cores analysed
AAFC-Scott	continuous wheat	3	2	1	9
	canola-wheat	3	2	1	9
	pea-wheat	3	2	1	9
AAFC-Swift	continuous wheat	3	2	1	9
	lentil-wheat	3	2	1	9

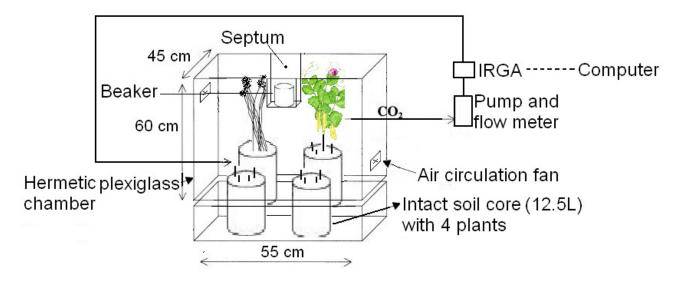


Figure 2. Design of sTable <sup>13</sup>C labelling chamber, with four soil cores per chamber and four plants per core.

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# Reducing $N_2O$ emissions from nitrogen fertilisers with the nitrification inhibitor DMPP

**Helen Suter**<sup>A</sup>, Deli Chen<sup>A</sup>, Huilin Li<sup>AB</sup>, Robert Edis<sup>A</sup> and Charlie Walker<sup>C</sup>

### **Abstract**

Emission of nitrous oxide (N<sub>2</sub>O) from fertilisers applied to soils comes from the process of nitrification, carried out by ammonia oxidizing bacteria (AOB) such as *Nitrosomonas*, and subsequent denitrification. Nitrous oxide emissions from agricultural soils are estimated at around 3% of the total greenhouse gas budget for Australia (Department of Climate Change 2009). A nitrification inhibitor, such as 3,4-dimethylpyrazole phosphate (DMPP) suppresses the activity of the AOB and thereby reduces nitrification and associated losses. This paper reports on a study of the impact of DMPP on N<sub>2</sub>O emissions from four soils fertilised with urea (100-160 kg N/ha) over a range of temperatures (5-35°C) in small scale (40-150g soil) incubation studies. DMPP was highly effective at reducing N<sub>2</sub>O emissions in one soil (Pin Gin, Qld Australia) by more than 93% at 25 and 35°C and temperature had no impact on the reductions. DMPP was less effective in reducing N<sub>2</sub>O emissions from the other soils examined (19-89% reductions) and temperature influenced the reductions. The ability of DMPP to reduce emissions was related to the pH, organic C and mineral N status of the soils examined. The results show that DMPP has the potential to be used as a tool for mitigation of N<sub>2</sub>O emissions from Australian agricultural systems.

# **Key Words**

3,4-dimethylpyrazole phosphate; nitrification rates; incubation studies.

## Introduction

Losses of applied fertiliser nitrogen (N) as leachable nitrate ( $NO_3$ ) and as emissions of nitrogenous gases ( $N_2$ ,  $N_2O$ ,  $NO_x$ ) can occur from both nitrification and subsequent denitrification. There is increasing concern about the contribution of greenhouse gas (GHG) emissions to climate change, from industry, transport and agriculture. Nitrous oxide ( $N_2O$ ) from agricultural soils accounts for 3% of the Australia's total GHG emissions.

One method of reducing N losses from nitrification is to reduce the rate of nitrification by inhibiting autotrophic ammonia oxidizing bacteria (AOB), increasing plant uptake of ammonium (NH<sub>4</sub><sup>+</sup>), and this can be achieved using nitrification inhibitors. Various nitrification inhibitors have been tested in cropping systems and have shown variable reductions in N<sub>2</sub>O emissions (Chen *et al.* 2008; Hatch *et al.* 2005; Li *et al.* 2008; McCarty 1999; Yu *et al.* 2007). This is partly because nitrification inhibitors are affected by soil properties and climatic variables such as temperature and moisture (Barth 2006; Kelliher *et al.* 2008). 3,4-dimethylpyrazole phosphate (DMPP) is one inhibitor which can be used at lower concentrations than other inhibitors with similar results (Zerulla *et al.* 2001).

DMPP has not been tested in Australian dryland agriculture and knowledge of its viability for high temperature situations is unknown, with studies covering temperatures to a maximum of 30°C (Irigoyena *et al.* 2003).

This paper reports on laboratory studies investigating the effect of temperature and DMPP application rate on  $N_2O$  emissions from urea applications to Australian soils, in small-scale incubation experiments.

## Methods

Soils

Soils were collected from a number of locations, air dried and sieved to <2 mm. Table 1 provides details of the soils used.

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Table 1. Selected source and soil properties

	Pin Gin	Mackay	Dookie -topsoil	Dookie-subsoil
Source site	Far northern	Queensland	Northern Victoria	Northern Victoria
	Queensland			
Agricultural activity	sugarcane	sugarcane	pasture	pasture
colour	Dark reddish	Black	Very dark grey	Brown
	brown			
Texture				
%clay	39	15	21	33
%silt	10	12	28	30
%sand	51	72	50	37
pН	4.5	4.0	5.4	5.5
Org C (%)	3.9	1.5	10.0	2.4
Total N (%)	0.2	0.1	1.0	0.2
Nitrifying potential	1.8	1.2	18	4
(mg/kg/day)				

## Incubation trials

Soil (40-200g) was pre-wetted 2 days prior to commencement of the experiment. Granular urea was applied at a rate of 100 (pasture soils) and 160 (sugarcane soils) kg N/ha (175 and 1325 ug N/g soil). DMPP was applied as the commercial product Urea with ENTEC<sup>TM</sup> (1.84 kg DMPP active ingredient/t urea (0.7  $\Box$ g DMPP/g soil (pasture) 5.3  $\Box$ g DMPP/g soil (sugarcane)). Urea (1325  $\Box$ g N/g soil) was also applied as a solution with DMPP (2.8  $\Box$ g/g soil) to the sugarcane growing soils for temperature comparison. A control treatment (no fertiliser) was included to measure background N transformations. Samples were incubated at 5, 15, 25 and 35°C and at 60 % water filled pore space (WFPS). Experiments ran for 70 days with sample aeration and water replenishment at regular intervals. Nitrous oxide (N<sub>2</sub>O) samples were collected in triplicate and analysed using a Hewlett Packard 6890 GC with 2 Porapak Q columns and a carbosorb column with an ECD detector. Emissions on a per hectare basis were calculated from the area of the vials (35 cm<sup>2</sup>).

#### Results

Nitrous oxide emissions from the control treatments were generally lower than fertilised soils ( $<2.6 \text{ kg N}_2\text{O}$  /ha) with the exception of the Dookie topsoil (Table 2). Nitrous oxide emissions from the unamended urea were greatest from the Dookie topsoil at 25°C (Table 2) (55 kg N<sub>2</sub>O/ha), followed by the Mackay (11.8 kg N<sub>2</sub>O/ha), Dookie subsoil (10.5 kg N<sub>2</sub>O/ha) and Pin Gin ( $8.0 \text{ N}_2\text{O}$ /ha) soils. The high level of emission from the Dookie topsoil reflects the high emissions from the control treatment for this soil. Emissions of N<sub>2</sub>O from all treatments increased with temperature in the Dookie soils to 25°C but were reduced in the Pin Gin and Mackay soils when the temperature was increased from 25 to 35°C.

Table 2. Cumulative N<sub>2</sub>O emissions after 70 days

Soil	Temperature	DMPP rate	1	%		
	(°C)	(µg/g soil)	Control	Urea	Urea + DMPP	reduction with DMPP
Pin Gin	25	2.81	0.0	8.0	0.1	94
	25	11.5	0.0	5.8	0.3	93
	35	2.81	0.0	5.3	0.3	99
Mackay	25	2.81	0.9	12.1	4.4	64
	25	11.5	0.9	11.8	1.3	89
	35	2.81	1.2	7.9	6.3	19
Dookie - topsoil	5	1.6	0.6	1.6	0.6	65
	15	1.6	1.7	4.9	1.9	61
	25	1.6	44	55	35	37
Dookie - subsoil	5	1.6	1.7	3.6	0.8	76
	15	1.6	1.3	7.4	1.9	74
	25	1.6	2.5	10.5	7.2	31

The reduction in  $N_2O$  emissions due to application of DMPP was greatest in the Pin Gin soil (>93%) regardless of application rate or temperature (Table 2). In the Mackay soil the rate of DMPP applied did influence the inhibition achieved, with greater inhibition with higher rates of DMPP (5.3  $\Box$ g/g soil) (89%). In all the other soils increased temperature decreased the degree of reduction in  $N_2O$  emissions as a result of using DMPP, as observed in other studies (Irigoyena *et al.* 2003). At 25°C DMPP reduced  $N_2O$  emissions in the order Pin Gin > Mackay > Dookie topsoil > Dookie subsoil.

Linear regression, excluding the data for the Dookie topsoil, showed that the level of  $N_2O$  emissions measured with DMPP influenced the percentage reduction in  $N_2O$  emissions as a result of using DMPP ( $R^2$ =0.80). However there was no relationship between the level of  $N_2O$  emissions measured for urea and the percentage reduction in emissions due to DMPP, and no relationship between emissions from urea treatments and emissions from DMPP treatments.

Soil pH appeared to influence the level of reduction in  $N_2O$  emissions with less emission in the highly acidic Mackay soil compared to the Pin Gin soil. Soil texture may also influence inhibition with less inhibition in the sandier soil from Queensland (Mackay) than in the clayey soil (Pin Gin). The level of organic C and mineral N also influenced the level of emissions and the reduction achieved, with a high level of organic matter, such as found in the Dookie topsoil, leading to high emissions of  $N_2O$  and a lower ability for the DMPP to reduce these emissions. Where a greater number of AOB exist, greater levels of DMPP may achieve similar levels of inhibition as seen in less organic soils such as the Pin Gin. The composition of the biological community in the soil is likely to influence the level of reduction achieved also both in terms of numbers of heterotrophic and autotrophic organisms and also in the composition of the autotrophic populations.

### Conclusion

Reductions in N<sub>2</sub>O emissions with addition of DMPP to urea from four different soils at 60% WFPS and at temperatures of 5 to 35°C ranged from 19 to 99%. DMPP was very effective in reducing N<sub>2</sub>O emissions compared to urea, by more than 93% in a sugarcane growing soil from far northern Queensland (Pin Gin) under all conditions. DMPP was able to reduce N<sub>2</sub>O emissions in another sugarcane growing soil but to a lesser extent (19 to 89%) and in pasture soils from Victoria (31-76%), and the level of reduction in these instances was decreased with increasing temperature.

Soil pH, texture and organic C content are considered to be the factors influencing the level of  $N_2O$  emissions seen and the degree of reduction shown with the addition of DMPP.

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# Simulating $N_2O$ emissions from maize-cropped soil and the impact of climatic variations and cropland management in North China Plain

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## **Abstract**

The Water and Nitrogen Management model (WNMM) was applied to simulate N<sub>2</sub>O emissions from a semi-arid and maize-cropping system on a loam soil at Yuci in the North China Plain (NCP) from May 2007 to September 2007. WNMM satisfactorily simulated crop growth, soil water content and soil temperatures at depth and N<sub>2</sub>O emissions from the soil, compared with the field observations during calibration and validation. About 89% of total N<sub>2</sub>O emissions were estimated as nitrification-induced, according to WNMM simulation for this semi-arid and intensively cultivated maize-cropped soil. The calibrated and validated WNMM was then deployed to simulate N<sub>2</sub>O emissions from this soil from 1951 to 2007 for nine management scenarios of N fertiliser application at Yuci. This sensitivity test found that the annual N<sub>2</sub>O emissions for this system were significantly correlated to annual N fertiliser application rate (r=0.81) and maize yield (r=0.43). Based on this 57-year simulation, multivariate regression models for estimating annual N<sub>2</sub>O emissions were developed to account for climatic variation (including annual solar radiation and rainfall) for this semi-arid and intensively cultivated maize-cropping system in the NCP.

# **Key Words**

N<sub>2</sub>O Emissions, maize-cropped soil, WNMM simulation, impact of climatic variation.

# Introduction

Nitrous oxide (N<sub>2</sub>O) is a potent greenhouse gases contributing to global warming and the depletion of ozone in the stratosphere (IPCC2006). Consequently numerous studies have investigated N<sub>2</sub>O emissions from agricultural soils cropped with maize (Li *et al.* 2002; Timothy *et al.* 2006; Song *et al.* 2009). Process-based models not only be used to simulate the complex dynamic processes of soil nitrification and denitrification, and their contributions to N<sub>2</sub>O production and emissions, but also have powerful advantages to be used to identify main driving factors for N<sub>2</sub>O emissions, such as soil properties, crop rotation, management and climate (Gabrielle *et al.* 2006; Grant *et al.* 1993; Li *et al.* 1992; Li *et al.* 2007; Parton *et al.* 2001). The obvious advantages of using such process-based models are: i) to test the proposed theories of N<sub>2</sub>O production from nitrification and denitrification processes from agricultural soils, which were mostly developed from laboratory experiments, compared to the field observations, ii) to demonstrate continuous inter-annual variations of N<sub>2</sub>O emissions, and iii) to help us to find the knowledge gaps between what has been documented in the books and also been applied in the models and what is really happening in the fields, by comparing model predictions to field observations.

# Method

Field experiments were conducted from May 2007 to September 2007 at the Yuci in the NCP (37°38′ N, 112°51′ E, elevation 789 m). A completely randomised design with three replicates was deployed with two fertilization *treatments*: TF = traditional fertilization and OF = optimal fertilization. The study site and experiment treatment information had been detailed by Liu *et al.* (2008).

# Methodology

We used one-season (May-September 2007) field observations for  $N_2O$  emissions from TF and OF treatments for the model calibration and validation, respectively. Then, the WNMM was used to simulate long term  $N_2O$  fluxes using historic weather dataset from 1951 to 2007 (57 years) and simulated various N fertiliser application scenarios to investigate the sensitivity of  $N_2O$  emissions to climatic variation (annual air temperature, annual precipitation and annual pan evaporation), N application rate and crop yield.

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## Results and discussion

Soil water content, soil temperature and  $N_2O$  calibration

A tipping-bucket water balance module in WNMM was used to simulate soil water infiltration, redistribution and percolation at layers, and soil evaporation and crop transpiration. WNMM predicted the surface (0-10cm) soil water contents satisfactory without any parameter optimisation for the TF ( $R^2$ =0.81, RSE=0.032 cm<sup>3</sup>/cm<sup>3</sup>, n=130 and p<0.001) (Figure 1). In the calibration (the TF treatment), the observed and predicted soil temperature also demonstrated an impressive agreement at 10cm ( $R^2$ =0.82, RSE=1.35°C, n=130 and p<0.001 at 10 cm) (Figure 2).

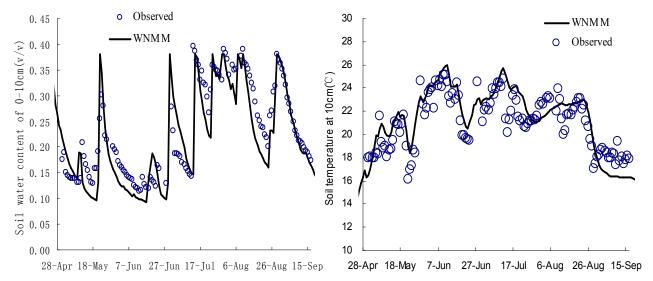


Figure 1. Field observed (hollow circle) and WNMM simulated (solid line) soil water content of 0-10 cm for the Trad treatment at yuci, NPC from May 2007 to September 2007.

Figure 2. Field observed (hollow circle) and WNMM simulated (solid line) soil temperature at 10 cm for the Tradition treatment at yuci, NPC from May 2007 to September 2007.

The WNMM predicted  $N_2O$  emissions for the TF (Figure 3) demonstrated a satisfactory agreement with the chamber observations at the daily basis ( $R^2$ =0.80, RSE= 7.28 g N/ha/d, n=130 and p<0.001). The predicted seasonal  $N_2O$  emissions for this year is 0.78 kg N/ha/yr, comparable to the chamber observed annual emissions of 1.08 kg N/ha/yr. In addition, nitrification-induced  $N_2O$  emissions predicted by the WNMM accounted for 89% of total  $N_2O$  emissions.

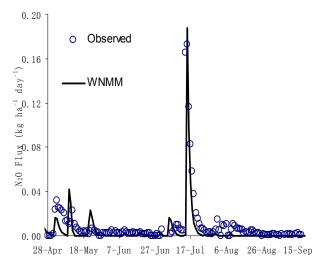


Figure 3. Chamber observed (hollow circle) and WNMM simulated (solid line)  $N_2O$  emissions in the TF.

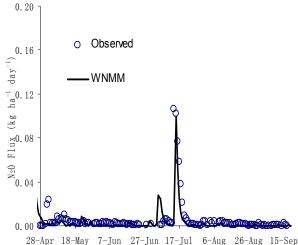


Figure 4. Chamber observed (hollow circle) and WNMM simulated (solid line)  $N_2O$  emissions in the OF.

# WNMM model N<sub>2</sub>O validation

The validation of daily  $N_2O$  fluxes for the OF was satisfactory ( $R^2$ =0.49, RSE=7.5 g N/ha/d, n=130 and p<0.001) (Figure 4). Based on the WNMM simulation, 0.47 kg N/ha/yr were emitted from May 2007 to September 2007, in which 89% are nitrification-induced, the observed chamber  $N_2O$  emissions for the same season were 0.68 kg N/ha/yr in the OF.

Impacts of N application rate and climatic variation on annual  $N_2O$  emissions

The 57-year averages of annual  $N_2O$  emissions for nine fertiliser N application scenarios indicated a positive correlation between annual  $N_2O$  emissions and fertiliser N application rates as shown in Figure 5. In addition,  $N_2O$  emission factor (EF, 0.25-0.61%) is smaller than 1% recommended by IPCC (2006) and decreases with the increase of the fertiliser N application rate. A Pearson correlation analysis was carried out to look at the statistical relationship between the 57-year WNMM-estimated annual  $N_2O$  emissions and related indices, such as climatic variables, fertiliser N application rate and crop yield, Annual  $N_2O$  emissions have positive and highly significant correlations with fertiliser N application rate (r=0.81) and maize yield (r=0.43) annual.

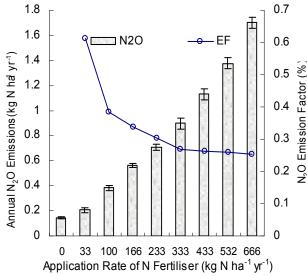


Figure 5. The 57-year averages of WNMM-estimated annual N2O emissions (gray bars) and N2O emission factor (solid line) (%, not corrected for background emissions) for nine fertiliser N application scenarios at yuci, NPC. The bars represent  $\pm$ standard deviations of annual N2O emissions.

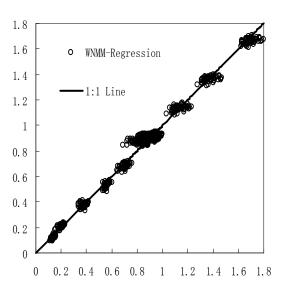


Figure 6. Annual  $N_2O$  emissions predicted by the multivariate regression (N rate, rainfall, minimum/maximum temperature, solar radiation, and yield are predictors) (N = 1207, p<0.001,  $R^2$ =0.99, S = 0.04105). The multivariate regression indicates that the fertilization and yield are the most important factors driving  $N_2O$  emissions.

In this semi-arid agroecosystem, maize yield is mainly controlled by annual precipitation (r=0.52) and fertiliser N application rate (r=0.38) based on WNMM simulations in this study. It is generally expected that higher rainfall results in more denitrification, therefore, potentially contributing to more N<sub>2</sub>O emissions from the soil. On the other hand, the increase in rainfall may increase crop growth resulting in more N uptake and possibly more nitrate leaching, consequently reducing the nitrate availability in the topsoil for soil denitrification process. Furthermore, 89% nitrification-induced N<sub>2</sub>O fraction estimated by WNMM also indicated that annual N<sub>2</sub>O emissions from this agroecosystem are mainly controlled by N inputs (organic N mineralisation and fertiliser N application) and abiotic factors (soil water content and temperature), which strongly impact soil nitrification process and crop growth as well. Thus, crop growth may be another important factor to effect annual N<sub>2</sub>O emissions from this soil.

Including climatic variables (annual average minimum air temperature, annual precipitation and annual pan evaporation) and the fertiliser N application rate and maize yield as predictor variables, multivariate regression models were developed for estimating annual  $N_2O$  emissions by the stepwise multiple linear regression process:

Y=0.1579+0.0023X1+0.0107X2-0.0153X3+0.0001X4+0.00001X5 (1) where Y is the annual N<sub>2</sub>O emissions (kg N/ha/yr), X1 is the annual N fertilizer application rate (kg N/ha/yr), X2 is the difference between annual average maximum temperature and annual average minimum

temperature difference ( ${}^{\circ}$ C), X3 is the average annual solar radiation, X4 is the annual rainfall (mm), and X5 is the maize yield (kg/ha). In general, Eq. (1) explained over 84% of the yearly variations of annual N<sub>2</sub>O emissions predicted by WNMM (n=1207 and p<0.001) (Figure 6).

## **Conclusions**

By comparing with the field observations for the TF, the simulation here indicated that WNMM is capable of simulating soil water and soil temperatures. And, the chambered-observed soil  $N_2O$  emissions were well predicted by the WNMM for the OF. The 57-year (1951-2007) backward simulations using the calibrated and validated WNMM under nine scenarios for fertiliser N application indicated that annual  $N_2O$  emissions simulated by WNMM were significantly correlated to the N fertiliser application rate and the maize yield. By applying a stepwise multiple regression, multivariate regression models with annual rainfall, fertiliser N application rate and maize yield as predictors were developed to estimate annual  $N_2O$  emissions, which explained over 84% of between-year variations in annual  $N_2O$  emissions predicted by WNMM.

