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Development of site specific guidelines for future land use at the Woodcutters lead zinc mine

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Abstract
The National Environment Protection Measures (NEPMs) guidelines for soil contamination in Australia require further assessment if the Health Investigation Levels (HIL) are exceeded. It was identified that the current NEPM's do not provide accurate close out criteria for mined land as the bioavailability of contaminated soil is usually a fraction of 100%. Absolute bioavailability is measured via animal uptake but is expensive and time consuming. A more practical approach uses in-vitro PBET (physiologically based extraction test) to determine the bio-accessibility of individual soils. A risk assessment conducted on a metal and metalloid survey of surface soils representing different categories of mine wastes employed as risk assessment tools: (i) in-vivo bioavailability measurement of composite wastes using rats; and (ii) the in-vitro PBET (physiologically based extraction test) determination of bio-accessibility of individual soils. All mine waste samples were tested for bioaccessibility (PBET) under various pHs in a synthetic gastric fluid system. pH values were 1.3, 2.5 and 4.0 simulating fasting, partially fed and fed stomach conditions respectively, and at pH 7.0 simulating the small intestinal pH condition. The bioavailability of arsenic was 1.6 – 8.9% but arsenic bioavailability is dependent on its oxidation states. Arsenate (AsV), the oxidized form of arsenic, is more likely to be found in mine waste materials. Arsenate bioavailability from these mining wastes was found to be <5% whereas arsenite (AsIII) could be as high as 8.9%. Conservatively, 10% bioavailability for arsenic could be used for exposure assessment. The bioavailability of lead was 0.6 – 1.4%. Similarly, bioavailability of 2% was used for risk assessment purposes. In-vitro bioaccessibility screening level using the PBET method was the more conservative approach. Based on the risk assessment approach that was used site specific health investigation levels for arsenic and lead could be proposed that may be adopted for mined land and enable future land uses to be determined.

Key Words
Lead, arsenic, mining, soil, site-specific guidelines.

Introduction
Developing closure criteria for Woodcutters Mine in Northern Australia has involved multiple investigations to support site specific thresholds for a number of key indicators including available metals concentrations in soils. In Australia "Enduring Value" of the Mineral Council of Australia promotes the need to have rigorous mine closure programs well in advance of mining completion and identifies the need to have quantitative indicators of rehabilitation success.

Base metal mining is accompanied with requirements to ensure that effects of heavy metals and metalloids do not impact on human health and the environment as part of the closure process. Australia has national guidelines for soil called National Environment Protection Measures (NEPMs) (NEPC 1999) to give an indicative protective measure of from contamination of heavy metals and metalloids. When the designated soil guidelines are exceeded, a Tier 2 health risk (or ecological risk) study is required to measure bioavailability and determine the % total concentration that is available to human or other biota uptake. Bioavailability (BA) is measured by animal uptake experiments using rats but is an expensive process. An alternative is to measure the bioaccessibility (BAc) using a physiologically-based extraction test or PBET (Bruce *et al.* 2007). Rat bioavailability is used to calibrate and confirm the wider use of the PBET method.

The Woodcutters soil anomaly was discovered in 1966 and mining commenced in 1984. The Woodcutters Mine was operational from 1985 until March 1999, producing 539,000 tonnes of zinc; 245,000 tonnes of lead; 16 million ounces of silver for export; and 3,650,000 tonnes of ore. Ore production commenced from the open pit in 1985 and became an underground operation in 1986. Mining ceased in March 1999 when economic ore was depleted. Newmont Asia Pacific took over the Woodcutters site in February 2002 and have progressed the mine closure program for the site.

This study seeks to: (i) Identify key hazards to map extent of contamination from mining; (ii) Undertake studies of PBET to map contamination; (iii) Confirm reliability of bioaccessibility through bioavailability measurement (rats): (iv) Establish site specific guidelines based on bioaccessibility and bioavailability assessments; and (iv) Undertake further remedial works and confirm if mine closure is satisfactory.