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## Soil C dynamics following the ploughing of a poorly-drained grassland

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#### **Abstract**

Perennial forage production is a predominant land use in northern temperate regions and soils under forage contain large stock of C. It is important to understand C dynamics under these systems to better assess their role in greenhouse gas budgets. Two plots, one that had received 100 m³ /ha of liquid swine manure (LSM) annually since 1978 and an unfertilized forage field, were (i) left with vegetation intact or killed by glyphosate in the autumn, and either (ii) left as an undisturbed chemical fallow, (iii) ploughed by full inversion tillage (FIT) in the autumn, or (iv) or in the spring. Following the autumn tillage operation, we monitored CO<sub>2</sub> emissions from the fallow soil surface, CO<sub>2</sub> concentrations in the soil profile, soil temperature and water content for one year. Soil aggregation, the intra-aggregate light fraction organic matter (LFOM) and microbial biomass were also analysed. Tillage significantly decreased the quantity of water-stable aggregates and with it the content of LFOM material protected by aggregates. Yet CO<sub>2</sub> emissions indicated that FIT reduced soil respiration compared to chemical fallow treatments by 19 to 33%. Regression analyses suggested that reductions in CO<sub>2</sub> emissions were due to the placement of surface C at depth where soil temperature and oxygen availability were attenuated. Our study indicates that in this cool poorly-drained soil, respiration is largely dependant on environmental factors and not physical protection mechanisms.

#### Introduction

Perennial systems, whether natural grasslands, pastures or forage fields contain between 10 to 50% more C than annual production systems located on the same soil. There is therefore interest in converting current arable land to forage systems due to their potential to sequester C. However, because forage soils are C rich, land use change of current forage fields and occasional renovation of heavily-fertilized forage fields could result in significant GHG emissions. In arable lands of temperate semi-arid regions where tillage is predominantly done by chisel ploughs, which mixes the surface soil, C stocks are reduced by tillage. In these regions, the differences between C in soils of no-till and tillage production systems indicate that mixing organic material from the surface into the soil often stimulates soil respiration. Similar observations have been made with the cultivation of grasslands and forage fields (Vellinga *et al.* 2004; Grandy and Robertson 2006).

Tillage of virgin soils modifies soil structure. The conversion of grasslands to arable lands reduces the mean weight diameter (MWD) of aggregates and releases light-fraction organic material (LFOM). On the other hand no-till production systems are observed to increase aggregate size and protected particulate organic matter (POM) and LFOM. Consequently, tillage of forage soils can be expected to disrupt soil structure and mix fresh organic material and fresh microbial C into the soil surface. The principle mechanism of C loss by tillage in semi-arid temperate soils is thought to be the physical disruption of the soil structure protecting SOM.

At the same time on the cool humid soils of eastern Canada where FIT using a mouldboard plough is the dominant tillage process, tillage has not always been observed to have an impact on soil C stocks (Angers *et al.* 1997). Carbon lost from the soil surface is compensated for by accumulation of C deeper in the soil profile. Similar observations were made at other locations (Angers and Eriksen-Hamel 2008). Because FIT buries surface C deep in the soil profile, the C is likely protected by the cool conditions and the lower concentrations of oxygen in the soil profile (Angers *et al.* 1997). Furthermore, by placing the C in contact with fresh mineral surfaces, it may also be stabilized by fixation of SOM on mineral surfaces. Forage fields can sequester large stocks of C relative to annual cropping systems (Soussana *et al.* 2004). It is therefore important to understand how management actions will influence the release of C during renovation and return of these fields to annual cropping systems. The objective of this work was to quantify the response and identify the processes that alter soil respiration in either full inversion tillage using mouldboard plough or notill seeding of two long-term forage fields (nutrient rich and nutrient poor) on cool moist soils of eastern Canada.

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#### Materials and methods

Study site and experimental design

The study was conducted at the research farm of IRDA located near Québec City, Canada. The site was on a Le Bras series, (270 g clay/kg, 420 g silt /kg, loamy, mixed, frigid, Typic Humaquept). The mean annual temperature in Québec City is 4.2°C and the mean annual precipitation is 1213 mm. In the fall of 2007, two long-term research plots (Angers *et al.* 2009) were divided into 24 subplots (4 treatments x 4 replicates x 2 long-term plots). The plots were left free of vegetation for one full year. One of the two long-term plots had received large doses of LSM annually since 1978 (100 m³/ha) and the other was an unfertilized grassland (0 m³/ha). The plots had been managed as typical forage fields since 1978. The subplots were randomly designated one of four treatments: ploughed by inversion tillage in the autumn (autumn-FIT), or in the spring (spring-FIT), chemically treated with herbicide (chemical fallow) or left as controls (grass, undisturbed). All subplots not designated as controls were chemically killed with herbicides on 10 Aug. 2007. Full inversion tillage, at a depth of 20 cm, was carried out on 4 Sept. 2007 and on 12 May 2008 using a four-share mouldboard plough.

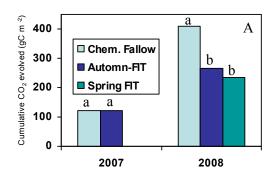
## Soil gas measurements, soil sampling and analyses

Soil surface fluxes of CO<sub>2</sub> were measured using non-flow-through non-steady state chambers (Rochette and Bertrand 2008). A soil profile was dug and instrumented within 1 metre of the chamber. Soil air samplers were inserted horizontally at depths of 5, 15, 25 and 45 cm to measure the concentrations of CO<sub>2</sub> and O<sub>2</sub>. Soil samples were taken on 29 Sept. 2007 and 22 July 2008 at depths of 0-5, 5-10, 10-20 and 20-30 cm. Water-stable aggregates (1-6 mm), intra and inter LFOM (NaI at a specific gravity of 1.7), microbial biomass C and bulk density were measured.

## Results and discussion

Soil respiration

Respiration rates in the fall of 2007 were consistent with other soils of eastern Canada and cooler humid regions with fresh organic material integrated into soils ranging from 0.10 to 0.3 mg  $CO_2$  m<sup>-2</sup>/s (e.g. Rochette and Angers 1999) (detailed data not shown). The seasonal respiration pattern was typical of cool humid temperate climates with long periods of low  $CO_2$  emissions in the spring due to the cool moist soils, followed by sharp increases in respiration associated with soil warming events (Rochette and Angers 1999). In the summer of 2008,  $CO_2$  fluxes were lower than the norm for this region, likely due to the cool wet summer and the lack of fresh organic material input.



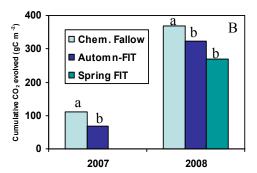


Figure 1. Cumulative CO<sub>2</sub>-C emissions from unfertilized (A) and fertilized (B) long-term grasslands subjected to autumn or spring full-inversion tillage (FIT), and compared to a chemical fallow.

After one year, total respiration, as represented by CO<sub>2</sub> emissions, decreased in the order of chemical fallow fertilized>chemical fallow unfertilized>autumn-FIT fertilized > autumn-FIT unfertilized > spring-FIT fertilized > spring-FIT unfertilized (Figure 1). Soil respiration was reduced by 27% by A-FIT and 33% by S-FIT on unfertilized soils and 19% by A-FIT and 21% by S-FIT on fertilized soils (unfertilized (p=0.07) and fertilized (p<0.001), respectively). Total emissions from the spring-FIT treatments on both unfertilized and fertilized sites were equivalent to the autumn-FIT treatments during the summer of 2008. These results are surprising, as it is often taken for granted that the ploughing of grassland will have a stimulatory effect on respiration (Vellinga *et al.* 2004; La Scala Jr *et al.* 2009).

Physical effects of tillage on the soil profile

Tillage resulted in a disruption of aggregate structure. On the fertilized site, compared to chemical fallow subplots, tillage reduced the percentage of soil in water stable aggregates by 13 and 20% in soils of the autumn-FIT subplots in autumn 2007 and summer 2008 respectively, and spring-FIT reduced stable aggregates by 7% (data not shown). On the unfertilized site, the quantity of stable aggregates in soil of the autumn-FIT treatments also tended to be lower by 7% (p=0.09) and 6% (p=0.16) in autumn 2007 and summer 2008, respectively, and the spring-FIT unfertilized tended to be lower by 6% (p=0.14) than the chemical fallow.

In the autumn of 2007, on the unfertilized site, aggregate disruption caused by tillage resulted in a decrease of 23% and 19% in the intra-aggregate light fraction organic material (iLFOM) relative to control and chemical fallow treatments. A similar trend was observed on the fertilized site where average quantities of iLFOM in samples taken from the spring-FIT plots decreased by between 25 and 35% relative to the undisturbed chemical fallow and control sites. These results are typical of the physical impact of tillage on soils. The occlusion of LFOM is a primary means of physically protecting SOM and the destabilization of aggregates is thought to be the primary mechanism for the reduction in SOM when soils are converted to arable land. Reductions in soil aggregation and associated POM or LFOM following cultivation of native prairie have been related to increased soil respiration (e.g. Grandy and Robertson 2006). Our results on poorly-drained soils confirm the negative impact of cultivation on aggregation and occluded SOM, but differ from other studies where a concurrent increase in soil respiration is observed.

Environmental factors: soil temperature and water content influencing respiration The destabilization of soil structure and release of aggregate-occluded LFOM in combination with the reductions in microbial biomass (data not shown) that we observed in FIT subplots would also suggest that an increase in easily available C for decomposers should result in accelerated decomposition and respiration. However, losses of C-CO<sub>2</sub> were much lower on FIT plots. Regression analysis indicated that, overall, emissions from chemical fallow subplots were strongly related to the temperature of the soil at 5 cm depth (R<sup>2</sup>=0.63\*\*), while emissions from autumn-FIT treatments are correlated with temperature (partial R<sup>2</sup>=0.42\*\*) at depth (40 cm). Furthermore, the slope of the temperature-CO<sub>2</sub> emission relationship is very similar in the two treatments. In real terms this result simply means that the peaks in CO<sub>2</sub> emissions under the FIT soils tended to be attenuated in the same way that temperature is attenuated with depth. The slope of the temperature-CO<sub>2</sub> emission relationship in spring-FIT subplots is much lower than that of autumn-FIT and chemical fallow treatments, but this likely due to the aging of the fresh residues as the spring tillage plots were killed with herbicide at the same time as the autumn-FIT and spring-FIT plots. Respiration generally responds in an exponential manner to increases in soil temperature, however in field studies such as these, it is difficult to separate non-linearity associated with the aging of soil residues from non-linearity associated with increased soil temperature. Average temperature during the snow-free season was only one degree warmer at the soil surface (5cm) of chemical fallow treatments, compared 25 cm depth. However in mid summer, there were differences of up to 10°C between 5cm and 15cm and throughout the spring, peak temperatures were on average 5°C greater close to the soil surface than at 15 cm (data not shown). The inversion of the soil profile with FIT places the majority of carbon at roughly 15-20 cm. Due to the exponential response of respiration to temperature differences, it is likely these peak temperatures that result in greater overall respiration.

However a negative effect related to the amount of oxygen in the soil profile ( $R^2$ =0.08\*\*) was also observed in FIT plots in the fall. Emissions from spring-FIT were strongly influenced by the amount of oxygen in the soil profile (partial  $R^2$ =0.31\*\*), and temperature was only a secondary factor in explaining emissions (partial  $R^2$ =0.24\*\*). Temperature and soil water content are understood to be the controlling factors on soil respiration. What is often neglected however is that the relationship between soil water content and soil respiration is a quadratic relationship (Linn and Doran 1984) and emissions tend to decrease as soils approach saturation? Due to the very moist fall of 2007 and summer of 2008, soils were often close to saturation in our case. This point is emphasized by the strong relationship observed between  $O_2$  quantities in the soil profile and emissions in the spring-FIT treatment.

## **Conclusions**

In poorly-drained soils under long-term perennial forages, we observed reductions in soil respiration with full inversion tillage relative to a chemical fallow treatment. The physical placement by FIT of residues and

C deeper in the soil profile where they are exposed to cooler temperatures and when soils are moist, reduced oxygen can reduce soil respiration. Tillage did physically disrupt soil aggregates and appeared to reduce the protection of light fraction organic material. Many studies make the assumption that the physical disruption of soils results in an eventual depletion in C stocks. Our study indicates that in this cool and poorly-drained soil, respiration is largely dependant on environmental factors and not physical protection mechanisms. In the context of climate change it will be important to understand how different soils may react to management practices in order to provide reasonable estimates of C loss under different land use and land management strategies. Carbon loss due to tillage must be estimated and modeled taking into account the complex interactions between the vertical distribution of environmental factors such as soil temperature and water content, and impact of different tillage procedures on physical and physico-chemical protection mechanisms.

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# Soil gas fluxes of N<sub>2</sub>O, CO<sub>2</sub> and CH<sub>4</sub> under elevated carbon dioxide under wheat in northern China

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#### **Abstract**

Fluxes of nitrous oxide  $(N_2O)$ , carbon dioxide  $(CO_2)$  and methane  $(CH_4)$  were measured from soils under ambient  $(420 \pm 18 \ \mu mol/mol)$  and elevated  $(565 \pm 37 \ \mu mol/mol)$   $[CO_2]$  at the Free-Air Carbon dioxide Enrichment (FACE) experiment in a wheat field in northern China.  $N_2O$  and  $CO_2$  emissions under elevated  $CO_2$  were increased by 47% (p < 0.05) and 11% (p = 0.063), respectively, but had no effect on  $CH_4$  flux. A significantly greater emission of  $N_2O$  (1812%) and  $CO_2$  (69%) was observed from high-N (190 kg N/ha) than low-N (50 kg N/ha) plots only after simultaneous addition of water and urea. The fluxes of  $N_2O$  and  $CO_2$  were positively and significantly correlated with both soil moisture and organic C contents, but  $CH_4$  flux with organic C content only. There was no significant relationship between soil mineral N and gas fluxes.

## **Key Words**

Free air carbon dioxide enrichment, nitrous oxide, carbon dioxide, methane, nitrogen fertilizer, wheat soil.

#### Introduction

Nitrous oxide (N<sub>2</sub>O), carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>) are important greenhouse gases to agriculture. Elevated [CO<sub>2</sub>] affects crop growth resulting in changes in soil C and N dynamics as well as greenhouse gas fluxes (Liu and Greaver 2009). Yet, the information on the responses to elevated [CO<sub>2</sub>] of these gas fluxes from cropping systems is limited. Emissions of N<sub>2</sub>O have been reported to either increase with soil moisture and C input under elevated [CO<sub>2</sub>], or decrease as a result of N immobilization (Hungate et al. 1997; Arnone and Bohlen 1998), CO<sub>2</sub> emissions were mostly stimulated under elevated [CO<sub>2</sub>], which was attributed to enhanced microbial and root respiration (Zak et al. 2000; Kou et al. 2007). The enhanced CH<sub>4</sub> emissions under elevated [CO<sub>2</sub>] in rice paddies were associated with greater amount of root exudates, root autolysis products and tillers (Inubushi et al. 2003), but the response of CH<sub>4</sub> oxidation in dryland cropping systems remains unclear. Application of N-fertilizer is a major contributor to greenhouse gas emissions. A recent review indicated that N stimulation of global N<sub>2</sub>O and CH<sub>4</sub> emission from multiple ecosystems, including croplands, could largely offset (53–76%) the reduction of CO<sub>2</sub> (via global terrestrial C sink) (Liu and Greaver 2009). However, the interaction between N addition and elevated [CO<sub>2</sub>] needs further research. The present study was conducted on a wheat field in northern China using Free-Air Carbon dioxide Enrichment (FACE) facility. The objectives are to investigate (i) the interactive effect between elevated [CO<sub>2</sub>] and fertilizer-N application on the fluxes of N<sub>2</sub>O, CO<sub>2</sub> and CH<sub>4</sub>; and (ii) the relation between these fluxes and soil moisture, organic C and mineral N contents.

#### Methods

Experimental site

The study site is located in an experimental farm in a soybean-wheat rotation on meadow cinnamon soil in Changping, Beijing, China (40°10'N, 116°14'E), with an average rainfall and temperature of 165 mm and 7.9°C during wheat growing season. The present experiment was conducted from early May to late June in 2008 (from booting to harvest of wheat crop).

## Carbon dioxide elevation

The elevation of  $[CO_2]$  was achieved from FACE system, consisting of 12 4 m diameter experimental areas, six elevated and six ambient. The two target  $CO_2$  concentrations were 420 (ambient) and 565  $\mu$ mol/mol (elevated). Carbon dioxide exposure commenced at sowing time and terminated at harvest time.

Wheat cultivation, fertilization and irrigation

Winter wheat (Triticum aestivum L. cv. Zhongmai 175) was sown on 10 October 2008 with a seeding rate of

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150 kg/ha. The experimental site was fertilized with granular urea before sowing and at jointing stage at a total rate of 50 and 190 kg N/ha to low-N (LN) and high-N (HN) plots, respectively. The immediate (1 h) and short-term (4 h) effects of irrigation on gas fluxes were tested by adding 1.5 L water (equivalent to 75 mm rainfall) to microplots in each treatment at 0900 h on 7 June. The granular urea dissolved in 0.5 L water was applied to HN microplots at 95 kg N/ha and same amount water without urea was applied to LN microplots on 10 June, and gas samples were collected one hour later.

## Gas sampling and flux determination

Gas samples for  $N_2O$ ,  $CO_2$  and  $CH_4$  analysis were taken from closed flux chamber (0.15 m height by 0.16 m diameter) on 5, 15 and 25 May and 4, 7 and 10 June between 1300 and 1500 h of the day, and one additional measurement was taken between 1000 and 1200 on 7 June one hour after irrigation. One chamber was inserted a day before the first measurement to a soil depth of 70 mm, and remained *in situ* throughout the experimental period. On each sampling day, the chamber was closed for 0.5 h prior to the first gas sampling. Three gas samples were then collected from the chambers at 10 minute intervals (chambers remained closed) using a gas tight syringe through a rubber bung. Gas of 30 mL was transferred into evacuated glass vials and transported to the laboratory within the same day for analysis by gas chromatography. Flux rates of  $N_2O$ ,  $CO_2$  and  $CH_4$  were calculated from the linear change in gas concentrations in the chamber.

## Soil analysis

Two auger samples (0-0.1 m) of top-soil from each microplot in each experimental ring were bulked. Subsamples (10 g) of the fresh soil were extracted with 2 M KCl in a 1:5 ratio of soil to extractant. The concentrations of ammonium  $(NH_4^+)$  and nitrate  $(NO_3^-)$  in the filtered extract were determined by continuous flow analysis (FOSS Fiastar 5000). Organic C was determined by Walkley-Black partial oxidation method.

## Statistical analysis

Data were analysed with MINITAB 14 statistical package using a factorial model analysis of variance with main effects as [CO<sub>2</sub>], N application and sampling time. Gas flux rates were regressed against soil properties.

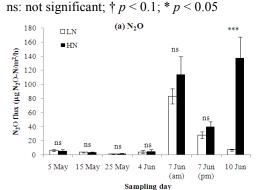
## **Results**

## N<sub>2</sub>O flux

Positive N<sub>2</sub>O fluxes were observed for all treatments over the experimental period. N<sub>2</sub>O emissions were 47% higher (p < 0.05) from elevated than from ambient [CO<sub>2</sub>] plots (Table 1), regardless of N application rate and sampling time. Interaction between N application rate and sampling time was significant (p < 0.001), with significantly higher (1812%) flux recorded from HN than LN plots after addition of dissolved urea in 0.5 L water on 10 June, but there were no significant differences at other sampling times (Figure 1a). The addition of 1.5 L water resulted in 37% and 43% increase, though not significant, in N<sub>2</sub>O flux from HN plots 1 h and 4 h after irrigation on 7 June (Figure 1a). N<sub>2</sub>O fluxes were positively correlated with CO<sub>2</sub> fluxes (r = 0.87, p < 0.001), soil moisture content (r = 0.65, p < 0.001) and organic C content (r = 0.36, p < 0.001).

Table 1. Effect of [CO<sub>2</sub>] on N<sub>2</sub>O, CO<sub>2</sub> and CH<sub>4</sub> fluxes (mean  $\pm$  SE, n = 42).

[CO <sub>2</sub> ] (µmol/mol)	N <sub>2</sub> O flux (μg N	$_{2}O-N/m^{2}$	$^{2}/h)$ CO <sub>2</sub> flux (mg	$g CO_2$ - $C/m^2/h)$	CH <sub>4</sub> flux (µg CH	$I_4$ -C/m <sup>2</sup> /h)
420	$25.6 \pm 5.7$	*	$39.7 \pm 4.4$	4.	$-5.5 \pm 1.0$	ng
565	$37.6 \pm 9.6$	·	$44.0 \pm 4.9$	Ť	$-4.6 \pm 0.8$	118



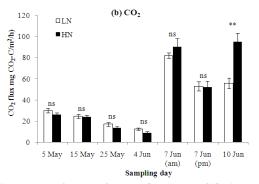


Figure 1. The effect of N addition and irrigation on the fluxes of (a)  $N_2O$  and (b)  $CO_2$  in LN and HN plots. Bars indicate standard errors. ns, no significant difference, \*\* p < 0.01, \*\*\* p < 0.001.

## CO2 flux

 $CO_2$  fluxes during the experimental period were always positive. Elevated [ $CO_2$ ] marginally increased (p = 0.063)  $CO_2$  emission by 11% (Table 1), regardless of N treatment and sampling time. Interaction between N application rate and sampling time was significant (p < 0.001), with 69% increase in  $CO_2$  emission from HN compared to LN plots on 10 June, but no significant differences were seen during other sampling times (Figure 1b), which was consistent with the aforesaid significant increase in  $CO_2$  flux.  $CO_2$  fluxes were positively correlated with soil moisture ( $CO_2$ ) and organic C contents ( $CO_2$ ) contents ( $CO_2$ ).

## CH<sub>4</sub> flux

Net CH<sub>4</sub> consumption was detected at all samplings, except on 10 June from HN plots with 1.65 and 0.12  $\mu$ g CH<sub>4</sub>-C/m<sup>2</sup>/h under ambient and elevated [CO<sub>2</sub>], respectively. [CO<sub>2</sub>] and N application rate had no significant effect on CH<sub>4</sub> fluxes throughout the course of the measurement period. CH<sub>4</sub> fluxes were positively correlated with organic C content (r = 0.32, p < 0.01).

## Soil moisture, mineral N and organic C

Gravimetric soil moisture content averaged 4–9% in the early stage of experimental period and increased (p < 0.001) to 15–18% after water addition on 7 and 10 June, but no significant effect of [CO<sub>2</sub>]. Elevated [CO<sub>2</sub>] increased organic C by 11% (p < 0.01) in HN plots, but not in LN counterparts. More NH<sub>4</sub>-N (27%, p < 0.05) and NO<sub>3</sub>-N (250%, p < 0.001) was detected from HN than LN plots, regardless of [CO<sub>2</sub>] and sampling time. Soil mineral N did not significantly affect the fluxes of the three gases.