Methods

A risk assessment was conducted based on a metal and metalloid survey of 60 surface soils representing 4 categories of wastes. In a soil survey conducted in September 2005, 60 soil samples representing 4 different categories of mine waste materials encompassing tailings, waste rock, processed material and contaminated ground. The soils were ground finely, digested in aqua regia and the concentration of each element determined by ICP-AES. Mean concentration data of various arsenic and metals in categories of mine wastes is summarised in Table 1.

Table 1. Concentrations (mean ± s.e.) of arsenic and metals in 4 categories of mine waste materials

Element (mg/kg)	Category 1	Category 2	Category 3	Category 4
Arsenic	180±50	1340±720	330±40	450±50
Cadmium	120±70	70±40	9±3	5±1
Cobalt	44±9	23±2	27±2	37±3
Copper	105±10	130±30	120±30	110±8
Nickel	120±16	52±8	65±8	110±9
Lead	840±280	5450±2700	870±230	550±80
Zinc	7800±2400	7700±4400	1200±470	820±120

Two different approaches were employed as the risk assessment tools: (i) in-vivo bioavailability measurement of composite wastes using rats; and (ii) the in-vitro PBET (physiologically based extraction test) determination of bioaccessibility of individual soils. All mine waste samples were tested for bioaccessibility (PBET) under various pH values in a synthetic gastric fluid system. pH values for the extraction tests were 1.3, 2.5 and 4.0 simulating fasting, partially fed and fed stomach conditions respectively, and at pH 7.0 simulating the small intestinal pH condition.

A desk top risk assessment was prepared focusing on metal concentrations which are higher than current health guideline values. In the absence of site specific bioavailability and exposure data, a worst case scenario initially is necessary to identify potential “hot spots” based on an accepted risk assessment framework (enHealth 2004).

In-vivo bioavailability test – rat study

The mine materials of each area were used to make a composite of equal amount of each element. Rats weighted at approximately 180 g each were divided into groups each of 4 rats. For positive controls, rats were injected intravenously using the salt solution and the other groups were given slurry of mine material by oral gavage. The mine materials were weighted for each rat separately according to the dose rate and body weight. The rats were kept in individual metabolic cages and were fasted over the night before the dosing day. The dose rates were: arsenic 0.5 mg/kg (in the form of sodium arsenate or sodium arsenite); and lead 0.01 to 2.7 mg/kg (lead acetate) dependent on waste concentration. Urine samples were collected 24 h prior to dosing and then daily over 10 days post dosing.

In-vitro bioaccessibility test – PBET

All mine waste samples were tested for solubilised fraction (bioaccessibility) under various pH values in a synthetic gastric fluid system (PBET – physiologically based extraction test). Mean percentages of bioaccessibility for arsenic, cadmium, cobalt, copper, nickel, lead and zinc from 4 categories of waste materials are shown in Table 2.

Results

Historical investigations into the distribution and concentrations of metals at the Woodcutters mine site indicate that there was an elevated natural background of various minerals. Accordingly, in 2006 site specific remediation guidelines were developed by EnTox following bioaccessibility studies. The approach adopted follows the procedure established by the NEPC (1999) and led to the further refinement of the proposed remediation guidelines (Table 2). The measure of % BAc using PBET and confirmed by rat bioavailability (%BA) on key soil types enable the development of site specific remediation guidelines and indicated that the extent of contamination was limited to a number of small discrete locations.

Table 2. Summary of guidelines for Woodcutters mine site remediation

Metal/metalloid	% BAc 2005	% BA 2005	%BAc 2006	NEPM Level E	EnTox 2006 Remediation Guideline
Arsenic	3-10	1.6-8.9	2-22	200	1000
Cadmium	17-30	-	1-46	40	80
Cobalt	6-18	-	6-18	200	1,000
Copper	5-13	-	4-22	2000	10,000
Lead	10-18	0.6-1.4	11-38	600	1,500
Nickel	4-17	-	4-17	200	2,000
Zinc	23-27	-	10-36	14,000	40,000

Although the EnTox 2005 soil survey results for total Pb and As were relatively high in the rehabilitated areas, the results for % BAc indicated that the contamination was not a significant health risk (Table 1). Only Cd at one site and Pb at 4 sites were considered to be contaminated and significant compared to the EnTox 2006 remediation criteria.