### **Discussion**

Effect of  $[CO_2]$ , N addition and irrigation on soil  $N_2O$  emissions

Elevated [CO<sub>2</sub>] significantly increased N<sub>2</sub>O emissions by 47%. This is in agreement with a 40% increase in N<sub>2</sub>O emissions recorded in a mixed perennial ryegrass/white clover sward in a FACE experiment (Baggs et al. 2003), and a 30% (though not significant) increase in a glasshouse experiment growing timothy under elevated [CO<sub>2</sub>] (Kettunen et al. 2005). The increase was possibly due to a stimulation of root biomass and root exudation for denitrifiers (Arnone and Bohlen 1998; Kettunen et al. 2007), as suggested by the positive correlation between N<sub>2</sub>O and CO<sub>2</sub> fluxes, as well as the significant increase in organic C content under elevated [CO<sub>2</sub>] in HN plots. Nitrogen addition increased N<sub>2</sub>O flux throughout the experimental period, with significant increase after irrigation and additional N treatment, for both CO<sub>2</sub> concentrations. This is expected as nitrification is mainly stimulated by the NH<sub>4</sub>-N (Bouwman et al. 1993) while denitrification is enhanced by high soil moisture and NO<sub>3</sub>-N contents (Bolan et al. 2004). The interaction between elevated [CO<sub>2</sub>] and N application rate on N<sub>2</sub>O flux was not significant. This finding differs from Baggs et al. (2003) who showed a significant increase in N<sub>2</sub>O emissions only under 560, but not 140 kg N/ha/y. This implies at low N application rates, N supply might be a limiting factor for N<sub>2</sub>O emissions despite the greater C availability under elevated [CO<sub>2</sub>]. This is possible as N immobilization was observed as a result of enhanced root production and the higher C/N ratio of residue under elevated [CO<sub>2</sub>] (Hungate et al. 1997; Pleijel et al. 1998). In the present study, elevated [CO<sub>2</sub>] increased N<sub>2</sub>O emissions under both LN and HN plots, which suggests that N is not limiting. This highlights the importance of striking a balance between the increases in N<sub>2</sub>O emissions and the grain yield achieved by applying N-fertilizer.

## Effect of $[CO_2]$ , N addition and irrigation on soil $CO_2$ emissions

Elevated [CO<sub>2</sub>] marginally increased soil CO<sub>2</sub> efflux, which is consistent with results obtained from other FACE sites growing cotton (Wood *et al.* 1994), spring wheat (Prior *et al.* 1997), winter wheat (Kou *et al.* 2007) and soybean (Peralta and Wander 2008). The stimulation of efflux was associated with increased biomass under elevated [CO<sub>2</sub>] (Kimball *et al.* 2002). Increases in CO<sub>2</sub> emission were observed however only when both water and urea were simultaneously added, indicating they were important factors affecting the immediate response of soil microbes. In summary, the negative environmental impact of elevated CO<sub>2</sub> on greenhouse gas emissions from soil need to be balanced by reductions in CO<sub>2</sub> resulting from increased C capture in crop biomass.

## Effect of $[CO_2]$ and N addition on net $CH_4$ consumption

During most of the study period, there was a net oxidation in  $CH_4$ , which is common for agricultural soils in temperate and well-drained sites (Ineson *et al.* 1998). Net  $CH_4$  consumption was overall lower, albeit not significantly, under elevated than ambient [ $CO_2$ ] (Table 1). This is consistent with Ineson *et al.* (1998), who observed an average net  $CH_4$  consumption of 25.5 and 8.5  $\mu$ g/m²/h respectively for the control and enhanced

CO<sub>2</sub> plot of perennial ryegrass. Incubation of soils taken from forest also indicated a significantly lower net CH<sub>4</sub> consumption under elevated than ambient [CO<sub>2</sub>] (Philips *et al.* 2001; McLain and Ahmann 2008). These results indicate that less CH<sub>4</sub> being removed from the atmosphere under elevated [CO<sub>2</sub>], which is comparable to a higher CH<sub>4</sub> production under elevated [CO<sub>2</sub>] in wetland systems like rice paddies (Inubushi *et al.* 2003). Increases in CH<sub>4</sub> production (or reduction in CH<sub>4</sub> oxidation) under elevated [CO<sub>2</sub>] are associated with the stimulation of methanogenic activity (Wang and Adachi 1999), reduction of methanotropic activity (Philips *et al.* 2001) and/or increased moisture in deep (>25 cm) soils (McLain and Ahmann 2008). The effect of N addition was not significant in the present study, which agrees with Ineson *et al.* (1998). However, an interaction between [CO<sub>2</sub>] and N addition on CH<sub>4</sub> oxidation was observed by Baggs and Blum (2004).

#### **Conclusions**

Fluxes of  $N_2O$  and  $CO_2$  from the soil were positive while  $CH_4$  negative overall under elevated  $[CO_2]$ . Under elevated  $[CO_2]$ , the higher  $N_2O$  and  $CO_2$  emissions probably resulted from increases in substrate availability while net  $CH_4$  consumption was not changed. N addition generally increased  $N_2O$  and  $CO_2$  production, particularly when the soil was wet, but not  $CH_4$ . There was no interaction between elevated  $[CO_2]$  and N addition on the fluxes of these gases in the short-term from this wheat field. These findings have major implications on global climate change. In particular, there is a positive feedback relation between elevated  $[CO_2]$  and the concentrations of these gases. Although N application generally boosts crop yield, in terms net greenhouse gas production, excessive N application will offset only part of the extra C sequestered, and should be avoided from both environmental and financial grounds.

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# Soil inorganic carbon pool changed in long-term fertilization experiments in north China plain

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#### **Abstract**

While soil organic carbon (SOC) concerned soil component in most research on the global carbon cycle, soil inorganic carbon (SIC) was given less attention. New evidence shows there was significant change in SIC in around 30 years, especially in the systems with intensive human being activities. The present work focused on the change of total amount, active form proportion, and soil profile distribution of SIC in different fertilization systems of 4 long-term experiments in the North China Plain (NCP). The change in percentage of secondary carbonate of SIC was estimated with  $\delta^{13}$ C values of SOC and soil carbonate. Results showed that the fertilization system had a great impact on the size of SIC pool, profile distribution, and the proportion of active and secondary carbonate of SIC. The result indicated that the SIC pool would change in 20-30 year farming system and  $CO_2$  from SOC decomposition was involved in the transformation process of soil carbonate in the NCP. Both pool balance and transformation processes of SIC should be considered as a component of C cycling in the soil-plant system in semi- and/or arid zone areas like the NCP.

#### **Key Words**

Inorganic carbon, balance, active form, secondary carbonate, north China plain.

#### Introduction

Soil organic carbon (SOC) is a hot topic in global carbon cycling researc while soil inorganic carbon (SIC) is a relatively cool one. But in arid and semi-arid region, SIC is the most important C form in soils (Eswaran et al. 2000). Recently, several researchers had shown that long term (about 30 years) effects of land use and agronomic activities on SIC balance and transformation could be demonstrated by conventional methods (Silva and Alexandre 2004; Reeder et al. 2004; Mikhailova and Post 2006). In North China Plain (NCP), agricultural practices changed a lot during the last 30 years. Manure application to arable soil, which was a traditional way to sustain soil fertility in China, stopped totally around 1980s in NCP, while more and more chemical N and P fertilizers were used instead. Irrigation area had increased more than 2 times since 1980s and irrigation pattern changed a lot after 2000. In suburban areas, horticulture was becoming the predominant form of land use, with an extra huge amount of fertilizers (up to 1000 N kg/ha) and irrigation applied. Greenhouse production systems became more popular, which changed soil fertility in a significant way. All these activities had great possibility to impact on SIC. The present work focused on the change in pool size, active form, profile distribution, and secondary carbonate ratio of SIC for different fertilization systems from 4 long-term fertilization experiments in NCP. The aim of the work was to evaluate soil total C pool to give a more correct assessment of the effects of human being activities on the soil carbon pool, which would give a clear answer to the question of whether soil is a C sink or source to atmospheric CO<sub>2</sub>.

## Methods

Study sites location

Four long-term fertilization experiments with 47 treatments in total within NCP were chosen to do the research. The experimental periods of the 4 experiments were 22 to 27 years. They were all winter wheat and summer maize cropping system, the most common system in NCP. The average temperature was around 13 °C and rainfall around 550 mm. All soils were long-term cultivated arable soil for a long time, except for Quzhou, which was converted from salty soil 30 years ago. The altitude of the 4 sites was 4 to 43 m above sea level, and groundwater table was about 1 to 3 m. Flood irrigation was about 300 mm every year. Mean yield of winter wheat and summer maize was about 6.0 and 5.7 t/ha, respectively.

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Table 1. Basic information of the 4 long-term experiments selected in NCP.

Site	Changping	Tianjin	Hengshui	Quzhou
Experimental span (a)	25	23	27	22
Location	N: 40°02′	N: 39°10′	N: 37°42′	N: 36°52′
Location	E: 116°10′	E: 117°06′	E: 115°42′	E: 115°01′
Relief	Plain	Sea shore plain	Low plain	Plain before mountain
Climate	monsoon	monsoon	monsoon	monsoon
Soil type	alluvial soil	alluvial soil	alluvial soil	Once salt-affected soil
Soil texture	loam	loam	sandy loam	sandy loam
ET <sub>0</sub> by FAO (mm)	2002	1684	1935	1841
Mean sunshine hours	2684	2468	2617	2593
accumulated T (>0°C)	4606	4722	4904	4982
frostless season (d)	195	198	190	201

### Sampling and measurements

Samples were taken in 2006 and 2007. Three to 6 samples were taken with soil drill from each plot deep to 180 cm at 20 cm interval. After air drying, samples were passed through 0.5mm sieve.

Soil organic carbon (SOC) was measured with a traditional method. Total carbonate content was measured by  $CO_2$  volume after HCl addition to samples in air-tight system. Active carbonate was measured by the method of Loeppert and Suarez (1994).  $\delta^{13}$ C of SOC and soil carbonate was measured by MAT-253.

## Data statistics

The treatment effects were assessed with the Analysis of Variance (ANOVA) using SPSS. Treatments were compared using two statistical tests (LSD and Tukey HSD tests).

#### Results

## SOC and STC pool

The change tendency of SOC and STC (SOC+SIC) among the 47 treatments of 4 long-term experiment sites was not the same, especially for the treatments with addition of organic matter or straw (Fig 1). This discord indicated that SIC pool size was changeds in the opposite direction of SOC. The result gave us evidence to consider STC, but not SOC alone, as soil C pool concerning soil carbon balance in arable soil-cropping system in semi- and/or arid zone.

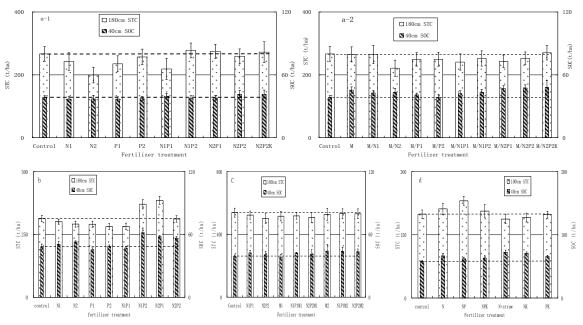


Figure 1. SOC and STC pool of different fertilization treatments in 4 long-term experiments in NCP. a-1 and a-2 was treatments of fertilizer only and manure+ fertilizer in Changping, respectively. b, c, and d was treatments in Quzhou, Hengshui, and Tianjin, respectively.

### Soil profile distribution of SIC

Not only the SIC pool size changed, the distribution of SIC along soil profile was also changed. In general, more carbonate moved down to deeper layers (120-160cm in most cases, or 40-80cm in Tianjin), comparing

to CK treatment at each site (Fig 2). With organic manure or straw addition, SIC in top soil was significantly reduced, indicating a negative influence of SOC happened to SIC. The deeper movement of SIC may became more difficult to convert to be  $CO_2$ , but be easily to move into groundwater.

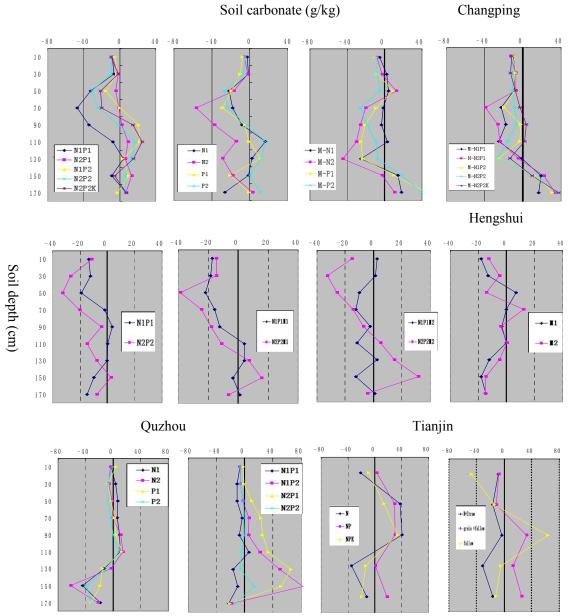


Figure 2. Soil profile distribution of SIC of different treatments in 4 long-term experiment sites in NCP.

## Proportion of Active and secondary carbonate

The proportion of active carbonate (AC) changed among treatments in 4 experiment sites (Table2), especially in plots of Changping. This change indicated that carbonate stability was influenced by fertilization and would have great impact on SIC pool size in the future. In view of long term, the stability of SIC in soils of semi-arid and arid zone was important issue concerning global C balance, especially in arable soils where intensive disturbance was put by human being. Secondary carbonate (SC) formed in soil profile with CO<sub>2</sub> mostly provided from SOC decomposition. More SC mean more CO<sub>2</sub> from SOC decomposition was converted to carbonate without emitting out to atmosphere. In 0-20cm, fertilizer and manure generally reduced the SC proportion, especially in Changping and Quzhou. However, in 60-100cm, SC proportion generally increased in fertilizer and manure plots. This result indicated that the amount of CO<sub>2</sub> from SOC decomposition precipitated into carbonate in soil would depend on the mode of fertilization and organic matter addition. Detailed research was needed to quantify these processes.

Table 2. Proportion of active and secondary carbonate in selected treatments of 4 sites (%)

Site	Treatment			Soil lay	er (cm)		
		0-	20	60-	-80	140-	160*
		AC	SC	AC	SC	AC	SC
Fertilizer plot	CK	47	100	45	89	36	78
Changping	N2	55		87		56	
	N2P2	65	88	32	95	42	70
Fertilizer/manure plot	CK-M	53	100	34	100	40	75
Changping	N2-M	62		34		39	
	N2P2-M	69	95	63	100	50	73
Quzhou	CK	31	77	20	56	35	45
	N2	29	70	31	84	55	76
	N2P2	33	64	33	70	44	64
Tianjin	CK	60	78	82	74	66	69
-	N	54	79	100	73	71	68
	NPK	48	77	73	68	95	62
	N-S	49	62	100	79	86	57
Hengshui	CK	41	80	68	94	69	89
•	N1P1	41		66		72	
	N2P2	41	79	73	95	70	88
	N2P2-M	38	92	69	92	65	89

<sup>\*</sup> For SC, AC and SC in Tianjin, the depth was 80-100cm.

#### Conclusion

It was important to include SIC pool balance in the accurate evaluation of the impact of fertilization on the balance of soil carbon pool in arid and semi-arid region. The negative relationship between SIC and SOC, though not significant in some cases among the 4 experiment sites, showed that SOC could accelerate the losing of surface SIC. In this context, the present results had great significance in proper evaluation of the effect of fertilization on soil carbon balance. Moreover, the process and scale of soil CO<sub>2</sub> from SOC decomposition converting into carbonate in soil was also an important potential reduce CO<sub>2</sub> emission in arable soils.

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## Soil N<sub>2</sub>O fluxes are low from a grain-legume crop grown in a semi-arid climate

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#### **Abstract**

Understanding nitrous oxide (N<sub>2</sub>O) fluxes from grain-legume crops in semi-arid and arid regions is necessary if we are to improve our knowledge of global terrestrial N<sub>2</sub>O losses resulting from biological N fixation. Nitrous oxide fluxes were measured from a rain-fed soil, cropped to grain-legume in a semi-arid region of south-western Australia for one year on a sub-daily basis. The site included plots planted to narrow-leafed lupin (*Lupinus angustifolius*; 'lupin') and plots left bare ('no lupin'), with no N fertiliser applied to treatments. Fluxes were measured using soil chambers connected to a fully automated system that measured N<sub>2</sub>O using gas chromatography. Daily N<sub>2</sub>O fluxes were low (-0.5–24 g N<sub>2</sub>O-N/ha day<sup>-1</sup>), not different between treatments, and culminated in an annual loss of 118 g N<sub>2</sub>O-N/ha. Greatest daily N<sub>2</sub>O fluxes occurred during the post-harvest period, and following a series of summer rainfall events. At this time of the year soil conditions were conducive to soil microbial N<sub>2</sub>O production: elevated soil water content, available N, and warm soil temperatures (>25 °C). To the best of our knowledge, this is the first paper to report annual N<sub>2</sub>O emissions from a rain-fed, grain legume crop in a Mediterranean-like semi-arid region.

## **Key Words**

Greenhouse gas, nitrogen fixation, agriculture, soil nitrogen, plant residue.

#### Introduction

Legume crops contribute valuable nitrogen (N) inputs to farming systems throughout the world. Conservative estimates suggest cultivated crop and pasture legumes provide 33 to 55 Mt N to agriculture on a global basis, despite the progressive replacement of legume rotations with synthetic N fertilisers over the past four decades (Crews and Peoples 2004; Smil 2001). Nitrogen fixed by legumes contributes to human food production, via fresh pods and dry grains, or as a feedstock and pasture for animals. Non-N fixing crops have been shown to benefit from legume crops through a variety of mechanisms including soil N inputs, disease breaks and improved soil fertility (Peoples *et al.* 2008). However, N fixation by cultivated legumes is also considered to enhance anthropogenic N<sub>2</sub>O emissions (Stehfest and Bouwman 2006).

Nitrous oxide fluxes from legume crops is mainly derived from decomposition of the above- and below-ground legume residues, with losses from the biological N-fixation process *per se* considered to be negligible (Rochette and Janzen 2005). Nitrogen released from legume residues is at risk of being emitted as  $N_2O$  via a number of soil biological processes including nitrification, denitrification and nitrifier denitrification (Wrage *et al.* 2005). These soil biological processes, and the emission of  $N_2O$ , are greatly enhanced by increased N availability. Although estimated  $N_2O$  emissions appear low into relation to legume residue inputs (1.25% of N fixed) (IPCC 2006), the high global warming potential of  $N_2O$  (298 times greater than  $CO_2$ ) means accurate estimates are required when assessing net greenhouse gas fluxes from legume based systems.

Legumes systems are estimated to emit  $0.4 \text{ Mt N}_2\text{O-N}$  annually, around 10% of total anthropogenic  $N_2\text{O}$  emissions, however this value is largely estimated from studies conducted in temperate agricultural systems (Stehfest and Bouwman 2006). Legume crops are widely grown in semi-arid and arid regions, which constitute one third of the global land area (Harrison and Pearce 2000). Yet,  $N_2\text{O}$  fluxes from legume crops grown in the absence of synthetic N or organic N inputs does not appear to have reported for these regions (Rochette and Janzen 2005; Stehfest and Bouwman 2006). Our understanding of global  $N_2\text{O}$  fluxes from legume crops would be improved by investigated losses from semi-arid and arid agricultural systems.

The south-western Australian grain belt includes 18 million ha of semi-arid land, and is responsible for 40% of Australia's annual grain production. The region has a strong seasonality characterised by cool, wet winters and hot, dry summers. The aim of the following study was to acquire a unique, one year data set of continuous sub-daily  $N_2O$  fluxes from a rain-fed, grain-legume (lupin) crop grown in a semi-arid region, and at the same time investigates the relationship between  $N_2O$  fluxes and other soil/environmental parameters.

#### Materials and methods

Soil and site

Nitrous oxide fluxes were measured on the Cunderdin Agricultural College (31°36′ S, 117°13′ E), in the central wheat belt of Western Australia, approximately 156 km east of Perth. Cunderdin has an annual rainfall of 365 mm, which mainly falls during the winter months (June–August), a mean daily maximum temperature of 25.1 °C and a mean daily minimum temperature of 11.4 °C. The experimental site was located on flat to gently undulating land, and consisted of a free-draining sand overlying a poorly draining clay (Natric Haploxeralf and Typic Natrixeralf; USDA, 1992). The surface soil (0–120 mm) had a pH of 6.0 (1:5 soil : 0.01 M CaCl<sub>2</sub> extract), electrical conductivity (EC) of 170 µS cm<sup>-1</sup> (1:5 soil : water extract), cation exchange capacity of 3.3 cmol/kg, C concentration of 9.38 mg/g, N concentration of 0.76 mg/g and bulk density of 1.4 g cm<sup>-3</sup>. The surface soil contained 93% sand, 4% silt, and 3% clay. For site history details see Barton *et al.* (2008).

## Experimental design and approach

Plots (105 m² per plot) were planted to narrow-leafed lupin (*Lupinus angustifolius* cv Mandelup) on the 14<sup>th</sup> May 2008, with no prior cultivation. A completely randomised design with two treatments, and three replicates, was employed. Plots were either planted with inoculated and fumigated narrow-lupin seed 'lupin') or remained unplanted ('no lupin'). The lupin plots were topdressed with 100 kg/ha of K₂SO₄, and direct-drilled (to 30 mm) with 100 kg/ha of 'Superphosphate CuZnMo'® at planting; no N fertiliser was applied to either treatment. An area (6.76 m²) within each plot was designated for measuring N₂O fluxes, while the remainder of the plot was used for soil sampling. Four weeks after seeding, plant numbers in the chamber base areas were adjusted, by either removing or adding seedlings, to reflect the average plant density in the field (32 plants m⁻²). Lupin was harvested from the chambers on the 5<sup>th</sup> November 2008 and the stubble was retained for the remainder of the study.

#### Nitrous oxide, soil and climatic measurements

Nitrous oxide fluxes were measured for approximately one year (14<sup>th</sup> May 2008–28<sup>th</sup> April 2009) using soil chambers (one per plot) connected to a fully automated system. The system included a gas chromatograph fitted with a <sup>63</sup>Ni electron capture detector for N<sub>2</sub>O analysis, an automated sampling unit for collecting and distributing gas samples, and six chambers (one per treatment plot). Chambers (500 mm x 500 mm) were placed on metal bases inserted into the ground (100 mm), and fitted with a top that could be automatically opened and closed. Four bases were located in each treatment plot to enable the chambers to be moved to a new position every week so as to minimise the effect of chambers on soil properties and plant growth. The height of the chambers was progressively increased to accommodate crop growth, with a maximum height of 650 mm, and opened if the air temperature in the chamber exceeded a set value (43 °C when lupin was growing in the chamber, 60 °C at other times) or if it rained (> 0.4 mm in five minutes). For further details of automatic gas sampling system see Barton *et al.* (2008).

Soil mineral N, water-filled pore space (WFPS) and climatic variables were measured to explain seasonal variations in  $N_2O$  fluxes. The mineral N of the surface soil (0–50 mm) was measured at least every two weeks. Mineral N was extracted from soil samples by adding 80 ml of 1 M KCl to 20 g of field-moist soil (sieved < 4 mm) and shaking for 1 h. The filtered solution (Adventec 5C) was frozen until analysed for  $NO_3$  and  $NH_4^+$  colorimetrically using a modified hydrazine reduction method (Downes 1978). Gravimetric soil water content was determined at the same time soil samples were collected for mineral N, and after drying sub samples at 105 °C for at least 24 h. Water-filled pore space was calculated by dividing volumetric water content by total porosity (Linn and Doran 1984). All climatic and soil temperature data from the weather station were collected and stored automatically by the weather station.

## Data analyses

A general linear model (using completely randomised design) in Genstat (2007) was used to determine if annual  $N_2O$  fluxes varied between the lupin treatments. Post-hoc pair-wise comparisons of means were made using LSD (significance level of 5%). Hourly  $N_2O$  ( $\mu g N_2O-N m^{-2}/h$ ) fluxes were calculated from the slope of the linear increase in  $N_2O$  concentration during the chamber lid closure period, and corrected for chamber air temperature, air pressure and the ratio of cover volume to surface area (Barton *et al.* 2008). Daily losses for each plot were calculated by averaging hourly losses for that day. Annual fluxes for each plot were calculated by integrating hourly losses with time.

#### Results

#### Environmental conditions

A total of 299 mm fell at the site during the study period (14<sup>th</sup> May 2008–28<sup>th</sup> April 2009), of which 206 mm fell during the period between planting and harvesting the lupin (Figure 1). The 2008 annual rainfall (304 mm) was 83% of the 30-year average (1971–2000), while rainfall during the growing season (May 2007–Oct. 2007) was 82% of the 30-year average. Mean minimum daily air temperature was 9.5 °C and mean maximum daily air temperature was 25.8 °C. The lowest hourly air temperature (-1.4 °C) was recorded in June 2008, while the greatest maximum hourly temperature (45 °C) was recorded in January 2009. Average daily soil temperatures in the surface 100 mm ranged from 9 to 37 °C. Temperatures were lowest during July 2008 (mid-winter) and greatest in January 2009 (mid-summer).

## Mineral N and WFPS

The amount of mineral N ( $NO_3^-$  and  $NH_4^+$ ) in the surface soil (0–50 mm) varied during the year, and in a similar way for both treatments (Figure 1). Soil mineral N were greatest for the first two months following planting (May–July 2008), and then again in following successive summer rainfall events following harvest (November 2008 – April 2009; Figure 1). In winter (July), the amount of mineral N in both lupin treatments declined to < 5 kg N/ha (Figure 1). A large proportion of mineral N in the surface soil was in the  $NO_3^-$  form, rather than  $NH_4^+$ . For example, soil  $NO_3^-$  in both treatment ranged from <1 to 48 kg N/ha, while the soil  $NH_4^+$  ranged from <1 to 8 kg N/ha (data not shown). Soil WFPS varied seasonally in response to rainfall, and varied from <2 to 39% (data not shown).

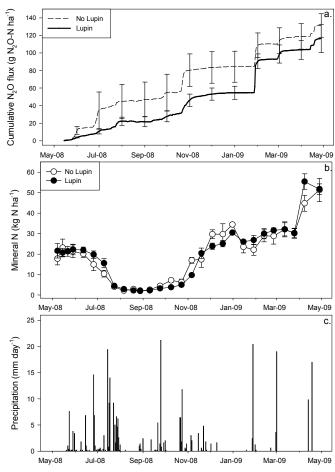


Figure 1. Cumulative daily  $N_2O$  fluxes (a), soil mineral N contents (b), and daily precipitation with time at a cropped site at Cunderdin, Australia ( $14^{th}$  May 2008– $28^{th}$  April 2009). Values in plots (a) and (b) represent means ( $\pm$  standard errors) of three replicates. Standard errors only shown monthly for plot (a) for clarity.

#### N<sub>2</sub>O fluxes

Daily  $N_2O$  fluxes ranged from -0.5 (October 2008) to 24 g  $N_2O$ -N/ha day<sup>-1</sup> (January 2009) in the lupin treatment, and -0.7 (August 2008) to 10 g  $N_2O$ -N/ha day<sup>-1</sup> (January 2009) in the no lupin treatment (Figure 1). Daily  $N_2O$  fluxes from the lupin treatment were greatest during summer and autumn following rainfall

events  $\geq 5$  mm day<sup>-1</sup>. Fluxes from the no lupin treatment also increased following summer and autumn rainfall, but similarly high fluxes were also reported from the no lupin treatment in response to rain ( $\geq 5$  mm day<sup>-1</sup>) in July and October. Hourly N<sub>2</sub>O fluxes following summer and autumn rainfall events tended to peak on the day of rain, or the day following; with greater losses from the lupin treatment than the no lupin treatment. For example on the 29 January 2009, mean hourly N<sub>2</sub>O fluxes following summer and autumn rainfall were as high as 164 µg N<sub>2</sub>O-N m<sup>-2</sup> hr<sup>-1</sup> (standard error, 8 µg N<sub>2</sub>O-N m<sup>-2</sup> hr<sup>-1</sup>) for the lupin treatment and 95 µg N<sub>2</sub>O-N m<sup>-2</sup> hr<sup>-1</sup> (standard error, 27 µg N<sub>2</sub>O-N m<sup>-2</sup> hr<sup>-1</sup>) for the no lupin treatment. Greatest hourly N<sub>2</sub>O fluxes following summer rainfall occurred after the first rainfall event, and was not exceeded by subsequent rainfall of similar magnitude. The total amount of N emitted as N<sub>2</sub>O after almost one year (351 days) did not differ between the lupin and no lupin treatment, with an average of 118 g N<sub>2</sub>O-N/ha (P<0.05) (Figure 1). For the lupin treatment, a large proportion (58%; 68 g N<sub>2</sub>O-N/ha) of the emissions occurred post-harvest, whereas for the no lupin treatment only 33% (44 g N<sub>2</sub>O-N/ha) of the annual loss occurred post-harvest. However, post-harvest cumulative N<sub>2</sub>O losses did not vary between treatments (P<0.05).

#### **Conclusions**

This study is the first to report daily  $N_2O$  fluxes from a rain-fed, legume crop grown in a semi-arid region without N fertiliser, and in the absence of grazing animals. Daily  $N_2O$  fluxes were low (-0.5–24 g  $N_2O$ -N/ha day<sup>-1</sup>), not different between the legume cropped or bare soil, and culminated in an annual loss of 118 g  $N_2O$ -N/ha. Greatest daily  $N_2O$  fluxes occurred when the soil was fallow, and following a series of summer rainfall events. The contribution of the biological N fixation process to  $N_2O$  emissions appeared negligible, while  $N_2O$  emissions from the decomposition of legume crop residue following harvest were also low.

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# Soil nitrous oxide emissions under dryland N-fertilised canola and $N_2$ -fixing chickpea in the northern grains region, Australia

Graeme Schwenke<sup>A</sup>, Bruce Haigh<sup>A</sup>, Guy McMullen<sup>A</sup>, and David Herridge<sup>B</sup>

#### Abstract

Nitrous oxide ( $N_2O$ ) emissions from cropping soils contribute to increasing atmospheric  $N_2O$ . Planning to reduce emissions requires real-world measurements. Crop production systems that partially rely on nitrogen (N) fixed by legumes may emit less  $N_2O$  than systems that are totally dependent on fertiliser N inputs. We measured  $N_2O$  emissions from a dryland vertosol in northwest NSW, Australia during the growth of N-fertilised canola (*Brassica napus*) and  $N_2$ -fixing chickpea (*Cicer arietinum*). At sowing, canola received 80 kg N/ha as urea, and chickpea was inoculated with effective rhizobia. Emissions of  $N_2O$  were monitored seven times per day using an automated system of chambers connected to a gas chromatograph. Daily  $N_2O$  emissions ranged from -1.7 to 39.6 g  $N_2O$ -N/ha/day in canola plots and -1.6 to 12.5 g  $N_2O$ -N/ha/day for chickpea. During crop growth, the N-fertilised canola plots emitted a total of 293 g  $N_2O$ -N/ha, equivalent to 0.37% of the urea N applied. Chickpea plots emitted 29 g  $N_2O$ -N/ha. The canola plots emitted a further 241 g  $N_2O$ -N/ha in the first months of the post-crop fallow, mostly during a short period of high rainfall, compared with 58 g  $N_2O$ -N/ha for chickpea. We hypothesise that the canola residue may have mineralised N earlier than chickpeas.

## **Key Words**

Nitrous oxide, nitrogen, urea, canola, chickpea.

#### Introduction

Cropping soils are an important anthropogenic source of nitrous oxide  $(N_2O)$ , a greenhouse gas with 298 times the global warming potential of carbon dioxide. The soil-emitted  $N_2O$  originates from the processes of nitrification (oxidation of ammonium to nitrite then nitrate) and denitrification (reduction of nitrate or nitrite to  $N_2O$  and  $N_2$ ). As both processes are biologically driven, soil moisture and aeration are key factors in emissions, along with availability of inorganic nitrogen (N) and organic carbon (C) substrate. In the north-eastern Australian dryland cropping region, inorganic N requirements of cereal crops are mainly supplied by inorganic fertilisers and soil organic matter mineralisation, with low reliance on  $N_2$ -fixing legume crops or pastures.

Partial substitution of fertiliser N inputs with biologically-fixed legume N should reduce N<sub>2</sub>O emissions through (a) reduced reliance on fertiliser N, whose manufacture alone produces 1.5-2.2 kg CO<sub>2</sub>-equivalent emissions for every kg N fertiliser produced (Wood and Cowie 2004), and (b) reduced availability of soil mineral N for loss through moderated release during crop residue decomposition. N<sub>2</sub>O emissions factors for non-irrigated cropping in Australia have been reduced from the IPCC default of 1.25% of fertiliser N applied down to 0.3%, but the lack of local data for emissions from legume-derived N has meant that 1.25% still applies (DCC 2009). Elsewhere, Rochette and Janzen (2005) reviewed published data on N<sub>2</sub>O emissions from a range of legume crops; with averages of 1.0 kg N/ha for annual crops, 1.8 kg N/ha for pure forage crops and 0.4 kg N/ha for grass legume mixes. These averages were only slightly above background soil emissions. Detailed phenological studies with soybean demonstrate that N<sub>2</sub>O emissions associated with a legume crop are insubstantial until the plant has matured and senesced plant parts begin to decompose (Ciampitti et al. 2008). Therefore, it is not the growth of the legume plant and its biological fixation of N from the air, per se, that is responsible for N<sub>2</sub>O emissions, but rather it is the release of mineral N into the soil from decomposing leguminous residues, including roots and nodules. Dalal et al. (2003) stated that the extent of N<sub>2</sub>O emissions during and following a pulse crop in the Australian cereal-growing region was unknown. There has been little published work in Australia since this document, so the situation remains unchanged. As a result, the comparison of soil N<sub>2</sub>O emissions from fertiliser N and legume-derived N in crop production systems is the focus of our research on a vertosol (cracking clay) soil near Tamworth in the northern grains region of north-eastern Australia.

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#### Methods

Field trial

The experiment was located on a black vertosol at the Tamworth Agricultural Institute, near Tamworth, NSW, Australia. This alkaline, cracking medium clay soil is typical of the majority of the soil used for dryland cropping in the northern grains region of eastern Australia. The crop rotation trial was established in standing wheat stubble in June 2009, and was designed as a three year experiment using a randomized complete block design consisting 6 treatments and 4 replicates. Plots were 12 m length and 6 m width. Rainfall at the site was measured using a rain gauge equipped with tipping bucket and data logger.

Canola (*Brassica napus*) and chickpea (*Cicer arietenum*) were sown in 50 cm rows with a zero-tillage planter on the 19<sup>th</sup> June 2009. Urea (80 kg N/ha) was banded at sowing, just below the soil surface mid-row between every alternative canola row. Canola was harvested by small plot header on the 23<sup>rd</sup> November, and chickpea on the 26<sup>th</sup> November. All crop residues from each plot were returned to and spread across the surface of those plots. Aboveground residues from plants grown within the measurement chambers were returned to the chambers after the grain was removed and held in place by netting during the fallow. There was no cultivation of the plots. Weeds were controlled with herbicides and hand-weeding.

#### Nitrous oxide measurements

We used an automated greenhouse gas measuring system (Breuer *et al.* 2000) to measure N<sub>2</sub>O emissions from 3 replicates of 2 treatments (N-fertilised canola and unfertilised chickpea) within the rotation trial. The system consisted of one 50 cm x 50 cm polycarbonate chamber located on each plot, clamped to a stainless steel base inserted 10 cm into the soil. Three bases were located in each treatment plot and chambers moved to a new position periodically to minimise any negative effects on soil properties or plant growth. We increased the height of the chamber using extensions to match the crop's height during the growing season. For chickpea, the chambers were placed from mid-row to mid-row, while for canola, the chambers were placed to cover both the plant row and the mid-row urea fertiliser band. In every 192 minute cycle, the lids of all chambers shut for the first 90 minutes, then re-opened for the remaining 102 minutes. During the 90 minute closed chamber period, the air in each chamber was sampled sequentially four times and N<sub>2</sub>O measured using a gas chromatograph equipped with an electron capture detector. N<sub>2</sub>O emissions were calculated from the slope of the linear increase in N<sub>2</sub>O concentration during the closed chamber period, then corrected for chamber air temperature, air pressure and chamber volume.

#### Results

Figure 1 depicts the daily emission of  $N_2O$  from soil under N-fertilised canola and unfertilised chickpea through the period of crop growth from mid June till harvest in late November 2009, then two months into the summer fallow period until late January 2010. Daily  $N_2O$  emissions ranged from -1.7 to 39.6 g  $N_2O$ -N/ha/day in the canola plots and -1.6 to 12.5 g  $N_2O$ -N/ha/day for chickpea. The higher results were recorded for both crops during a week of rainfall from 26<sup>th</sup> December 2009 that totalled 134 mm. Most daily emissions however were low, with the canola soil emitted more than the chickpea soil, which was often below detection. Both the range in our results and the low averages were of the same order as other soil  $N_2O$  emissions measured under dryland wheat crops (Barker-Reid *et al.* 2005, Galbally *et al.* 2005, Barton *et al.* 2008, Officer *et al.* 2008).

In the 157 days from sowing until harvest, soil under N-fertilised canola emitted a total of 293 g N<sub>2</sub>O-N/ha. Much of this occurred in the first two months after N application in conjunction with rainfall events that would have stimulated soil nitrification after the urea had hydrolysed to ammonium. Emissions from canola plots equated to 0.37% of the N applied as urea at sowing, although we did not correct for background, i.e. nil fertiliser N. Over the same period the soil under chickpeas emitted only 28.5 g N<sub>2</sub>O-N/ha. If we consider this as the background N<sub>2</sub>O emission then the emission factor for N fertiliser under canola during crop growth was 0.33% of that applied. This is close to the Australian emission factor used for accounting emissions from non-irrigated crops (DCC 2009), and therefore of similar magnitude to previous research done on soil under cereals (Barker-Reid *et al.* 2005, Galbally *et al.* 2005). Rainfall during the cropping period totalled 179 mm, which is approximately half the longterm average at Tamworth. Despite this, crop growth was reasonable with canola yielding 1.7 t grain/ha and chickpea 1.3 t grain/ha, although chickpea yields were substantially depressed by insect damage at grain-filling.

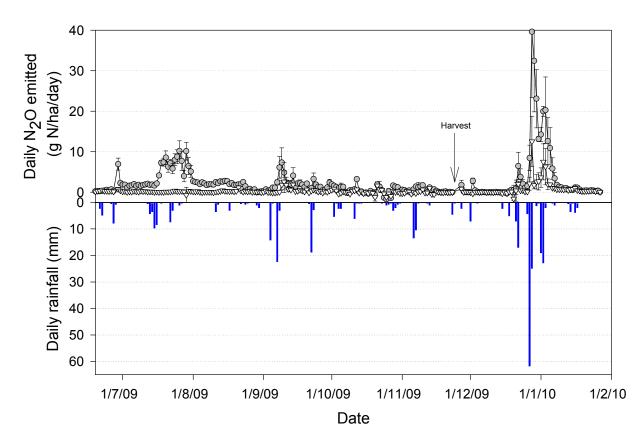


Figure 1. Daily emission of nitrous oxide emissions from soil under canola (circles) and chickpea (triangles) as influenced by date since urea fertiliser application (canola only) and daily rainfall (bottom graph). Data points are means of three replicates with standard errors of the means shown.

We expected that the  $N_2O$  emissions from the soil after canola would be minimal as the plant growth should have depleted the available soil N, but during the first two months of the summer fallow period, a further 241 g  $N_2O$ -N/ha was emitted from the soil after canola and another 57.6 g  $N_2O$ -N/ha were emitted from the soil after chickpea. Most of the fallow emissions occurred during a week of continued rainfall at the end of 2009. This is in concert with Barker-Reid *et al.* (2005) who found rainfall and mineral nitrogen status to be the main influence on  $N_2O$  fluxes, especially in conjunction with rainfall after extended hot, dry periods. Unprocessed data on crop residue N and soil mineral N concentrations post-harvest should shed further light on the suitability of conditions for denitrification, an uncommon event in dryland cropping for this region.

## Conclusion

Soil emissions of  $N_2O$  during a dryland canola crop were of similar magnitude to those observed from soils growing wheat in other Australian cropping regions, and also with some N-rates on cotton grown in the same region (Galbally *et al.* 2005). Emissions coincided with significant rainfall events, particularly soon after N fertiliser application (before significant plant uptake) and also post-harvest, when presumably the decomposing canola residues had released inorganic N in the surface soil. Pending analyses of soil and crop residues should confirm this. Emissions of  $N_2O$  from soil during chickpea growth were practically undetectable for most of the growing season, as found by researchers in the northern hemisphere (Rochette and Janzen 2005). Post-harvest decomposition would have released some of the biologically-fixed N from the crop residues, but this may not have led to as much available N as in the soil after canola. Continued monitoring during the summer fallow and into the following winter cereal crop will establish whether the total subsequent  $N_2O$  emissions from the chickpea residues are still less than that from N-fertilised canola.

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# Soil nitrous oxide fluxes following cover crops management under tillage and no tillage in South Brazil

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#### Abstract

Emissions of  $N_2O$  were measured following cover crops management (oat - O and vetch - V) under tillage (CT) and no tillage (NT) in a silt loam Acrisol in South Brazil. Effects of tillage systems and residue management on  $N_2O$  emissions were examined over 55 days in 2007 and 54 days in 2008. Larger emissions were measured in 2008 compared to 2007.  $N_2O$  emissions increased in the presence of crops residues and were further increased in NT V/M in 2007 (193±84  $\mu g$  N/m²/ha) and in CT V/M in 2008 (431±138  $\mu g$  N/m²/ha) and they are related to high water content and available soil nitrogen. Smallest fluxes of  $N_2O$  were measured from the NT O/M treatments, which 288±61  $\mu g$  N/m²/ha in 2007 and 274±19  $\mu g$  N/m²/ha in 2008.

## **Key Words**

Global warming, soil nitrogen, residue quality, rainfall, denitrification.

#### Introduction

Emissions of  $N_2O$  are of concern because of the role of this gas in the greenhouse effect and the destruction of the ozone layer (IPCC 2007). Direct and indirect emissions from agricultural systems are now thought to contribute 6.2 Tg  $N_2O$ -N/y to a total global source strength of 17.7 Tg  $N_2O$ -N/y. In Brazil the inventories of greenhouse gases indicated that agriculture is a principal source of  $N_2O$  (MCT 2006). Emissions this gas from agriculture are related to soil processes in that  $N_2O$  emission is increased by application of inorganic fertilizer, incorporation of crop residues and animal waste. Residue composition and the quantity of biomass incorporated influence the  $N_2O$  emission at different levels for no tillage and conventional tillage (Baggs *et al.* 2003). Tillage systems, such as no till and conventional, directly determine the proximity of residues and the relative spatial concentrations of  $N_2O$ .

#### Methods

Experimental area and treatments

The study was carried out in subtropical conditions of Southern Brazil. The experimental area is located at the 30° 50′ 52′′ S, 51° 38′ 08′′ W. The local climate is Cfa second Köpen classification, with an annual average temperature of 19.4 °C and precipitation of 1440 mm (Bergamaschi *et al.* 2003). Soil N<sub>2</sub>O emissions and soil and meteorological variables were measured frequently after application of cover crops residues in spring. In an Acrisol, we assessed the long-term effect (22 years) of soil tillage systems [no-tillage (NT) and conventional tillage (CT)] and cropping systems [oat/maize (O/M) and vetch/maize (V/M)] on N<sub>2</sub>O emissions.

## Air sampling and N2O emission

Air samples were collected in static chambers after cover crop management (O and V) in 2007 for 54 days and in 2008 for 55 days. Air samples were collected with syringes at 0, 15, 30 and 45 minutes after closing the chamber. The samples were analyzed for N<sub>2</sub>O concentration by gas chromatography.

## Soil and meteorological variables

Soil samples for determination of mineral N (nitrate and ammonium), soil moisture and dissolved organic carbon (DOC) were collected as composites of five replicate soil samples per plot, from a depth of 0–10 cm. A 10-g sub-sample of the soil was used to determine soil inorganic-N by extracting in 50 mL 1 M KCl. Concentrations of  $NH_4^+$  and  $NO_3^-$  were determined by Kjeldhal. Soil moisture was gravimetrically determined by drying a sub-sample to 105 °C. Soil moisture was used to calculate water filled pore space (% WFPS) using bulk densities collected each week in conventional tillage and one time in no tillage. Dissolved organic carbon was extracted in water, filtrated in regenerate cellulose membrane (0,45  $\mu$ m) and determined by C analyzer. The effects of soil and meteorological variables and  $N_2O$  fluxes were evaluated with multiple linear regressions.