Conclusion

The investigation and development of site specific thresholds demonstrates that careful examination of specific source characteristics and receiving context can greatly improve the focusing and application of resources in closure processes. This had a significant bearing on the focus and extent of remediation activities and success of this mine closure process.

Acknowledgements

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Extraction of cyanide from soil using alkaline phosphate solutions

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Abstract
A large amount of cyanide has been produced and used in a variety of industrial processes such as metal plating, gas production, mining and pigment production. Cyanide in the environment has attracted a concern due to its high toxicity. Toxicity and mobility of cyanide in soil strongly depend on its form. Chemical oxidation and biological degradation are commonly adopted for the remediation of cyanide contaminated soil. The chemical oxidation with the direct injection of oxidants revealed a limited remedial efficiency due to the degradation of oxidants by organic matter, manganese oxide and sulphide and to the low oxidation rate of adsorbed metal cyanide complex and solid metal cyanide. A new oxidation technology combined with soil washing to improve remedial efficiency is under development. For the first step in technology development, we tested the soil washing efficiency of alkaline phosphate solution. The tested solutions were 0 – 100 mM Na-orthophosphate, Na-hexametaphosphate and Na-pyrophosphate and the solution pH was adjusted to be 10 – 12 with 1N NaOH and 1N HCl. The kinetic study and the washing efficiency test were tested 1soil and 5washing solutions. After the reaction, the pH and the concentrations of cyanide species (free, weak acid dissociable, strong acid dissociable) and metal of washing solution were determined. The cyanide extraction sharply increased with reaction time for 100 minutes and then the cyanide extraction slowly increased. The cyanide extraction increased with pH and phosphate concentration. The cyanide extraction efficiency of phosphate solution at the same pH follows: pyrophosphate > hexametaphosphate > orthophosphate. More than ninety percent of the total extracted cyanide was strong acid dissociable (SAD) cyanide. The optimum cyanide extraction solution among the tested solutions was pH 12_30mM pyrophosphate. However, the extracted As increased with increasing the cyanide extraction. It implies that an additional wastewater treatment process is required for As removal.

Key Words
Cyanide species, Alkaline phosphate solution, Soil washing, As dissolution.

Introduction
Chemical oxidation is one of the commonly adopted methods for the remediation of cyanide contaminated soil. For the chemical oxidation, the oxidants such as H_2O_2, ozone and hypochlorite are directly injected into the contaminated soil to destroy cyanide (Akcil 2003). Free cyanide is easily destroyed but SAD cyanide and solid metal cyanide are resistant to the oxidation. The injected oxidants also are consumed by organic matter, manganese oxide and sulfide. For those reasons, the application of chemical oxidation frequently failed to achieve the remedial goal. We are developing a new chemical oxidation method combined with soil washing to overcome the limitation of existing chemical oxidation method. The new method consists of the extraction of cyanide from the contaminated soil by washing and the oxidation of separated cyanide in the solution. The extraction of cyanide from soil is strongly controlled by the type of cyanide. The cyanide in soil exists as free cyanide, metal cyanide complex and metal cyanide solid (Kjeldsen 1998). Free cyanide can be exists as $HCN_{(g)}$, $HCN_{(aq)}$ and CN^-. HCN is the dominant species at pH < 9.24 but CN^- is the dominant species at pH > 9.24. CN^- is weakly adsorbed on the soil particles. Iron cyanide complex [$Fe(CN)_6^{3-}$] is the most common species of metal cyanide complexes and has a high affinity to soil organic matter and oxides. Iron-iron cyanide {$Fe_4[Fe(CN)_3]_3$} is the most common solid phase of cyanide in soil. The adsorption of free cyanide ion and iron cyanide complex in soil is mainly controlled by the surface charge of variable charge mineral and organic matter. Previous study (Rennert and Mansfeldt 2002) on the adsorption of those species showed the adsorption decreases with increasing pH. The solubility of iron-iron cyanide is mainly controlled by the pH and redox potential and increased with increasing pH (Meeusen *et al.* 1992). We tested the cyanide extractability of alkaline phosphate solution and determined the optimum condition of the extraction solution.

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Methods

Collection and characterization of soil sample

A soil sample was collected from an abandoned gold mine site in Korea and the collected sample was stored in a light tight glass bottle at 4 ˚C for the further analysis and experiment. Mineralogical composition of the sample was determined with X-ray diffraction analysis. The pH and the concentrations of water soluble major cations, anions and heavy metals were determined with a pH meter and an ICP-AES after the reaction of 1 soil and 1 distilled water for 24 hours. The content of total S was determined with an S analyser and the contents of total cyanide, weak acid dissociable (WAD) cyanide and free cyanide were determined with the ASTM method. The cation exchange capacity was determined with the Ca-Mg method and the ignition loss was determined by heating at 450 ˚C.

Extraction of cyanide with alkaline phosphate solution

The extraction solutions were prepared with Na-orthophosphate, Na-heaxmetaphosphate and Na-pyrophosphate at 0 – 100 mM and the pH was adjusted to be 10 to 12 with 1N NaOH or 1N HCl. Four grams of soil and 40 ml of the extraction solution were reacted and the solution was separated with centrifugation and filtration after a presetting time of reaction. The concentrations of total cyanide, WAD cyanide and free cyanide of the separated solution were determined with the ASTM method. The concentration of SAD cyanide was determined by the subtraction of free cyanide and WAD cyanide from total cyanide. The pH and the metal concentration of the solution were determined with a pH meter and an ICP-AES, respectively.

Results

Quartz, feldspar and mica were the major minerals in the soil sampled. The cyanide extraction sharply increased with the reaction time for 100 minutes and then, increased more slowly. The extracted cyanide increased with increasing pH and phosphate concentration of the solution (Figure 1). The extraction sharply increased with phosphate concentration up to 30 mM and slightly increased at greater than 30 mM. The cyanide extraction capacity of the solutions at same pH follows: pyrophosphate > hexametaphosphate > orthophosphate. Greater than 90% of the extracted total cyanide consists of iron cyanide complex dissolved form iron-iron cyanide solid. Trace amount of free cyanide was extracted with the alkaline phosphate solution. The As dissolution during the reaction between the soil and the solution showed the same pattern of cyanide extraction. The extracted Cu, Zn, Pb, Ni, Al, Mn and Fe increased with increasing phosphate concentration and decreasing pH.

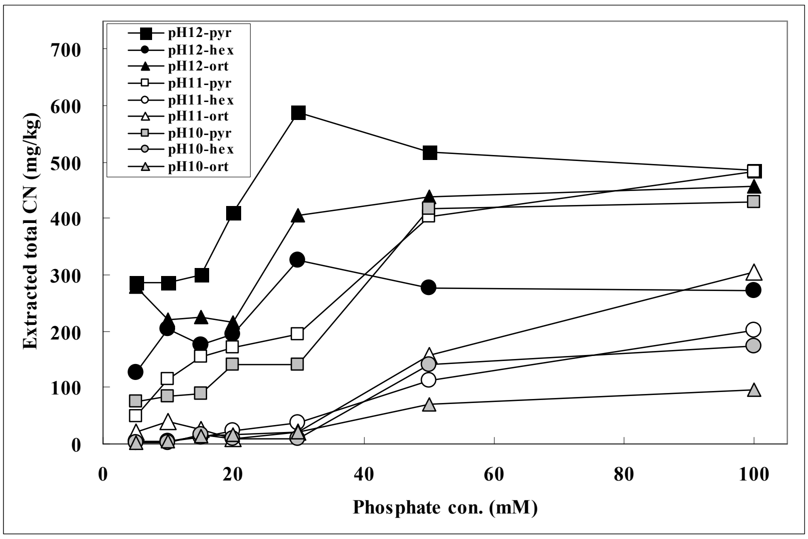

Figure 1. Extracted total cyanide from the soil using alkaline phosphate solutions.