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#### Results

Larger fluxes occurred in 2008 more than in 2007 (Figure 1 and 2). In 2008 the maximum fluxes occurred between 20 to 30 days in all treatments. In both years conventional tillage increased N<sub>2</sub>O emissions for O/M systems. Similar results were reported by Baggs *et al.* (2003; 2006). NT promotes the smallest fluxes in O/M systems. The accumulated N<sub>2</sub>O emission after cover crop rolling averaged for the years for NT soil was three times greater for V/M system (mean:886.3 g N/ha) than for the O/M system (mean:280.8 g N/ha), which is explained by the high quality of vetch residue accelerating N release in soil (Millar and Baggs 2005). In CT soil, however, such emissions were similar in those two crops systems: mean of 742.0 g N/ha in O/M and 739.8 g N/ha in V/M because CT increased N<sub>2</sub>O emissions in O/M systems. These results were contrary and higher than those in 2003 reported by Gomes (2006) in this same experiment. We believed that the high precipitation occurred after cover crops in 2007 and 2008 increased N<sub>2</sub>O emission potential because this coincided with nitrogen release by crops. It probably reflects oxygen deficiency in soils favoring to denitrification (Farquharson and Baldock 2008). In 2007 this was confirmed as emissions for no and conventional tillage were controlled mainly by NO<sub>3</sub> and dissolved organic C availability in soil and by water filled porosity (Eq. 1 and 2).

$$N_2O_{PC} = (\mu g N/m^2/ha) = -93.9 + 4.78NO_3 + 2.56WFPS + 0.26DOPC$$
 (1)   
  $(R^2 = 0.57, n = 20, p < 0.001)$ 

$$N_2O_{PD} = (\mu g N/m^2/ha) = -79.9 + 2.05NO_3 + 1.33WFPS + 0.22DOC$$
 (2)  
 $(R^2 = 0.45, n = 40, p < 0.001)$ 

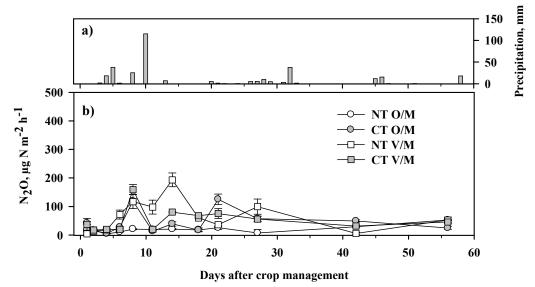


Figure 1. Precipitation (a) and soil nitrous oxide fluxes (b) during 55 days after oat (O) and vetch (V) management in tillage (CT) and no tillage (NT) in 2007. M=maize. Error bars represent standard deviation.

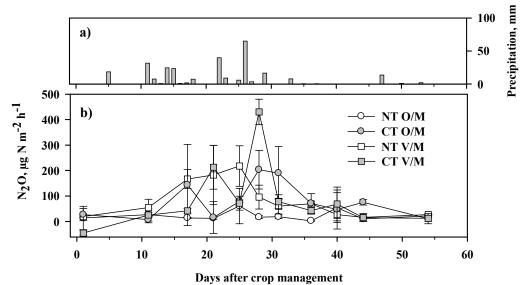


Figure 2. Precipitation (a) and soil nitrous oxide fluxes (b) during 54 days after oat (O) and vetch (V) management in tillage (CT) and no tillage (NT) in 2008. M= maize. Error bars represent standard deviation.

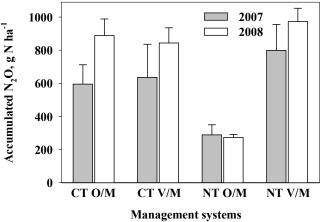


Figure 3. Accumulated N<sub>2</sub>O emitted over 55 days in 2007 and 54 days in 2008 after oat (O) and vetch (V) management in tillage (CT) and no tillage (NT). M=maize. Error bars represent standard deviation.

#### Conclusion

The emission of  $N_2O$  was smaller in no tillage when this system was combined with oat/maize. However in vetch/maize managed as no tillage and conventional tillage there were no differences. The emission for V/M was higher than for O/M just for no tillage. The relation of nitrate, dissolved organic carbon and water ships filled porosity indicate that  $N_2O$  emission was predominantely derived by denitrification in the soil.

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## Sorptive protection of organic matter in soil

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#### **Abstract**

Soils are a significant sink for organic carbon, which can be protected from chemical and biological change, and hence conversion into greenhouse gases, such as CO<sub>2</sub> and CH<sub>4</sub>. In order to mitigate global climate change, and improve soil quality, the chemical mechanisms behind the long-term protection of organic matter must be understood, and strategies developed to improve this protection. Organic matter can be stabilised and protected in soil by a range of mechanisms, especially sorption. Sorption of organic matter to the surface of clay minerals via strong multiple complex bonds prevents hydrolytic enzymes approaching and decomposing the organic matter. We used clay minerals to study the sorption processes between organic matter and mineral phases, hence protection of the organic matter, that typically occur in soils. Initial results from sorption experiments show that humic acid was adsorbed more strongly to goethite than with kaolinite or montmorillonite. For all three mineral phases sorption was pH-dependent, with maximum sorption occurring at lower pH. XRD analysis in montmorillonite systems show that the sorbed humic acid decreased the 'd' spacing of the 2:1 clay.

## **Key Words**

Preservation, organic compounds, bonding.

#### Introduction

A huge volume of organic carbon comes from anthropogenic sources, for example, from waste disposal, such as effluents from wastewater treatment, or biosolids used as crop manure. Storage of this organic carbon in soil is desirable in order to prevent rapid conversion to greenhouse gases; the organic matter could also add valuable plant nutrients to the soil. The extent to which a soil can store and protect carbon depends on the a) physicochemical properties of the organic matter, b) the nature of the minerals in soil, and c) on soil properties, such as pH, salinity and presence of natural organic matter. Colloidal clays and minerals abound in soils, and, through various processes, including sorption, can act as an ecological barrier for immobilization and protection of organic carbon. The organic matter can be adsorbed onto mineral phases by several different mechanisms.

## Ion exchange

Organic ions can be adsorbed via ion-exchange mechanisms. For example, the exchangeable cations on the surface of clay minerals may be replaced by organic cations. Cation exchange is involved in the sorption of various aminated benzenes by montmorillonite. Anionic organics may be adsorbed via interaction with amphoteric Al-OH groups of clays and soil minerals at low pH when these functional groups carry a net positive charge.

## Hydrogen bonding

Hydrogen bonding can occur between surface hydroxyl groups and hydrogen or electronegative atoms of sorbing molecules. For example, polar functional groups on hydrophobic compounds can enhance sorption with inorganic surfaces through non-hydrophobic bonding, including hydrogen bonding (Boily *et al.* 2000). Pyridine forms strong hydrogen bonds with water molecules coordinated with interlayer cations in montmorillonite (Kubicki *et al.* 1999).

## Intercalation into the interlayer region of expanding clays

Organic molecules may intercalate between the layers of expanding clays (Schnitzer 1987), and thereby help to increase sorption of non-ionic hydrophobic organic compounds (Spark *et al.* 1997). Such sorption of organic molecules by expanding clays such as montmorillonite, can involve interaction with external surface sites and/or the interlayer regions. For example, Schnitzer and Kodama (1966) proposed that the sorption of some pyridine derivatives involves sites on the external surfaces, as well as those between layers of montmorillonite (Schnitzer and Kodama 1966). Intercalation may involve several pathways, including a)

cation exchange (Chen *et al.* 1987), b) dipole-dipole attractions, whereby organic molecules replace interlayer water molecules, or c) interaction with interlayer water molecules, via hydrogen bonding (Kubicki *et al.* 1999). When organic molecules penetrate the interlayers of expanding clays, the basal spacing of the clay is often increased (Chen *et al.* 1987), decreased, or remains unchanged. X-ray Diffraction studies can provide information about the extent of the change in basal spacing, and thereby provide conclusive evidence for intercalation.

## Hydrophobic interactions

Sorption of hydrophobic compounds can also occur through interaction with the more hydrophobic surfaces of mineral particles. The siloxane face of the clay mineral, for example, is more hydrophibic than are hydroxyl surfaces, and therefore the siloxane face interacts more readily with hydrophobic compounds. The sorption of hydrophobic compounds can depend on physicochemical properties, such as the hydrophobicity; a character that can be represented by the octanol-water partition coefficient ( $K_{ow}$  value). For example, sorption of some neutral hydrophobic compounds is directly correlated with their  $K_{ow}$  (Zhang *et al.* 1991)

#### Methods

The clay samples came from the Clay Minerals Society Source Clays Repository : a) Na-Montmorillonite (Wyoming) SWy-2 from Wyoming, USA, and b) Kaolin KGa-2 from Warren County, Georgia, USA. The surface areas (nitrogen adsorption) and cation exchange capacities (provided by the Clay Minerals Society) of these clay minerals were 31.8  $\text{m}^2$  /g and 76.4 cmol/ kg respectively for SWy-2, and 23.5  $\text{m}^2$  /g, and 2.0 cmol/ kg respectively for KGa-2.

Goethite was prepared by the modified method of Boily *et al.* (2000). Polycarbonate apparatus was used throughout to prevent silica contamination. To about 1.2 L of 1 M Fe(NO<sub>3</sub>)<sub>3</sub>, (prepared from boiled milli-Q water), 5 M carbonate-free NaOH was added dropwise, under an atmosphere of N<sub>2</sub>, until the pH was 12.5. The dark brown precipitate was aged at 60 °C for 2 weeks. The suspension was then dialyzed against Milli-Q water under an atmosphere of N<sub>2</sub>, with the water changed twice daily until the conductivity was less than 1.0  $\mu$ S, after which the suspension was frozen before being freeze-dried.

Humic acid was purified from the sodium salt by a method similar to that of Susic and Boto (1989). Sodium humate was mixed with Milli-Q water, and the pH adjusted to about 10 by the addition of 25% aqueous  $NH_4OH$ . The mixture was centrifuged at 16 000 g for 10 min, and then concentrated HCl was added to precipitate the humic acid from the supernatant. The precipitate was collected by vacuum filtration (Whatman #1 filter paper), air-dried at 25 °C for 24 h, and oven-dried (80 °C) for 48 h.

Humic acid used in the experiments was added from a 5.0 g/L stock solution, prepared by dissolution of purified humic acid standard in water. Dissolution was assisted by the addition of a few drops of  $NH_4OH$ .

## Measurement of pH

Great care was taken to ensure accurate measurement of pH in all experiments. Metrohm 691 pH meters with Orion Ross 'Sure Flow' and/or Metrohm combined pH-glass microelectrodes were used to measure pH. Before each experiment, the electrodes were calibrated at  $25 \pm 0.05$  °C, with freshly-prepared NBS standard buffers at pH 4.01 and 6.86. The electrode calibration was checked at the end of each experiment to ensure that there had been no significant drift in the calibration during the experiment. Results were discarded if the re-calibration were outside 0.05 pH units. The pH electrodes were regularly checked and cleaned, according to manufacturer specifications.

## Humic acid determination

Humic acid was determined by a method similar to that used by Susic and Boto (1989), by a Shimadzu HPLC system (SCL-10AVP) with fluorescence detection (RF-10AXL) at an excitation wavelength of 340 nm and an emission wavelength of 455 nm. The mobile phase was about 0.003% ammonium hydroxide at pH 10, at a flow rate of 1.0 mL/min. A 150 x 4.6-mm I.D, 4 µm Synergy Fusion Reverse column (Phenomenex, Australia) (protected by a guard column with matching stationary phase material) was used for separation of humic acid. A six-point linear calibration curve (0-100 mg/L) with a correlation coefficient > 0.99 was used to calculate the humic acid concentrations in samples.

## Sorption experiments

Suspensions that contained sufficient substrate to give a BET surface area of  $100 \, \text{m}^2/\text{L}$  were prepared by an appropriate mass of solid ( $0.4800 \pm 0.0005 \, \text{g}$  goethite,  $0.9400 \pm 0.0005 \, \text{g}$  montmorillonite, or  $1.2800 \pm 0.0005 \, \text{g}$  kaolinite) measured into 300 mL of 10 mM KNO<sub>3</sub>. Suspensions were stirred with a magnetic stirring bar (covered with Pyrex) and equilibrated for about 20 h in a jacketed, borosilicate glass reaction vessel (maintained at  $25.0 \pm 0.5 \, ^{\circ}\text{C}$ ). The suspensions were continuously purged with humidified nitrogen to eliminate carbon dioxide. Sorption experiments were conducted in triplicate. At the start of each experiment, the pH of the suspension was adjusted to the required value by the addition of  $0.1 \, \text{M}$  HNO<sub>3</sub> or KOH, and then humic acid, to the required concentration. The suspension was periodically sampled over 48 h, and the concentration of HA determined as described above. The pH was continuously monitored, and the suspension continuously purged with nitrogen gas.

## Results

### Sorption experiments

The sorption of humic acid to goethite, kaolinite and montmorillonite is pH-dependent, with maximum sorption at low pH (Figure 1). This behaviour is typical for the sorption of humic and fulvic substances by mineral phases. At low pH, mineral surfaces may carry a positive charge, which can interact with a) ionized negatively-charged groups of dissolved organic matter, or b) by hydrogen bonding with –C=O from carboxylic acids. The sorption of humic acid on goethite was the highest of the three substrates. This is not surprising because the goethite surface is known to have a higher surface charge density than do phyllosilicate minerals. The point of zero charge (PZC) for the goethite sample used in this study was about 8.5, so the surface had a net positive charge below this pH. The lower sorption of the dissolved organic material observed for the clay minerals is probably because of the lower concentration of positive charged sites on their surfaces. Lower sorption of organic anions onto clays has often been observed. For example, various benzene carboxylates (simple analogues of complex humic and fulvic structures) were adsorbed significantly less to kaolinite than to goethite (Spark *et al.* 1997) The decrease in sorption at higher pH results from repulsion between the increasingly negative surface charge, and the negatively charged carboxylate groups on the humic acid.

The XRD data for the sorption of humic acid to montmorillonite (Figure 2) shows that the basal spacing of the montmorillonite decreases significantly when humic acid is present. Changes in basal spacing for swelling clays have often been used as diagnostic evidence for intercalation of solutes. However, the change in basal spacing observed with added humic acid is in the opposite direction to that expected for the intercalation of such bulky molecules. Furthermore, sorption of humic acid to montmorillonite was fully reversible, which was unexpected with the large molecules that intercalated into the clay structure. This suggests that the humic acid did not intercalate, but was rather adsorbed to the external surfaces of the montmorillonite.

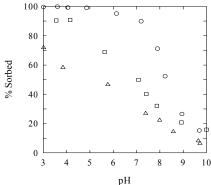


Figure 1. Sorption of humic acid at 25 °C to 100 m<sup>2</sup>/L to goethite ( $\circ$ ), kaolinite ( $\square$ ) and montmorillonite ( $\Delta$ ). Initial concentration of the humic acid was 50 mg/ L. Background electrolyte 10 mM KNO<sub>3</sub>.

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Figure 2. X-ray diffractograms of dried samples of montmorillonite suspensions at pH 4.5: (a) without humic acid, (b) with added humic acid; and pH 10.5: (c) without humic acid, and (d) with added humic acid.

#### Conclusion

Sorption is pH-dependent, with more humic acid adsorbing to the iron oxide compared with the clay minerals, probably because of the higher surface charge density on goethite compared with the clays. The sorption of humic acid to montmorillonite decreased the 'd' spacing, perhaps suggesting that intercalation was not the primary mechanism for uptake of humic acid on that clay. This may be significant, because surface-bound organic matter is generally thought to be more prone to degradation than is that which diffuses into micro porous clay structures.

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## Spatial-temporal variabilities of N<sub>2</sub>O emission from *Acacia mangium* soils

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## **Abstract**

We compared spatial structures of  $N_2O$  fluxes in an *Acacia mangium* plantation stand in Sumatra, Indonesia between drier (August) and wetter (March) season. A  $60 \times 100$  m plot was divided into  $10 \times 10$  m grids. The  $N_2O$  fluxes and soil properties were measured at 77 grid points of 10 m intervals in the plot. Spatial structures of the gas fluxes and soil properties were identified using geostatistical analysis. The mean of  $N_2O$  fluxes in a wetter season was significantly higher than that in a drier season.  $N_2O$  fluxes had a strong spatial dependence with a range of about 18 m in both the drier and wetter season. The spatial structure of  $N_2O$  fluxes in a wetter season was mainly governed by that of water-filled pore space (WFPS), while that in a drier season possibly depended on the spatial patterns of soil resource distribution. Our results indicate that we should consider factors controlling spatial structures of  $N_2O$  fluxes separately between the drier and wetter season, though the geostatistical parameters were comparable between the seasons.

## **Key Words**

Leguminous tree, fast wood plantation, nitrous oxide, seasonal change, spatial structure, Indonesia.

#### Introduction

Nitrous oxide (N<sub>2</sub>O) is a major greenhouse gas in the atmosphere and significantly contributes to global warming according to the latest data (IPCC 2007). Tropical rain forest soils have been identified as an important source of N<sub>2</sub>O (Keller et al. 1986). Industrial plantations of fast-growing tree species, in particular leguminous tree plantations, have been widely introduced into tropical Asia (FAO 2001). However, presence of leguminous and other nitrogen (N)-fixing trees in forests may enhance N<sub>2</sub>O emission from the soils, because they produce N rich litter through symbiotic N fixation, leading to high soil N availability and soil N cycling (Erickson et al. 2001). In the fast-growing leguminous tree plantations in tropical Asia, their soils have been demonstrated to be a significant source of N<sub>2</sub>O as well (Arai et al. 2008; Konda et al. 2008). Therefore, it is necessary to elucidate the N<sub>2</sub>O emissions and underlying mechanisms involved in the emission in fast-growing leguminous tree plantations, in order to estimate the accurate magnitude of mitigating global warming by the plantations, and to develop management options to mitigate N<sub>2</sub>O emissions as well. Soil surface N<sub>2</sub>O fluxes show large seasonal (Kiese et al. 2003) and spatial variability (Folorunso and Rolston 1984), and these are serious problems in precisely estimating the source and sink strength of N<sub>2</sub>O in tropical rain forest ecosystems. It is essential to understand the seasonal and spatial variations of these gas fluxes to conduct accurate quantitative evaluations of these gas emissions in the leguminous tree plantation soils. Our objectives were (1) to evaluate the seasonal and spatial variation in N<sub>2</sub>O fluxes in the fast-growing leguminous tree plantation, and (2) to clarify the major factors controlling the variation of these fluxes from the relationship between the gas fluxes and soil properties.

## Methods

Site description

The field measurements were done in an A. mangium plantation area (3°52'40''S, 103°58'40''E) in South Sumatra, Indonesia, in August 2005 and March 2006. The mean annual temperature and precipitation from 1991 to 2002 were 27.3°C and 2,750 mm, respectively (Hardjono *et al.* 2005). Although there are no distinctly pronounced dry and wet seasons, the period from June to September is relatively dry (average monthly precipitation < 150 mm (Hardjono *et al.* 2005)). This study was conducted once during the drier and wetter season, respectively. The topography is undulating and the soils are Acrisols, derived from Tertiary sedimentary rock. A  $60 \times 100$ -m plot was established in an A. mangium plantation. The  $60 \times 100$ -m plot was divided into  $10 \times 10$ -m grids, and gas and soil samples were collected once at each grid point (n=77) on 8 August 2005 and on 3 March 2006.

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## Gas sampling and analysis

We measured N<sub>2</sub>O and CO<sub>2</sub> fluxes using the static chamber method (Arai *et al.* 2008). Polypropylene chambers (22.2 cm upper diameter, 18.7 cm lower diameter, 12.0 cm high) were inserted into the soil to a depth of 2 cm 1 day before sampling. The chamber diameter at the soil surface was 19.4 cm. After sealing the chambers with lids containing a sampling port and an air bag to equilibrate the inside pressure to atmospheric pressure, we took 40-mL gas samples with a syringe after 0, 15, and 30 min. The gas samples were ejected into previously evacuated 30-mL glass vials with butyl rubber stoppers. These glass vials were analysed in the laboratory for the concentrations of N<sub>2</sub>O and CO<sub>2</sub> using gas chromatographs (GC-14B, Shimadzu Co. Ltd., Kyoto, Japan) equipped with an electron capture detector and a thermal conductivity detector, respectively. We calculated the gas flux by linear regression because the increase in gas concentration in the chamber during this sampling period appeared linear.

## Soil sampling and analysis

After gas sampling, we collected all litters from 0.059 m² area near the chambers and separated them into fresh (L layer) and decayed (FH layer) litter. The dry weights of the L and FH layer were determined on an oven-dry basis (105 °C, 24 h). After litter sampling, we took top 10 cm mineral soil using two 200-mL (5.1 cm diameter, 10 cm height) sampling cylinders in a drier season and one 200-mL soil cylinder in a wetter season. One cylinder soil sample (200 mL) of drier season was used for analyses of bulk density, expressed in an oven-dry basis (105 °C, 24 h). We used the bulk density in the drier season as well for the wetter season. The 200ml soil samples in each season were homogenized and stored in a refrigerator at 4 °C. Gravimetric moisture was determined after drying soil subsamples at 105 °C for 24 h. We calculated water-filled pore space (WFPS) of soil using gravimetric moisture, bulk density and particle density (2.58 Mg/m³) determined by a pycnometer. Ammonium (NH<sub>4</sub><sup>+</sup>) and nitrate (NO<sub>3</sub><sup>-</sup>) nitrogen were extracted with tenfold 2M KCl for 5 g samples by shaking for 1 h within 3 d of sampling. The filtrate was stored in a freezer, and determined for NH<sub>4</sub>-N and NO<sub>3</sub>-N concentrations using a flow-injection analyzer (AQUA LAB Co., Ltd., Tokyo, Japan). Soil pH (H<sub>2</sub>O) was measured using a glass electrode for a suspension of 10 g soil and 25 mL distilled water.

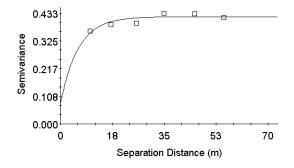
## Results and discussion

Averaged  $N_2O$  fluxes of 77 chambers showed a pronounced seasonal difference with significantly higher rates in the wetter season, 1.85 ( $\pm 1.18$ ) mg N/m²/d, than in the drier season, 0.55 ( $\pm 0.42$ ) mg N/m²/d (Table 1). Seasonal patterns of  $N_2O$  fluxes often can be explained by soil moisture (Kiese *et al.* 2003), decomposition rates of litter (Werner *et al.* 2007) and diffusion restriction of inorganic N (Davidson *et al.* 1993). In our study, the mean of WFPS was higher in the wetter season than in the drier season. In the wetter season, L layer accumulated in the drier season was almost disappeared, and FH layer amounts and  $CO_2$  fluxes increased significantly than in the drier season (Table 1) .This may indicate that higher supply of

Table 1. Statistical and geostatisitical data of gas fluxes and soil parameters in the drier and wetter seasons. Values followed by different uppercase letters are significantly different between seasons (P < 0.05).  $^{\dagger}$ Bulk density was measured once in the drier season.  $^{\ddagger}$ Spatial structures were not apparent.

Property	Season		SD	Range	Q value
$N_2O$ flux (mg N m <sup>2</sup> /d)	Dry	$0.55^{A}$	0.42	18.0	0.81
	Wet	$1.85^{B}$	1.18	17.4	0.97
$CO_2$ flux (g $C/m^2/d$ )	Dry	$2.73^{A}$	0.66	_‡	_‡
	Wet	$4.29^{B}$	0.91	_‡	_‡
Bulk density <sup>†</sup> (Mg/m <sup>3</sup> )	Dry	0.75	0.08	21.7	0.99
• • •	Wet	-	_	-	-
WFPS (%)	Dry	55.5 <sup>A</sup>	8.0	_‡	_‡
	Wet	$66.3^{B}$	1.0	17.1	0.94
Soil pH (H <sub>2</sub> O)	Dry	$4.88^{A}$	0.40	$70^{+}$	0.56
<b>1</b> , , ,	Wet	$5.03^{B}$	0.37	63.2	0.50
L amount (kg/m <sup>2</sup> )	Dry	0.27	0.09	_‡	_‡
	Wet	0.02	0.03	_‡	_‡
FH amount (kg/m <sup>2</sup> )	Dry	$0.78^{A}$	0.38	25.2	0.87
	Wet	$1.13^{B}$	0.31	_‡	_‡
Soil NH <sub>4</sub> -N (mg/kg)	Dry	29.4 <sup>A</sup>	3.2	33.7	0.55
, 2 0,	Wet	$68.7^{B}$	2.8	_‡	_‡
Soil NO <sub>3</sub> -N (mg/kg)	Dry	$20.6^{A}$	7.7	_‡	_‡
	Wet	$8.7^{\mathrm{B}}$	4.2	_‡	_‡

available carbon and nitrogen to soil microbes through accelerated litter decomposition in the wetter season. In the *A. mangium* soils during the wetter season, high water content and supply of available carbon and nitrogen into the soils can promote microbial activities, resulting in the enhancement of N<sub>2</sub>O emissions.



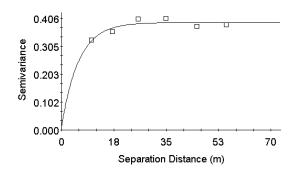


Figure 1. The Semivariogram of  $N_2O$  fluxes in the drier season.

Figure 2. The Semivariogram of  $N_2O$  fluxes in the wetter season.

 $N_2O$  fluxes had strong spatial dependence with a range of about 18 m in both the drier and wetter season (Table 1, Figure 1, 2), indicating that the degree and limit of spatial dependence at sampling scale (Gorres *et al.* 1997; Yanai *et al.* 2003) were comparable between the seasons. The  $N_2O$  fluxes significantly correlated with litter amounts (R=0.335, P<0.01) and  $CO_2$  fluxes (R=0.416, P<0.01) in the drier season, while they significantly did with WFPS (R=0.391, P<0.01) in the wetter season. Because FH layer of *A. mangium* plantation was not a direct source of  $N_2O$  in a drier season according to a litter removal experiment in the same plantation soils (Konda *et al.* unpublished data), the accumulated litter layer may function as a substantial soil resource for increasing  $N_2O$  fluxes during the drier season. We estimate that the spatial pattern of  $N_2O$  fluxes in the drier season was mainly controlled by the spatial distribution of fresh resource supplied from the litter layer to the soils, while anaerobic conditions in the soils could play an important role for the spatial pattern in a wetter season due to the enhancement of denitrification rates and also  $N_2O$  emission rate.

## Conclusion

The spatial structure of  $N_2O$  fluxes in the wetter season mainly depended on that of WFPS, while in the drier season it possibly depended on fresh resource supply from the litter layer to the soils. We should consider factors controlling spatial structures of  $N_2O$  fluxes separately between the drier and wetter season, though the geostatistical parameters were comparable between the seasons.

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# Temporal and spatial patterns of N<sub>2</sub>O and CH<sub>4</sub> emissions on an agricultural field containing ephemeral wetlands

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#### **Abstract**

It has been recognized that both  $N_2O$  and  $CH_4$  emissions vary with land use and slope positions. In various parts of the world, wetlands are imbedded in the agricultural landscapes. However, to date, no study has been carried out to examine the  $N_2O$  and  $CH_4$  emissions from agricultural fields containing ephemeral wetlands. In this study, gas samples were collected for four consecutive years (2003 to 2006) from different slope positions along three transects from a No-Till cropped upslope through the riparian area to the wetland. Additionally, gas samples were taken from three adjacent cropped depressions for a two-year period. Although the daily fluxes of  $N_2O$  and  $CH_4$  emissions were highly variable, there were distinctive temporal and spatial patterns. These patterns reflect the effects of the hydrological regime and land management practice which are related to the land use and slope positions. Overall, on an annual basis, the total non- $CO_2$  GHG emission rates from the wetland basin were much greater than those from the cropped area. The riparian zone served as a transition zone with the highest variability of  $N_2O$  and  $CH_4$  emissions. These findings suggest that the  $N_2O$  and  $CH_4$  emissions from ephemeral wetlands imbedded in the agricultural landscapes must be taken into account.

### **Key Words**

Green house gas, N<sub>2</sub>O, CH<sub>4</sub>, agricultural field, ephemeral wetlands.

## Introduction

In an agricultural field, both  $N_2O$  and  $CH_4$  emissions are highly variable, temporally and spatially. The distributions of  $N_2O$  and  $CH_4$  emissions are often skewed with so-called spatial "hot spots" and also temporal "hot periods" (Yates *et al.* 2006, Dalal *et al.* 2008). Field studies of  $N_2O$  and  $CH_4$  emissions have focused on the cropland. In the Prairie Pothole Region (PPR), wetlands are imbedded in the agricultural landscapes. The area is extensively farmed with more than half of the wetlands drained or altered for agriculture. Some big or deep wetlands are remained uncultivated but the upland areas around these wetlands are cropped. To date, no study has been conducted to examine both  $N_2O$  and  $CH_4$  emissions from complex landscapes containing both wetlands and cropland. Due to the lack of studies, in regional or national GHG inventories report, the  $N_2O$  and  $CH_4$  emissions from the cropped depressions usually were not distinguished from other cropped areas and those from the in-field wetlands have been ignored, not being accounted for in either the inventory of the wetland or that of the cropland (e.g., Gregorich *et al.* 2005). The objectives of this study were to examine the temporal and spatial patterns of the  $N_2O$  and  $CH_4$  emissions from agricultual fields containing ephemeral wetlands.

#### Methods

Study site and sample collection

The field site of this study is the 260 ha Parkland Agriculture Research Initiative demonstration farm located near the town of Mundare in central Alberta near the northern extent of the Prairie Pothole Region (Fig. 1). The farm has been farmed for about 100 years and contains cropped uplands and depressions and some uncultivated in-field wetlands. The in-field wetlands were all ephemeral wetlands — inundated after spring snowmelt but water receded in the summer. A stratified transect method was used in this study for the sample collection. Three adjacent in-field wetlands — referred to as East (E), Central (C) and West (W) wetland, respectively — were selected (Fig. 1). Each transect was stratified into different slope positions, each with a sampling point (Fig. 1c showing the central transect as an example). After the first year, three cropped depressions (CD) were also selected in the upland areas adjacent to the wetlands and a sample point was established in the middle of each depression. Locations of all sampling points were determined using a DGPS unit. Gas samples were collected using the chamber method at each sampling point in each year from before spring snowmelt near the end of March to after freeze up at the end of November. The sampling

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interval varied but averaged about one sample per week. The gas samples were taken using a 20 ml syringe from the chambers 30 minutes after the chamber installation. At least three ambient samples were taken at the time of gas sampling in the proximity of the chamber top to serve as a time-zero sample. All gas samples were taken between 10:00 and 14:00 at the sampling dates. The gas samples were analyzed for  $CH_4$  and  $N_2O$  simultaneously using a Varian 3600 gas chromatograph (GC) with manual injection and Varian Star Workstation version 5.3 software. Sample chamber gas flux was calculated from the measured concentrations using the ambient air concentration next to the chamber as the value at time-zero.

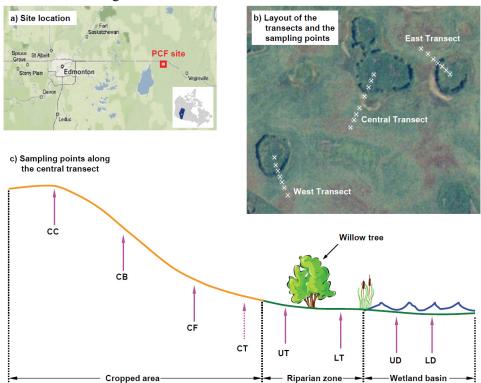


Figure 1. The location of the field site and the layout of the sampling points.

## Data processing and statistical analyses

Daily N<sub>2</sub>O and CH<sub>4</sub> fluxes between March 1<sup>st</sup> and December 1<sup>st</sup> in each year were calculated using a linear interpolation of the flux data measured at the sampling dates. Each year was divided into six periods based on the seeding date. The 35-day period before the seeding date was defined as the late-spring period (LSP) and the period from March 1st to the beginning of the LSP was defined as the early-spring period (ESP). The 35-day period immediately after the seeding date was defined as the early-summer period (ESM) and the two consecutive 35-day periods were defined as the mid-summer period (MSM) and late-summer period (LSM), respectively. The period after the LSM until December 1st was defined as the fall period (FAL). Cumulative N<sub>2</sub>O and CH<sub>4</sub> emissions within these periods (referred to as period cumulative data, herein) were calculated as the sums of the daily N<sub>2</sub>O and CH<sub>4</sub> fluxes in each period in each year, respectively. Annual cumulative N<sub>2</sub>O and CH<sub>4</sub> emissions were calculated as the sums of the daily N<sub>2</sub>O and CH<sub>4</sub> fluxes in each year (assuming no emissions between Dec 1<sup>st</sup> and March 1<sup>st</sup>), respectively. The annual cumulative data for these two gases were converted to the CO<sub>2</sub>-equivalent (CO<sub>2</sub>-eq) values using the global warming potential factors over a 100yr cycle (25 and 298 for N<sub>2</sub>O and CH<sub>4</sub>, respectively) proposed by the IPCC (2006). The converted values of the two gases were added up and used as the annual cumulative total non-CO<sub>2</sub> GHG emission. The period cumulative data were divided into sub-datasets based on the land use. The group means of the N<sub>2</sub>O and CH<sub>4</sub> emissions (data log-transformed) for each slope position and each period in each land use were calculated. The differences between the group means of the slope position (GM<sub>s</sub>) and the period (GM<sub>D</sub>) were tested using the Duncan's Multiple Range Test (DMRT, P = 0.05). Similar approach was taken for the analyses of the annual cumulative data except that one major factor was changed from the period to the year

## Results

Within-year variations of the  $N_2O$  and  $CH_4$  emissions The daily  $N_2O$  and  $CH_4$  emissions were highly variable with time and across the landscape. However, the

(GM<sub>v</sub>). The group means were then back transformed to their original units.

grouped means of the period cumulative data for each sampling point showed the distinctive within-year temporal patterns for different land uses on different slope positions (Table 1). In cropped area, the  $N_2O$  was mainly produced in the early-spring and early-summer, associated with the snowmelt and the seeding and fertilizing events. The  $CH_4$  emission was low and was not greatly affected by these two events. Overall, there was a low level of  $CH_4$  consumption in the cropped area, especially after the mid-summer. In the wetland basins, the  $N_2O$  was mainly produced after mid-summer and  $CH_4$  was produced year round but the hottest periods were the late-spring to the mid-summer. In the riparian zones, there were large differences between the two slope positions, indicating the high variability of  $N_2O$  and  $CH_4$  emissions in these areas, probably due to the fact that the riparian zones are the transition zone from the cropped area to the wetland basin.

Table 1. Group means of the period cumulative N<sub>2</sub>O and CH<sub>4</sub> emissions.

			Croppe	d area						Riparia	an zone			Wetland	basin		
		-	CC	СВ	CF	CT	CD	$GM_p$	$N_p$	UT	LT	$GM_p$	N <sub>p</sub>	UD	LD	$GM_p$	N <sub>p</sub>
	Days	n	3	3	3	1	3			3	3		_	3	3		
$N_2O$	emissi	on (	$N_2 O$ -	N, g ha	ı <sup>-1</sup> peri	od <sup>-1</sup> )											
ESP	52	4	196	220	340	593	694	292 a	43	89	-1	37 a	24	20	17	19 b	24
LSP	35	4	33	38	67	87	383	62 c	43	44	-1	19 a	24	8	-2	3 b	24
ESM	35	4	229	254	182	453	605	272 a	46	58	11	32 a	24	33	55	43 ab	24
MSM	35	4	169	92	95	204	191	131 b	46	49	29	39 a	24	106	172	137 a	24
LSM	35	4	10	1	17	21	20	12 d	46	1	5	3 ab	24	28	106	62 ab	24
FAL	60	3	14	26	21	11	23	20 d	33	-6	-19	-13 b	18	140	125	133 a	18
$GM_s$		_	92	87	100	167	212			37	4			46	66		
		-	В	В	В	A	A			A	В			A	A		
CH 4 6	emissi	on (	(CH 4-	C, g ha	ı <sup>-1</sup> peri	$od^{-1}$ )											
ESP	52	4	-43	-8	-41	232	291	14 ab	43	121	394	253 b	24	534	273	400 c	24
LSP	35	4	7	-33	20	-19	520	29 a	43	525	4017	1898 a	24	10286	8600	9412 ab	24
ESM	35	4	28	-24	59	-43	-49	6 ab	46	115	4617	1741 a	24	13362	28504	19647 a	24
MSM	35	4	-107	-193	-28	-57	-26	-95 c	46	-64	2052	801 ab	24	5219	10716	7581 b	24
LSM	35	4	-168	-113	-119	-57	-88	-121 c	46	-185	294	41 b	24	523	1242	860 c	24
FAL	60	3	-125	-91	-129	176	56	-75 bc	33	-107	410	136 b	18	1208	948	1075 с	18
$GM_s$		_	-67	-77	-37	29	52			62	1651			3639	4928		
		-	BC	C	ABC	AB	A			В	A			A	A		
$\mathbf{N}_{s}$			69	69	69	23	27			69	69			69	69		

Table 2. Group means of the annual cumulative N2O and CH4 emissions.

	Cropped area				pped area Riparian zone Wetland b				land basin		
	CC	CB	CF	CT	CD	UT	LT	UD	LD	$GM_y$	$N_y$
n	3	3	3	1	3	3	3	3	3	-	
N 2 O en	nission	(CO 2	-eq, kg	ha <sup>-1</sup> .	vr <sup>-1</sup> )						
2003	83	74	113	392	_	88	78	94	61	91 b	22
2004	428	422	384	329	_	53	-9	159	170	166 ab	22
2005	457	374	412	892	854	274	-6	223	693	318 a	25
2006	721	609	710	2049	1380	94	-20	479	484	374 a	25
$GM_s$	347	308	346	708	1088	110	1	206	263		
	ABC	ABC	ABC	AB	A	C	D	BC	BC		
CH 4 en	mission	(CO <sub>2</sub>	-eq, kg	ha <sup>-1</sup> .	yr <sup>-1</sup> )						
2003	-5	10	23	39	_	20	72	1139	2741	136 a	22
2004	-35	-30	0	21	_	-12	333	1330	1668	98 a	22
2005	-11	-27	-33	-14	18	-3	633	5328	5066	150 a	25
2006	-9	-15	-11	-7	30	33	621	2162	1786	137 a	25
$GM_s$	-17	-18	-9	7	24	7	338	2053	2541		
	С	C	C	C	C	C	В	A	A		
Total no	on-CO	<sub>2</sub> GHO	i emiss	sion (C	O 2-eq	, kg ha <sup>-1</sup>	yr <sup>-1</sup> )				
2003	86	85	138	431	_	122	152	1234	2870	288 b	22
2004	401	395	384	350	_	25	480	1517	1939	467 ab	22
2005	454	341	379	878	868	321	692	5811	6256	919 a	25
2006	714	593	700	2042	1407	145	566	2996	2766	910 a	25
$\mathbf{GM}_{s}$	342	301	353	733	1107	125	420	2401	3137		
	BCD	CD	BCD	BC	AB	D	BCD	A	A		
$N_s$	12	12	12	4	6	12	12	12	12		

## *Cross-year variations of the N₂O and CH₄ emissions*

There are cross-year variations of  $N_2O$  and  $CH_4$  emissions (Table 2), which could be explained by the different climate conditions and managements (e.g., crop type and fertilizer application) among the experimental years. Among different slope positions, the annual cumulative  $N_2O$  emission rates from the wetland basin were lower than but at a comparable level as those from the cropped area (Table 2). The annual cumulative  $CH_4$  emission rates from the wetland basin were orders of magnitude greater than those from the cropped area. Consequently, the total non- $CO_2$  GHG emission rates from the wetland basin were much greater than those from the cropped area. The riparian area served as a transition zone and the  $N_2O$  and  $CH_4$  emissions from the riparian area appeared to have the highest variability. The overall annual total non- $CO_2$  GHG emissions from the riparian area may be much lower than but could also be higher than those of the cropped area. Within the cropped area, significant differences in  $N_2O$  and  $CH_4$  emissions were also found on different slope positions, with the lower slope positions being the "hot spot" for both  $N_2O$  and  $CH_4$  emissions. These observed temporal and spatial patterns can largely be explained by the different hydrological regimes and in-field soil and nutrient transportations. which are determined by the land use and the slope position in the field scale.

## *Implications*

The high variability of  $N_2O$  and  $CH_4$  emissions observed in this study imply that in an agricultural landscape containing wetlands, large errors may exist when the average emission rates measured on random selected points (or plot data) at random dates are used for the upscaling of GHG emissions. Due to the skewness of the emission rates, the field inventory may be overestimated when the "hot spots" (e.g., the cropped depression or wetland basin points) or "hot periods" (e.g., snow-melt period) are included or may be underestimated when they are excluded. This also requires that the sampling design must take the temporal and spatial variation into account. More accurate results can be obtained by using a landscape stratification procedure (e.g., Pennock *et al.* 2005; Izaurralde *et al.* 2004) and through multi-year or long term monitoring.

#### Conclusion

The  $N_2O$  and  $CH_4$  emissions vary across the landscape and with time. However, there were distinctive temporal and spatial patterns for given periods, land uses and slope positions. Our findings suggest that it is necessary to take into account the temporal and spatial variability of the  $N_2O$  and  $CH_4$  emissions in the upscaling procedure, sampling design and the development of GHG mitigation strategies.

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## The Australian nitrous oxide research program

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## **Abstract**

Nitrous oxide emissions are highly variable across industries, soils, climates and management practices. The Australian Nitrous Oxide Research Program (NORP) is a network of six experimental sites developing spatial and temporal scaling tools using both automatic and manual chambers comparing best management practices to reduce emissions whilst maintaining agricultural productivity and profitability. NORP delivers multiple benefits to Australia's primary producers through a comprehensive database for advanced analysis of  $N_2O$  emissions datasets, aligned with soil C, climate, and management data with easy access for end users and the simulation community.

### **Key Words**

Nitrous oxide, mitigation, chambers, nitrogen, simulation.

#### Introduction

Full greenhouse gas accounting is critical when developing emissions reduction strategies for irrigated and dryland farming systems. The relatively short duration, episodic emissions of the most potent greenhouse gas (nitrous oxide -  $N_2O$ ) are closely related to water, carbon and nitrogen management require specific attention. To fully understand the implications of soil and plant management and the biophysical interactions requires the collection of long-term, high spatial and temporal resolution data afforded by automatic greenhouse gas monitoring systems. Australia is at the forefront of evidence based agricultural production and greenhouse gas research. It is also the only country which has taken the initiative of developing a purpose built Tier 3 greenhouse gas accounting system, the National Carbon Accounting System (NCAS) which includes both carbon and nitrogen emissions from soils. High quality calibration and validation data are critical elements in any predictive modelling examining the impact of management options and developing mitigation strategies.

An informal network of automated high (spatial and temporal) resolution greenhouse gas sampling devices has existed in Australia since 2005, the majority using the automated sampling and analysis system with gas chromatography and infra-red CO<sub>2</sub> analysis, based on the design of Butterbach-Bahl *et al.* (1997). Since 2009, the Australian Nitrous Oxide Research Program (NORP) has explicitly linked six experimental sites from around Australia collecting real-time N<sub>2</sub>O emissions data, as well as carbon dioxide (CO<sub>2</sub>), and (in some cases) methane (CH<sub>4</sub>) consumption data from a broad geographical range of irrigated and dryland, crop and pasture farming systems. Fourier Transform Infrared Spectroscopy (FTIR) and Tuneable Diode Laser (TDL) technologies are also being used at some sites.

The objective of NORP is to develop a detailed biophysical understanding of the processes and agricultural practices influencing  $N_2O$  emissions from agricultural systems of Australia. This will provide landholders with management strategies which have a significant impact on reducing  $N_2O$  losses whilst maintaining productivity and profitability as well as the base data for the further development and testing of the NCAS. NORP is principally funded by the federal Department of Agriculture, Fisheries and Forestry (DAFF) under its Australia's Farming Future (AFF) initiative (2009-1012), with additional funding from four Research and Development Corporations (RDCs) – Grains (GRDC), Sugar (SRDC), Dairy (SRDC), Cotton (CRDC) and Incitec Pivot, as well cash and in-kind contributions from state governments and university participants.