Conclusion

The pH 12_30 mM Na-pyrophosphate solution was the optimum cyanide extraction solution from the soil. In addition to the cyanide oxidation treatment for wastewater, an As removal process might be needed for the safe discharge of the solution.

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Gardening on Brownfields Sites: Evaluating trace element transfer from soil to plants and their transformations in soils

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Abstract
Tens of thousands of brownfields (abandoned or underutilized properties where known or potential environmental issues are an obstacle to redevelopment) can be found in cities, towns, and rural areas across the USA. Our work has focused, in part, on the conversion of brownfields to garden areas and is motivated by the increasing interest in locally produced foods. Challenges of converting brownfields to community gardening sites will be discussed using one newly established urban community garden site located in Kansas City as an example. This site had mildly elevated levels of lead (Pb) and some detectable levels of dichlorodiphenyltrichloroethane/ dichlorodiphenyldichloroethylene (DDT/DDE). Suitable safety/corrective measures were suggested and implemented after thorough evaluation of soil properties. Measures focused on reducing both direct (soil-human) and indirect (soil-plant-human) exposure of Pb and/or DDT/DDE to the gardeners and their children. In addition, field test plots were established within the community garden and three crop types with three very different growth and contaminant uptake patterns were planted. Effectiveness of selected site-specific soil amendments to reduce bioavailability of Pb will be evaluated. Different methodologies will be utilized throughout the project to understand the significance of potential soil-plant-human exposure pathway of contaminants while gardening on mildly contaminated sites. Efforts will be made to understand relationships between key soil properties and contaminant bioavailability.

Key Words
Brownfields, trace elements, bioavailability

Introduction
Vacant or abandoned properties with real or perceived contamination issues are called “brownfields”. In the U.S., approximately 450,000 brownfields sites cover an estimated 5 million acres (2 million hectares). Since 1995, the Environmental Protection Agency (EPA) provides funds for assessment and cleanup to bring these sites back to beneficial use. Our work focuses on the potential conversion of brownfields to garden areas and is motivated by the increasing interest in locally produced foods. In the U.S.,there was a 6.8% increase in farmers markets between 2006 and 2008, with 4,600 such markets in 2008, and approximately 18,000 community gardens present in the U.S. and Canada Gardening on brownfields presents challenges beyond more typical brownfields redevelopment projects because of increased chances of human exposure to contaminants through direct soil ingestion and indirect food-chain transfer. Lead from the use of leaded paint and gasoline, arsenic (As) from arsenate pesticides along with dichlorodiphenyltrichloroethane (DDT) and chlordane can be most common and significant contaminants. It is apparent that most of the community gardening groups interested in gardening on brownfields are disproportionately located in urban areas. Many of the brownfields that are candidates for urban gardening were formerly residential areas.
It is well known that the total concentration of trace elemental and other contaminants in the soil environment and/or plants does not strongly correlate to bioavailability or potential toxicity. Therefore, a careful assessment of site specific contaminants and soil characteristics is essential for designing suitable safety measures required for minimizing the direct or indirect transfer of contaminants to the gardeners.
Our objective is to work with select community-based gardening initiatives to evaluate uptake of trace elements and other contaminants by food crops and to develop recommendations for seedbed preparation and corrective/protective actions to address potential contaminant transfer to food crops and consumers.