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#### Methods

The major elements of NORP are an overarching integration and coordination project; six automated greenhouse gas sampling and analysis projects with multiple treatments at experimental locations throughout Australia; and a laboratory based project examining the impact of nitrification inhibitors on N<sub>2</sub>O production. The specific activities of the integration project are the development of standardised data collection protocols in concert with the analogous soil carbon program (also funded by DAFF through the AFF initiative); a methodological comparison at selected sites within the automated site network, specifically an investigation into the spatial-temporal relations between manual and automatic sampling methods; the development of a web-based remote data management; and the overall management and technical oversight of the NORP.

The integration project coordinates data acquisition, database development and maintenance, data entry and web-based management, synthesis, analysis and retrieval. The database is totally scalable to ensure addition of new sites as they come on-line. The objective comparison and development of scaling methods between chambers and methodologies also lays the foundation for future investments with respect to comprehensiveness in data acquisition and the timely identification of best management practices for mitigation. The integration project also provides a centralised data platform for the development of the NCAS as well as diverse farming systems simulation groups to improve their own models and collaborate with peers in the simulation of greenhouse gas emissions. Whilst N<sub>2</sub>O mitigation is the underlying premise, CO<sub>2</sub> and CH<sub>4</sub>, along with ancillary soil nutrient and water, plant growth, development and climate data is collected at high temporal and spatial resolutions at the majority of the experimental sites.

The location of the experimental sites and their specific objectives are:

- 1. Grains/cotton (Queensland) irrigated systems at Kingsthorpe, 10 km east of Toowoomba, examining the impacts of water management on emissions.
- 2. Grains (Western Australia) rainfed systems at Wongan Hills, examining the emissions of N<sub>2</sub>O associated with the substitution of grain legumes for sources of nitrogen, and the liming of cereals.
- 3. Grains (New South Wales) rainfed systems at Tamworth, examining the use of legumes as alternate nitrogen sources in cereals.
- 4. Sugar cane/grains (Queensland) rainfed systems at Mackay. The treatments include the use of nitrification inhibitors with fertilisers to reduce N<sub>2</sub>O emissions and substituting legume sources of nitrogen for fertilisers.
- 5. Dairy (Victoria) high rainfall pasture systems at Terang, measuring N<sub>2</sub>O and CO<sub>2</sub> emissions following the application of urine and inhibitors at the DemoDairy site.
- 6. Grains (Victoria) high rainfall systems at Hamilton, measuring N<sub>2</sub>O and CO<sub>2</sub> emissions from direct drilled and conventionally sown legume/wheat rotations, including the use of nitrification inhibitors.

## Results

The NORP sites have gradually been activated since May 2009, with the first full season of data available for release from the majority of sites in mid 2010. The data from each of the sites will be presented at the 19<sup>th</sup> World Congress of Soil Science.

## Conclusion

The basic biogeochemical processes underpinning  $N_2O$  emissions are generic across soils and climates, with the sharing of management specific information across the primary industries enhancing the development of robust mitigation strategies and the development of whole system accounting methods for reducing greenhouse gas emissions from mitigation simulation for all industries.

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# The impact of land uses on $N_2O$ emission in an intensive dairy farming region, Japan

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#### **Abstract**

Nitrous oxide ( $N_2O$ ) emission from agricultural soils highly depends on the land use and management methods. We investigated an intensive dairy farming region (upper Naka river watershed, East-Japan) to evaluate the  $N_2O$  emission from soil for different land uses and different soil textures. Nitrous oxide flux from 8 agricultural fields was taken by static chamber method from January 2008 to February 2009 with bimonthly intervals. Nitrous oxide flux ranged from -9.1 to 205.6  $\mu g$  N/m²/h in upland crop systems and from -13.0 to 283.3  $\mu g$  N/m²/h in paddy fields. It was mainly influenced by soil moisture, applied fertilizer and special weather conditions. Nitrous oxide emission from rice fields was higher than that of upland soils, especial during the non-flooding period. Summer season had a significant lower  $N_2O$  emission than winter season. The controlling factors changed with different scales. The concentrations of ammonia ( $NH_4^+$ -N) and nitrate ( $NO_3^-$ -N) in soil were the most important parameters for  $N_2O$  flux for paddy and upland systems at field scale, respectively. The soil moisture was the main controlling factor for  $N_2O$  flux at the regional scale.

## **Key Words**

Land uses, N<sub>2</sub>O, agricultural soils, scale.

## Introduction

The livestock sector grew rapidly to meet the increasing demand in meat and dairy productions. As a result, the increased manure applied to soil became one of the most important sources of  $N_2O$  emission from agricultural soils (Mosier *et al.* 1998). Nitrous oxide flux from agricultural soils was strongly influenced by different crop systems, especially whether they are paddy or upland fields (Li *et al.* 2004). Many researchers have studied  $N_2O$  emission at field scale. It was difficult to find the main influence factors and to establish strong predictive relationships between field fluxes and field scale parameters such as temperature, soil moisture, soil texture and so on (Groffman 1991). This study was conducted at an intensive dairy farming area, where high amount of manure is applied. The data of  $N_2O$  flux from a field scale was analysed at regional scale, which contains different soil textures and different crop systems. The objectives of this research were (i) to explore the character of  $N_2O$  fluxes from different crop systems, and (ii) to evaluate the  $N_2O$  emission at the whole target region.

## Methods

This study was conducted from January 2008 to February 2009 at upstream of Naka River watershed in Japan (36°49`- 37°01`N, 139°54`-139°59`W). In this region, major crop systems are one season cultivation of rice (R), maize (M), and a rotation of grass and maize (G/M). Dairy cow manure is the main fertilizer source. Five sampling sites (marked with I-V) were chosen according to different land uses, soil textures and location. There are 8 sampling fields in total. Three samples were taken at each field randomly. In G/M system, Italian ryegrass (*Lolium multiflorum* L.) was planted in October and harvested in May, immediately followed by the planting of maize, which was harvested in September. For R system, the field was flooded from May to late August; the rice seedlings were transplanted in May and harvested in October. N<sub>2</sub>O fluxes in the fields were measured using static chambers. The basic information about soil and fertilizer for all the sampling sites are shown in Table 1.

#### Results

N<sub>2</sub>O fluxes in whole region

 $N_2O$  flux ranged from -9.1 to 205.6  $\mu$ g N /m²/h in M and G/M systems and from -13.0 to 283.3  $\mu$ g N /m²/h in R systems (Figure 1a and 1b). The highest  $N_2O$  fluxes were found in January, 2008, and then it decreased with the time. The fluxes were less than 50  $\mu$ g N/m²/h in March 2008 for M and G/M systems and in May 2008 for R systems. An exception was the G/M system on loam and R system on silt loam in December of 2008 and sandy loam in February 2009, which had high  $N_2O$  fluxes of 121.3, 128.5 and 142.9 $\mu$ g N /m²/h, respectively. The cumulative  $N_2O$  emission of winter period from November to April ranged from 1.7 to 5.3

kg N /ha/ period and was significantly higher than that of summer period from May to October which ranged from -0.1 to 1.7 kg N /ha/period (Figure 2) (p<0.01). R systems had significantly higher  $N_2O$  emission than G and G/M systems (p<0.01). Significant interactions were found between the period and land uses, and between land uses and soil types (p<0.01). As a result, the annual  $N_2O$  emission of M and G/M systems ranged from 2.0 to 3.4 kg N /ha/yr with an average of 2.8 kg N /ha/yr, and that for R systems ranged from 2.5 to 6.0 kg N /ha/yr with an average of 4.1 kg N/ha/yr.

## The character of N<sub>2</sub>O emission from different land uses

Land uses strongly influenced the N<sub>2</sub>O fluxed in the fields. The N<sub>2</sub>O emission from paddy fields was 1.5 times higher that of upland field. Winter period from November to April showed 10 and 3 times higher N<sub>2</sub>O emission compared to summer period from May to October for rice fields and upland systems, respectively. Those results may be due to the different soil moisture, the application of fertilizer and special weather condition. Davidson et al. (2000) showed that soil water-filled pore space (WFPS) is an import factor to control N<sub>2</sub>O emission from soil. Nitrous oxide flux mainly occurs when WFPS is between 40% and 80%. When WFPS exceeds 80%, N<sub>2</sub>O consumption occurs and di-nitrogen (N<sub>2</sub>) becomes the major end product of denitrification. In this study, the paddy fields were kept flooding from early May to end of August 2008, leading to low N<sub>2</sub>O emissions. However, during non-flooding time, WFPS was around 46% and promoted N<sub>2</sub>O emission. For uplands, the WFPS was less than 40% during the whole season, and only little N<sub>2</sub>O emission from nitrification might have occurred. High N<sub>2</sub>O emission can happen after fertilizer application (Mori et al. 2008). In this region, the fertilizer is generally applied in paddy fields in winter period around November. Thus, N<sub>2</sub>O emission can be stimulated during that time. For silt loam soil, slurry with the same amount N as winter period has been applied in August 2008, few days before sampling. However, no high N<sub>2</sub>O emission was found during that time (Figure 1a). It can be explained that the main end product of denitrification was N<sub>2</sub> rather than N<sub>2</sub>O. In uplands, the manure was applied both in winter and summer seasons. For the summer period, farmers applied manure around end of May to early June in all G and G/M systems. Thus, high N<sub>2</sub>O flux during this time might not be captured since no sampling was conducted after manure application. Thus, the N<sub>2</sub>O emission during summer period might be underestimated. Comparing different soil textures, there was no significant correlation between N<sub>2</sub>O emission and soil texture parameters through the whole year for all of the crop system. However, a significantly high N<sub>2</sub>O emission was observed in silt loam soil at R system (Figure 2). It may be due to the 2 times higher fertilizer application rate compared to clay loam and sandy loam fields (Table 1). Many studies have shown that high N<sub>2</sub>O emission can occur during special weather conditions such as freezing-thawing period or rain events (Neilsen et al. 2001). The high N<sub>2</sub>O fluxes during winter were coincided due to freezing-throwing event in surface soils.

## The character of $N_2O$ emission from whole region

The present study showed different influence parameters at different scales (Table 2). At field scale, the influence factors of N<sub>2</sub>O flux included the concentration of soil NO<sub>3</sub> -N and soil temperature (0-10cm). But for regional scale, it is also the concentration of NH<sub>4</sub><sup>+</sup>-N, CO<sub>2</sub> emission, the difference between air and soil temperature, the WFPS, contentment of silt and organic C and the ratio of C/N. As expected, NO<sub>3</sub> -N availability was found to limit  $N_2O$  flux at M and G/M systems (Table 2). Unlike upland soils,  $NH_4^+$  -N of soil significantly influenced the N<sub>2</sub>O emission at R systems (Table 2). However, the NO<sub>3</sub> -N concentration with an average of 95 mg N/kg was much higher than that of NH<sub>4</sub><sup>+</sup>-N, which had an average of 9.3 mg N/kg at both flooding and non-flooding period. This result suggests that there are different processes to control N<sub>2</sub>O emission in upland systems and rice systems. Carbon dioxide emission was significantly positively correlated to N<sub>2</sub>O flux at R systems during non-flooding period (Table 2). It indicates that microbe activities are closely related to N<sub>2</sub>O emission for rice flooding period. A negative correlation between CO<sub>2</sub> emission and N<sub>2</sub>O fluxes was also found in all R systems for all season. High CO<sub>2</sub> flux from soil in August 2008 was stimulated by high temperature, which promoted the soil microorganisms' activities, soil animal and crop root respiration. Since N<sub>2</sub>O emission in soil is produced by microbial processes of nitrification and denitrification, soil temperature affects N<sub>2</sub>O flux by regulating those microbial activities (Granli and Bøckman 1995). In this study, a significant negative correlation was found between soil temperature and N<sub>2</sub>O fluxes (Table 2). It may be masked by other factors such the amount of applied fertilizer and the freezing-thawing event. The difference between air and soil temperature can drive N<sub>2</sub>O diffusion from soil (Granli and Bøckman 1995). The difference between air and soil temperature was also significantly correlated with N<sub>2</sub>O flux in this study. All of the results indicated that N<sub>2</sub>O emission at this region was controlled by the mineralization N of soil, microbe activities, temperature, water regime, soil texture and the turnover of soil nitrogen and carbon.

Table 1. The basic informations of soils of the 8 study fields.

Land uses	I	I	II		IV		V	
	G/M	G/M	R	G/M	G/M	R	G/M	R
TN(mg N/g)	0.85a	0.87a	0.48b	0.80a	0.43bc	0.36b	0.37c	0.87a
TC(mg C/g)	11.85a	12.17a	6.64c	10.41b	4.62de	3.83e	5.23d	9.61b
pН	6.15	6.95	6.56	6.27	5.69	6.1	6.16	6.15
Fertilizer(kg N/ha)								
Winter (Nov-Apr)	430	455	100	315	410	295	250	250
Summer( May-Oct)	430	455	100	415	470	0	250	270
Soil texture		Clay loam		Loam	Sandy	loam	Silt l	oam

Table 2. Coefficients factors for the linear model of N<sub>2</sub>O at different spatial scales.

	Constan	t NH4	NO <sub>3</sub>	CO <sub>2</sub>	Soil temp	. Air-soil temp.	WFPS	Silt	С	Ratio C/N	Mo	del
		mg	N/kg	mg C/m <sup>2</sup> /h		°C	%	%	mg N/g	<del>-</del> ;	R	P
Field scale												
IVG/M	122.29	-	-	-	-	-	-	-	-	-	0.87 <	0.001
V M	-21.08	-	0.44	-	-	-	-	-	-	-	0.71 0	.003
II R	171.33	-	-	-	-10.48	-	-	-	-	-	0.69 0	.007
IV R	101.71	-	-	-	-5.51	-	-	-	-	-	0.72 <	0.001
V R	214.27	-	-	-	-11.13	-	-	-	-	-	0.700	.002
Regional scale												
Uplands	695.50	-	0.43	-	-9.17	-	4.66	-	-9.17	-	0.990	.001
Non-flooding F	R 137.21	8.96	-	-	-12.11	-	-	-	-	-	0.76 <	0.001
Flooding R	1.93	-	-	0.20	-	-	-	-	-	-	0.55 0	.022
All season R	131.00	5.84	-	-9.55	-	-	-	-	-	-	0.71 <	0.001
Whole region	209.31	-	-	-	-6.04	5.65	-	1.03	-	-10.65	0.53 <	0.001

#### Conclusion

The results of this research demonstrate that  $N_2O$  emission in soils was regulated by land use types, application of fertilizer and special weather conditions. Annual  $N_2O$  emission from R systems was higher than that of upland soils. Summer season had a significant lower  $N_2O$  emission than winter season. The controlling factors changed with the different scales. For R systems, the water regime and the concentration of  $NH_4^+$ -N in soil were the most important factor for  $N_2O$  flux. The concentration of  $NO_3^-$ -N and the WFPS in soil were the main factors of  $N_2O$  emission in G and G/M systems. At the whole region, the soil moisture was the important factor to drive  $N_2O$  emission.

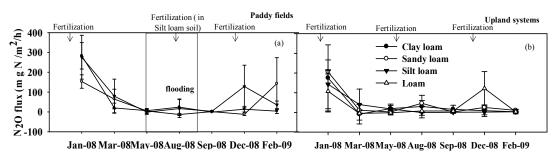


Figure 1. Seasonal patterns in  $N_2O$  emission at (a) paddy rice systems and (b) Maize and grass/maize rotation systems. Black error bar stands for standard deviation (n=3).

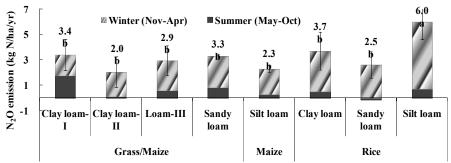


Figure 2. Annual N<sub>2</sub>O emission from different land uses. Black error bar stands for standard deviation (n=3).

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# The isolation and identification of useful bacteria that decrease nitrous oxide emission from agricultural field

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#### **Abstract**

Increases in atmospheric concentration of nitrous oxide (N<sub>2</sub>O) are partly attributed to soil denitrification. To overcome the problem, we propose utilising useful bacteria *in situ* to suppress N<sub>2</sub>O emission from agricultural soil by inhibiting the activities of microorganisms that produce high levels of N<sub>2</sub>O. The useful bacteria are the bacteria that convert nitrate ion (NO<sub>3</sub><sup>-</sup>) to another nitrogen compound under aerobic conditions, or aerobic denitrifyfing bacteria that reduce NO<sub>3</sub><sup>-</sup> to nitrogen under aerobic condition. Therefore, we attempted screening to find bacteria that have either of those properties, and then, four strains (K, N-I, N-II, and N-III) that could remove NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> under aerobic conditions were isolated and identified. Of the total nitrogen originally provided, 55% to 75% was taken up into the cells and the residual nitrogen went into the culture supernatant. The strains K, N-I, and N-II were identified as *Enterobacter cloacae*. The strain N-III showed 98.2% gene sequences identical to *Enterobacter cloacae* and 98.1% to *Klebsiella pneumonia*, indicating that the strain N-III has the potential to be a new species of bacterium.

## **Key Words**

Aerobic denitrifying bacteria, identification, nitrous oxide.

#### Introduction

Nitrous oxide  $(N_2O)$  has a 200- to 300-fold-stronger greenhouse effect than carbon dioxide  $(CO_2)$ . It has been reported that  $N_2O$  has the potential to destroy the ozone layer (Takaya *et al.* 2003). Recently, the concentration of  $N_2O$  in atmosphere is increasing. One of the proposed sources of  $N_2O$  is soil denitrification of nitrogenous compounds (Figure 1), resulting from excess agricultural fertilizer. The nitrate ion by fertilization is reduced by denitrifying bacteria to gaseous nitrogen  $(N_2)$  under anaerobic condition. However, the agricultural field is aerobic, so the reduction of  $N_2O$  to  $N_2$ , that is, the final step of denitrification, is suppressed by oxygen . Therefore, considerable amounts of  $N_2O$  are released in agricultural fields. To decrease  $N_2O$  emission, we propose dispersing useful bacteria over the agricultural field where the aerobic denitrifers grow and suppress activities of microorganisms that produce high levels of  $N_2O$ . The useful bacteria we propose convert  $NO_3$  to another nitrogen compound or denitrify releasing low levels of  $N_2O$  under aerobic condition. Therefore, we attempted the isolation and identification of bacteria that have either of those properties.

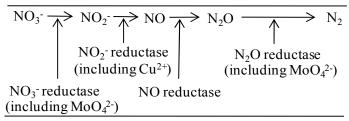


Figure 1. The given course of denitrification steps.

## **Materials and Methods**

Isolation of aerobic denitrifiers

At first, we collected 77 samples of rhizosphere soil from agricultural fields in Kurokawa, Machida, and Nishinomiya (Japan), and then transferred to them saline (0.8%) to adjust the suspensions. Some drops of the suspensions were transferred to 5 mL of screening media in flasks with cotton plugs, respectively and cultured by shaking at 130 rpm at 30 °C. The screening medium contained the following compounds: 0.1% NH<sub>4</sub>NO<sub>3</sub>, 2% Glucose (Glc), and trace metallic salts. Two of the trace metallic salts, molybdate ion (MoO<sub>4</sub><sup>2-</sup>) and copper ion (Cu<sup>2+</sup>), are needed for enzymes to catalyze some steps of denitrification (reduction of NO<sub>3</sub><sup>-</sup> to NO<sub>2</sub><sup>-</sup>, of NO<sub>2</sub><sup>-</sup> to NO, and of N<sub>2</sub>O to N<sub>2</sub>) (Figure 2). Bacterial growth, consumption of NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup> (N-

compounds), and Glc and production of NO<sub>2</sub> were monitored by quantitative analysis. After some independent experiments as described previously, positive strains were isolated and cultured further in 3mL of the same media at 130 rpm at 30 °C, to study the properties of isolated strains.

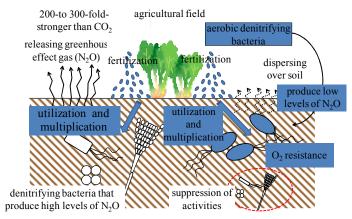


Figure 2. Suppression of releasing N<sub>2</sub>O by aerobic denitrifying bacteria.

Analysis of total nitrogen concentration in cultural supernatant and cells

Total nitrogen in the culture supernatant and the cells was determined by Kjeldahl apparatus.

## Identification of the strains

The 16S rRNA genes (1500 bp) from the total DNA extracted from the four strains were amplified by PCR. The PCR products were ligated into a pGEM-T easy vector and transformed into *Escherichia coli* cells and then, clones were sequenced. Sequence results were compared with reference sequences using DNA Data Bank of Japan (DDBJ) service.

## Results

Isolation of aerobic denitrifiers

It was found that four strains of 77 samples have the potential to be aerobic denitrifers and we defined the four strains as K, N- I, N- II, and N- III. N- III was able to remove more  $NO_3^-$  and  $NH_4^+$  than other three strains, so the result of N- III was shown in Figure 3. The remaining  $NO_3^-$ ,  $NH_4^+$ , and Glc in the medium decrease sharply for the first 20 hours. The production of  $NO_2^-$  was too little to detect. Although  $NO_3^-$  and  $NH_4^+$  were almost removed, the value of growth was under 6 (optical density at 660 nm  $[OD_{660}]$ ). This result may indicate that  $NO_3^-$  is not being assimilated because this would expect a growth value much higher than 6. To further study the nitrogen prevalence, the four strains were cultured in 50 mL of same media under same conditions. After  $NO_3^-$ ,  $NH_4^+$  were removed, to analyze total nitrogen, the cultural supernatant and cells were collected.

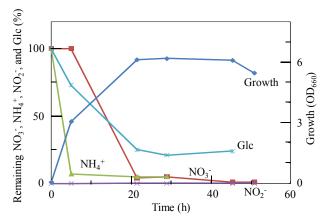


Figure 3. Growth profile of strain N-II and of N-compounds in the medium with MoO<sub>4</sub><sup>2-</sup> and Cu<sup>2+</sup>consumption

Analysis of total nitrogen in cultural supernatant and cells

Table 1. shows utilization of 0.1% NH<sub>4</sub>NO<sub>3</sub> (initially 1.24 mmol) and total nitrogen. *Paracoccus denitrificans* and *Pseudomonus stutzeri* were used as controls in that they are known to denitrify releasing

low level of  $N_2O$  under aerobic conditions. The controls removed almost all  $NH_4^+$  but did not remove  $NO_3^-$ . With the four isolated strains, 58% to 82% of the total nitrogen originally provided was observed in the cells and 18% to 42% of total residual nitrogen was in the cultural supernatants. Considering remaining  $NH_4^+$  and  $NO_3^-$ , it was found that the supernatants contained another nitrogen compound.