Materials and Methods
Evaluation of sites throughout the U.S. to be included in this project is on-going. Several suitable sites have been identified thus far and one of them will be discussed below as an example.
The Washington Wheatley (WW) site in Kansas City, Missouri is located in a residential neighborhood. The site is approximately 42m x 37m and was formerly occupied by four residences. The site was screened for trace metals using a hand-held x-ray fluorescence spectrometer (XRF). Screening locations were established

by using a 10 feet grid system, including 39 screening locations, to facilitate generating spatial distribution maps of trace elements of interest. GPS was used to log the exact screening pointsBased on the screening results, soil samples were collected at four locations showing the highest trace element readings. The soil samples were collected from two depths (0-15 cm and 15 to 30cm) for analysis of selected soil chemical properties (available N, pH, electrical conductivity (EC), organic C (OC) and available phosphorus (P) using appropriate procedures (Sparks 2005)) and confirmation analyses of total trace elemental concentration in soils. Additionally, three soil samples (C1 through C3, Figure 1) were initially collected for chlordane analyses and six (C4 through C9, Figure 1) additional soil samples were collected later for DDT and dichlorodiphenyldichloroethylene (DDE) analyses.

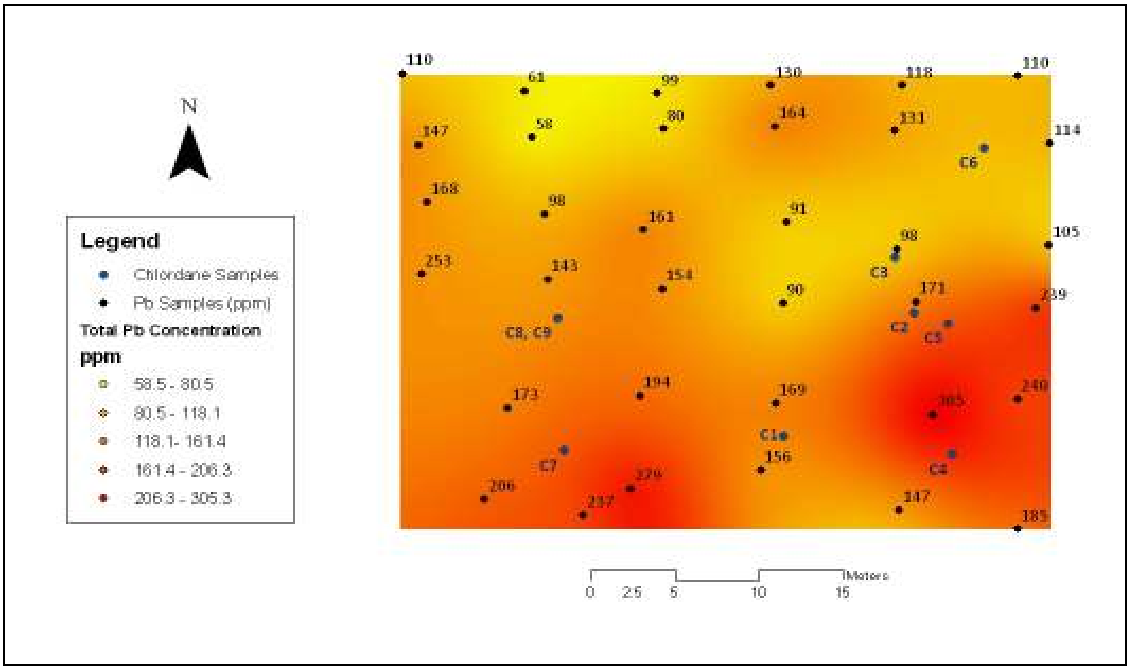

Figure 1. Total Pb concentration map of the Washington Wheatley site generated using the Pb concentrations measured by the portable x-ray fluorescence analyzer. Soil sampling locations for DDT and DDE (C1 through C9) are also shown.