Table 1. Total nitrogen in cultural supernatant and cells

strain	Initial	(mmol	) Finish (mmol) re	emaining rate
	Sup.	Cells	Sup. (NO <sub>3</sub> -)(NH <sub>4</sub> +) Cells	(%)
K	1.24	0	0.60 (0.21)(0.04) 0.79	112
N-I	1.24	0	0.57 (0.15)(0.04) 0.75	106
N-II	1.24	0	0.33 (0.00)(0.03) 1.02	109
N-III	1.24	0	0.59 (0.14)(0.03) 0.73	106
Paracoccu denitrificar	s 1.24	0	1.00 (0.58)(0.04) 0.48	119
Pseudomon stutzeri	us <sub>1.24</sub>	0	1.08 (0.67)(0.05) 0.41	121

## Identification of the strains

All of the identification results of four strains are shown in Table 2. The strain K showed 99.0% identity to *Enterobacter cloacae* isolate 766 and 98.4% identity to *Enterobacter cloacae* B5. The strain N- I showed 99.1% identity to *Enterobacter cloacae* isolate 766. The strain N-II showed 98.6% identity to *Enterobacter cloacae* isolate 766 and 98.0% identity to *Enterobacter cloacae*. The strain N-III showed 98.2% identity to *Enterobacter cloacae* isolate 766 and 98.1% identity to *Enterobacter cloacae*. The strain N-III showed 98.2% identity to *Enterobacter cloacae* isolate 766 and 98.1% identity to *Klebsiella pneumoniae* strain TCCC1, indicating that N-III does not have significantly-high identity.

Table 2. The identification of strains K, N-I, N-II, and N-III

Isolate	Homologous strains	Identity (%)
K	Enterobacter cloacae isolate 766	99.0
	Enterobacter cloacae strain B5	98.4
N-I	Enterobacter cloacae strain FR	99.1
	Enterobacter cloacae isolate 766	98.6
N-II	Enterobacter cloacae isolate 766	98.6
	Enterobacter cloacae strain B5	98.0
N-III	Enterobacter cloacae isolate 766	98.2
	Klebsiella pneumoniae strain TCCC	C1 98.1

## **Conclusions**

Isolation of aerobic denitrifiers

Four strains removed  $NO_3^-$  and  $NH_4^+$  under aerobic conditions but by analysis of total nitrogen in the supernatant and cells, denitrification did not occur. Considering the remaining  $NH_4^+$  and  $NO_3^-$ , it was postulated that the supernatants contained another nitrogen compound.

#### Identification of the strains

The strains K, N- I, and N- II were identified as *Enterobacter cloacae*. The nucleotide sequence of 16S rRNA of N-III could not be identified with known sequences, so we conclude N-III has the potential to be a new species of bacterium.

## Acknowledgements

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## The role of biochar in reducing nitrous oxide emissions and nitrogen leaching from soil

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#### **Abstract**

This study examined the influence of four biochars on nitrous oxide (N<sub>2</sub>O) emission and nitrogen (N) leaching from the two contrasting soils (an Alfisol and a Vertisol) using repacked soil columns over three wetting–drying (W–D) cycles and two leaching events spanning five months. A control (acid-washed sand) was also included for each soil. The four different biochars used were:

- (i) W400 woodchip (Eucalyptus saligna) biochar prepared at 400 °C, non-activated
- (ii) PM400 poultry manure/rice hull biochar prepared at 400 °C, non-activated
- (iii) W550 woodchip (Eucalyptus saligna) biochar prepared at 550 °C, activated
- (iv) PM550 poultry manure/rice hull biochar prepared at 550 °C, activated

During the first two W–D cycles, W400 and W550 had inconsistent effects on soil N<sub>2</sub>O emissions; however, the soils amended with poultry manure biochars, especially PM400, generally produced higher soil N<sub>2</sub>O emissions, relative to the control. The greater initial N<sub>2</sub>O emissions from the PM400-amended soils (*cf.* control) can be ascribed to its higher intrinsic N content, which may be relatively labile, compared with the other biochars. Notably, during the third W–D cycle, all biochars, including PM400, consistently decreased soil N<sub>2</sub>O emissions (cumulatively by 14–73% from the Alfisol and by 23–52% from the Vertisol) than the control soil. In the first leaching event, after two months, none of the biochars influenced the leaching of NH<sub>4</sub><sup>+</sup>-N and NO<sub>3</sub><sup>-</sup>-N, except for PM400, which caused higher leaching of NO<sub>3</sub><sup>-</sup>-N than the other treatments. In the second leaching event, after four months, the leaching of NO<sub>3</sub><sup>-</sup>-N was not affected by the biochar treatments; whereas, leaching of NH<sub>4</sub><sup>+</sup>-N was significantly reduced by 55–93% from the W550- and PM550-amended Alfisol and Vertisol, and by 87–94% from the W400- and PM400-amended Vertisol. We hypothesize that the increased effectiveness of biochars in reducing N<sub>2</sub>O emissions and NH<sub>4</sub><sup>+</sup>-N leaching over time is due to an increase in sorptive properties as biochar 'ages' in soil through oxidative reactions on the biochar surfaces.

#### **Kev Words**

Biochar, nitrous oxide emission, nitrate, ammonium, leaching.

## Introduction

Soil biochar application is promoted as a climate change mitigation tool due to its potential to increase longterm soil carbon pools and reduce greenhouse emissions. Biochars are reputed to affect soil N transformation processes, but only a few studies have tested in detail the influence of biochars on soil N<sub>2</sub>O emissions and inorganic N leaching. Biochar is generally produced from biomass materials at temperatures between 300 to 600°C under partial or complete exclusion of oxygen (pyrolysis) and is considered highly resistant to biological degradation due to its increased chemical recalcitrance (aromaticity) compared with the parent biomass (Baldock and Smernik 2002). Biochars are highly porous, usually alkaline, and exhibit large specific surface area (Glaser et al. 2002; Downie et al. 2009). Oxidation of biochar in soil leads to the development of negatively-charged organic functional groups on its surfaces (Cheng et al. 2008). Due to these inherent chemical and physical properties, biochars can potentially influence a number of soil properties including soil pH, porosity, bulk density, and water holding capacity (Glaser et al. 2002; Chan et al. 2007). Furthermore, biochars sorb ions from soil solution by a combination of electrostatic, complexation, and capillary forces on their surfaces and in pores (Major et al. 2009; Moreno-Castilla 2004). These properties of biochars can potentially decrease leaching of nutrients from soil (Lehmann et al. 2003) and accessibility of ions to soil microorganisms. However, the influence of biochars on soil properties could be highly variable (Glaser et al. 2002) because biochar properties vary widely, depending on the biomass source and pyrolysis conditions (Baldock and Smernik 2002; Downie et al. 2009; Major et al. 2009).

Biochar application to soil could affect N<sub>2</sub>O emissions by (a) altering soil properties (e.g. pH, aggregation, CEC) and the availability and distribution of key electron acceptors (O<sub>2</sub>, NO<sub>3</sub>), and donors (NH<sub>4</sub><sup>+</sup>, dissolved organic matter), (b) inducing catalytic reduction of N<sub>2</sub>O to N<sub>2</sub> following oxidation and subsequent reactions of biochars with soil minerals and (c) influencing microbial community structures, and microbial enzymes and processes (N mineralisation-immobilisation turnover, nitrification, denitrification) involved in N cycling in soil (Šimek and Cooper 2002; Yanai *et al.* 2007 Van Zwieten *et al.* 2009). Some of these effects are expected to be a function of chemical composition (ratio of aromatic to aliphatic groups, intrinsic N content and form, ash content, etc.) and physical nature (specific surface area, porosity) of biochars produced from a range of biomass sources and pyrolysis conditions. Furthermore, through the development of charged functional groups on biochar surfaces during their oxidation, biochars may further affect abiotic and biotic N cycling processes governing soil N<sub>2</sub>O emissions. The aim of the present study was to assess the influence of four biochars on the emission of N<sub>2</sub>O and leaching of NO<sub>3</sub>-N and NH<sub>4</sub>+N from two contrasting soils subjected to 3 W–D cycles over a 5-mo period.

#### Methods

Four biochars, Agrichar<sup>TM</sup>, made from woodchips (W) or poultry manure + rice hulls (PM) at 400 °C, non-activated, or at 550 °C, activated, abbreviated as: W400, PM400, W550, PM550, were used; these biochars varied widely in important properties (pH 6.93 to 10.26; CEC 7.3 to 28.3 cmol(+)/kg; total C 415 to 802 g/kg; ash content 3.5 to 44.4%) (see further details in Singh *et al.* 2010). Biochars or acid-washed sand (control) were mixed with a sandy loam (Kurosol) and a clay (Vertosol) soil. According to the USDA Soil Classification, these soils are classified as an Alfisol and a Vertisol, respectively. Soil–biochar mixtures, adjusted to 0.85 water-filled pore space (WFPS), were repacked to 1.3 g/cm³ bulk density in PVC columns (Figure 1). Glucose-C and nutrient (N, P, K) solution were added. Gas samples were collected from the enclosed headspace and analysed for N<sub>2</sub>O. Following drying to ~0.3 WFPS, the soils were rewetted and gas sampling was continued. In total, soils were subjected to three W-D cycles during the five-month study period. Leachate was collected at the start of the second and third W-D cycles, and analysed for NH<sub>4</sub><sup>+</sup>-N and NO<sub>3</sub><sup>-</sup>-N.

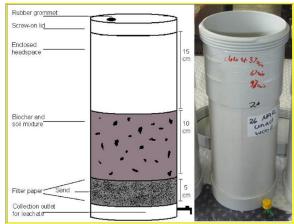


Figure 1. A schematic representation and photo of experimental column.

## Results

Nitrous oxide emissions

- During the first two W–D cycles, W400 and W550 had inconsistent effects on soil N<sub>2</sub>O emissions and the soils amended with poultry manure biochars, especially PM400, produced higher soil N<sub>2</sub>O emissions relative to the control. The initially greater N<sub>2</sub>O emissions from the PM400-amended soils (cf. control) initially can be ascribed to its higher intrinsic N content, which may be relatively labile, compared with other biochars.
- During the third W–D cycle, all biochar treatments consistently decreased soil N<sub>2</sub>O emissions, cumulatively by 14 to 73% from the Alfisol and by 23 to 52% from the Vertisol, relative to their controls.

## Nitrogen leaching

- In the first leaching event, biochars did not decrease the leaching of NH<sub>4</sub><sup>+</sup>-N and NO<sub>3</sub><sup>-</sup>-N from soils (cf. control); PM400 caused higher leaching of NO<sub>3</sub><sup>-</sup>-N than the other treatments, including control.
- In the second event, NO<sub>3</sub><sup>-</sup>-N leaching was not affected by the biochar treatments (*cf.* control); whereas, NH<sub>4</sub><sup>+</sup>-N leaching was reduced by 55–93% from the W550- and PM550-amended Alfisol and Vertisol and by 87–94% from the W400- and PM400-amended Vertisol.

## **Conclusion**

Results show that biochar application can be effective in reducing  $N_2O$  emissions and inorganic-N leaching from soils. The most effective biochars were: (a) both the low- (400°C, non-activated) and high-temperature (550°C, activated) wood biochars and (b) the high-temperature (550°C, activated) poultry manure biochar. Initially, in comparison with the control, the application of high-N poultry manure biochar synthesized at low temperature (400°C, non-activated) increased  $N_2O$  emissions and  $NO_3^-$ -N leaching whereas other biochar treatments either decreased  $N_2O$  emissions or did not affect inorganic N from soil. However, after four months, all biochars decreased  $N_2O$  emissions by up to 73% and  $NH_4^+$ -N leaching by up to 94%, relative to the control. We hypothesise that the increased effectiveness of biochars in reducing soil N losses is due to an increase in sorptive properties as biochar 'ages' through oxidative reactions on biochar surfaces and their subsequent interactions with soil minerals.

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# Topographical variations of soil respiration in the deciduous forest -In the case with extremely immature soil from weathered granite-

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#### **Abstract**

This study considers the time series data of soil respiration and its spatial variation in a small mountainous catchment which is located on complex terrain in Japan. Soil respiration rate was measured for 96 soil collars in the small mountainous catchment (1.6ha) in this study. The relationships between soil temperature, soil moisture content and measured soil respiration rate could be expressed by one function in spite that measured places were located at different topographical locations. The relative difference between calculated and measured soil respiration rate was 23%. The time series data of daily soil respiration was estimated by this function used with the monitoring data of soil temperature and soil moisture content ratio at 5 places in this cachment. These daily soil respiration rates fluctuated at almost the same time and relative variation ranges between 73-122% in one year.

#### **Kev Words**

Soil respiration, complex terrain, time series data, soil temperature, soil moisture content ratio.

## Introduction

In recent years, the eddy correlation method for measuring CO<sub>2</sub> flux has been used increasingly to evaluate the carbon uptake capacity of forests (e.g., Nakai et al. 2003). This method, however, is generally used for forests growing on flat terrain. Evaluating the carbon fixing of forests on the more topographically complex terrains typical of Japan requires measuring tower CO<sub>2</sub> flux, and comparing the value obtained with CO<sub>2</sub> flux measurements from both foliage and at the forest floor. For example, Kominami et al. (2003) measured CO<sub>2</sub> flux at night (CO<sub>2</sub> efflux measured from foliage and at the forest floor using the chamber method), when wind speed is low and atmospheric stability is high, and compared the results to tower flux using the eddy correlation method. Their results indicated that the estimated flux in the former case was only 40% of the latter, which suggests that CO<sub>2</sub> gas migrated down inclined surfaces due to its being denser than air. Thus, it is necessary to compare data on CO<sub>2</sub> flux at the forest floor with tower-flux data from above the forest canopy using the eddy correlation method. To do so, the evaluation of soil respiration rate as 1) time series data and 2) spatial representative data at the scale of small watersheds in mountainous terrains is required. This study focused on providing time series data on soil respiration rate, and on spatial variation in those data, by determining the relationships between soil respiration rate, soil temperature, and soil moisture content, based on multipoint year-round observations in a small mountain watershed. Soil temperature and soil moisture content can be monitored easily and nondestructively.

#### Methods

Site description

Measurements were conducted in the 1.6-ha Yamashiro Experimental Watershed (34°47'N, 135°50'E; 180–250 m ASL) in Japan. A broadleaf secondary forest covers the watershed and is dominated by *Quercus serrata*. In 1999, the total basal area occupied by stems larger than 3 cm diameter at breast height (DBH) was 20.7 m²/ha, and the aboveground biomass was 105.05 t /ha. From 1999 to 2002, the average litter fall was 5.16 t/ha/y, the average air temperature was 15.5 °C, the average monthly temperature was 5.1–26.1 °C, the warmth index was 125.6 °C ·month, and the average annual precipitation was 1,449.1 mm (Goto *et al.* 2003). Bedrock underlying the site is weathered granite, and the soil is generally sandy, immature, and thin (Araki *et al.* 1997).

Measurements of soil respiration rate, soil temperature, and soil moisture content The relationships among soil respiration rate ( $F_c$ ; mg  $CO_2/m^2/s$ ), soil temperature ( $T_s$ ;  ${}^{o}C$ ), and soil moisture content ratio ( $\theta$ ; m $^3/m^3$ ) are expressed by Equation (1):

$$F_{c} = aEXP(bT_{s})\left(\frac{\theta}{c+\theta}\right)$$
(1)

where 'a', 'b' and 'c' are constants.

Various methods have been proposed for measuring F<sub>c</sub>, including the dynamic closed-chamber method, the static closed-chamber method, the open-top chamber method, and the measurement of eddy correlation on the forest floor. The advantages and disadvantages of these methods have been compared by Norman *et al.* (1997). The present study used a manual chamber with an enclosed IRGA sensor, which is a highly portable system developed by Nobuhiro *et al.* (2003). This is a variation of the static closed-chamber method, and uses an IRGA sensor (GMT-222; VAISALA, Helsinki, Finland) inserted into a cylindrical chamber (diameter 9.1 cm, height 13.5 cm). The concentration of CO<sub>2</sub> in the chamber is measured every 10 s. F<sub>c</sub> is calculated from the increased CO<sub>2</sub> concentration, based on Irvine *et al.* (2002), although these studies did not use identical dynamic closed-chamber methods or static closed-chamber methods. After confirming that the CO<sub>2</sub> concentration in the chamber increased linearly, the soil respiration rate was calculated from the rate of increase. Actively photosynthesising plants were not present in all of the soil collars.

## Measurements to identify variables

In order to obtain data for identifying the constants a, b, and c used in Equation. (1), measurements were made at four plots (each 3 m  $\times$  0.5 m) on a ridge, a north-facing slope, a valley bottom and a south-facing slope (plots 1–4; Figure. 1) in the Yamashiro Experimental Forest. Each plot from 1 to 4 has Twenty-four soil collars (total of 96 collars). Spacing between soil collars was about 10–20 cm. Soil respiration was measured 74 times, with a frequency of one to four times per month between June 2002 and May 2003. Each measurement consisted of one respiration rate measurement for each of the 24 soil collars. Chamber attachment time was 32 min in the winter months (December 2002–April 2003), and 12 min for measurements during the rest of the year. The shorter time for chamber attachment is better. Because more frequent observation is possible. However, the digit of the  $CO_2$  concentration rate is 10ppm with the system in this study. Thus longer attachment time was needed to obtain the linear increased data of  $CO_2$  concentration when  $F_c$  was low in winter (Nobuhiro *et al.* 2003). The soil respiration rate was calculated using the values measured 2 min after chamber attachment.

One soil moisture/temperature sensor (HYDRA; Stevens Vitel, Chantilly, VA, USA) was buried near the center of each plot, and soil temperature and soil moisture content at a depth of 5 cm were measured at 10-min intervals from June 2002 to June 2003.



Figure 1. Topography and location of observation sites, Numbers show the location of the observation sites.

#### Results and discussion

Data used in identifying variables

 $F_c$ ,  $T_s$ , and  $\theta$  were used in identifying the variables to minimize the relative error indicated by Equation. (2):

$$RRSE = \frac{\sqrt{\Sigma(F_{cal} - F_{c})^{2}}}{\Sigma(F_{c})},$$
(2)

where  $F_{cal}$  is the calculated value for  $F_c$  and  $\Sigma$  is the sum of all applicable data.

The results yielded by Equation. (3), are: a = 0.0566, b = 0.0717, and c = 0.1089, with a RRSE of 23%:

$$F_{c} = 0.0566EXP(0.0717T_{s}) \left( \frac{\theta}{0.1089 + \theta} \right).$$
(3)

 $F_c$  and  $F_{cal}$  are indicated in Figure 2. A satisfactory result was obtained, with data plotting roughly along a 1:1 line. This supports the validity of using the functions given by Equation. (1) for this study.

The soil respiration rate is affected not only by soil temperature and soil moisture content ratio, but also by a

variety of other factors, including the amount of organic matter and roots in the soil, and the tree species present. The standard deviation of the soil respiration rate in the plots was large (roughly 20–40% of the average value), which was probably due to factors other than soil temperature and soil moisture content ratio. However, the  $F_c$  for all plots roughly matched the  $F_{cal}$  estimated from the soil temperature and moisture content ratio, as indicated in Equation. (3). This may indicate that effects due to factors other than soil temperature and soil moisture content ratio were canceled by averaging the measurements from the 24 soil collars. This issue will need to be investigated further.

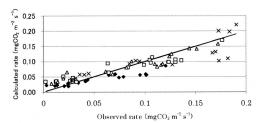
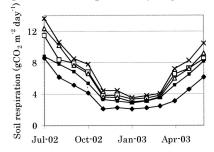
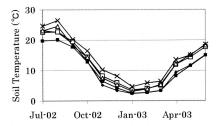


Figure 2. Comparison of observed  $(F_c)$  and calculated  $(F_{cal})$  rate of soil respiration, Black diamond: Plot 1, White square: Plot 2, White triangle: Plot 3, Cross: Plot 4.

## Estimation of annual soil respiration

The spatial variation in soil respiration rates was investigated by calculating and comparing rates at plots 1–5 from July 2002 to June 2003. The daily average soil temperature and soil moisture content ratio at 5 cm depth, as monitored at plots 1–5, were entered into Equation. (3), and the calculated value was taken to be the daily soil respiration rate. The average value for each month is shown in Figure. 3. The highest soil respiration rate for all months was in plot 4, the lowest in plot 1, and the second lowest in plot 5. This is because the soil temperature was low at ridge plots 1 and 5, soil moisture content was low at plot 1, and soil temperature was high at plot 4. The likely reason why soil temperature was high at plot 4 is that it is a south-facing slope with good sun exposure, and ridge plot 1 probably had a lower soil temperature because wind speed was comparatively high, causing major heat loss.





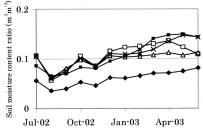


Figure 3. Estimated soil respiration rate in Plots 1-5, Upper: soil respiration, Middle: Soil temperature, Lower: Soil moisture content ratio, Black circle: Plot 1, White square: Plot2, White triangle: Plot 3, Cross: Plot 4, Black square: Plot 5.

Estimation of annual soil respiration rate and its validity

The validity of Eq. (9) was confirmed by comparing the annual soil respiration rate estimated using Eq. (9) against values given in previous reports. The cumulative value for 1 year, obtained from the average values for daily soil respiration rate, was  $21.3 \text{ t CO}_2/\text{ha}^2/\text{y}$ . The cumulative values obtained from maximum and minimum values were, respectively,  $26.0 \text{ t CO}_2/\text{ha}^2/\text{y}$  (122% of the cumulative value obtained from average values) and  $15.6 \text{ t CO}_2/\text{ha}^2/\text{y}$  (73% of the cumulative value obtained from average values).

#### Conclusion

This study has yielded an equation that estimates soil respiration rate using soil temperature and soil moisture content ratio with a precision of 25% (relative error). The equation was used to calculate time series data for daily soil respiration rate at four plots in a forest watershed. The four plots represented different topographical categories in the watershed (ridge, valley bottom, and south/north-facing slope), such that the time series and spatial variation results adequately reflect the overall characteristics and spatial variations within the Yamashiro Experimental Forest. For the purpose of evaluating spatial variation in time series data, it is best to have a high spatial density of measurements. Soil respiration, however, is difficult to measure at a large number of points. Fortuitously, we were able to estimate time series data on soil respiration rate based on soil temperature and soil moisture content, which are considerably easier to monitor. The time series data on soil respiration rate and its spatial variation from this study will be used in future work to evaluate the carbon-fixing capacity of forests on complex topographies by comparing them with time series data on CO<sub>2</sub> flux above the forest canopy.

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