Test plots were established in early June for the summer 2009 gardening season and initial soil samples from each subplot (18) were collected. The basic experimental design was a split plot design with three replications. The main plot factor was compost treatment (2, no compost or compost added) and was arranged in a randomized complete block. The subplot factor was plant type. The three vegetables planted were Swiss chard (cultivar Gator Perpetual Spinach, seed was obtained from Fedco, Waterville, ME), sweet potato (cultivar Beauregard sweet potato from Kansas State Research and Extension Center, Haysville, KS) and tomato (cultivar Biltmore from Seminis, Oxnard, CA). At the end of the growing season, plants were harvested from test plots as well as from some randomly selected community gardening plots located in the site. Two cleaning methods was applied to the harvested plant material: One subset of plant materials was only washed once with deionized water (to mimic the "kitchen style washing") while the second subset was thoroughly cleaned following the laboratory cleaning procedure described in Hettiarachchi *et al.* (2003). Dried and ground plant materials were digested with trace metal grade, concentrated HNO_3 acid (4 hours at 120^{o}C) and the filtered digest solutions were analyzed for trace elements using an ICP-AES or GF-AAS. Soil samples collected at the end of the growing season will be analyzed for various soil parameters including pH, EC and the extractable metals to assess changes in soil chemistry after the growing season. Moreover, Pb bioavailability will be determined with a modified physiologically based extraction test (PBET) to determine the effects of soil amendments (compost).

Results and Discussion

All the sites evaluated so far are located in urban or sub-urban environments. Most commonly found trace element contaminant was Pb. It was apparent from the site history and previous land use that Pb based paint and leaded gasoline could be the most probable sources of Pb in these environments. Out of those sites, the WW site in Kansas City was available for gardening in the summer 2009. Results and discussions are focused on the WW site.

All three soil samples collected from WW site for chlordane analysis showed chlordane concentrations were non-detectable. While analyzing for chlordane, however, it was found that all samples contained detectable amounts of DDT ranging from 0.04 mg/kg to1.3 mg/kg. DDE was detected in two of the submitted samples at 0.03mg/kg and 0.04 mg/kg, respectively. Initial in situ XRF analysis showed elevated levels of Pb in soils. A spatial distribution map of lead levels in soil across the site was prepared from the XRF data (Figure 1). The color scheme employed utilizes dark orange for high concentrations and light orange-yellow for low concentrations. The distribution of Pb was highly heterogeneous and there were several areas of high Pb concentration hotspots scattered thoughout the site. Laboratory results were in close agreement with the in situ XRF analyses and showed elevated lead concentrations of up to 352 mg/kg (Table 1). The soil pH ranged from 6.6 to 7.6 and therefore, no pH adjustments was recommended for this site. Mehlich-3 extractable phosphorous (P) concentrations ranged from 57 mg P/kg (high) to 154 mg P/kg (excessive). Addition of organic matter was recommended for this site (one fourth by volume). Moreover, a variety of methods to reduce any potential risk associated with relatively immobile soil contaminants such as Pb and DDT was recommended to the WW community gardeners. Some of those were: root vegetables should be washed and peeled before consumption; all other vegetables should be thoroughly washed prior to consumption; removal of outer leaves of leafy crops before cleaning.

Table 1. Selected chemical properties of soils collected from the surface 0 to 15 cm (S) and 15 to 30 cm deep (D).

Sample ID	pH[†]	Mehlich-3 P	Available K	Available NH_4-N	NO_3-N	Pb[‡]	OM[§]
		mg/kg					%
9S	6.6	130	624	53.6	73.2	243	3.9
9D	6.6	93	455	9.6	35.1	352	3.4
21S	7.2	116	417	11.8	22.7	117	3.0
21D	7.2	123	221	9.3	15.0	129	3.1
26S	7.8	57	255	8.3	4.3	80	1.5
26D	7.6	80	260	8.2	2.2	60	1.1
39S	6.9	154	488	15.0	24.2	237	4.7
39D	6.9	149	334	9.6	13.3	207	3.3

[†]1:1 Soil: Water
[‡]by 4M HNO_3 acid digestion followed by analysis using ICP-AES
[§] by dry combustion on a LECO CN2000 elemental analyzer

Total soil Pb concentration in the subplots that received compost treatment was lower compared to the subplots that did not receive any compost. This difference can be explained through a dilution effect due to the addition of compost (Table 2) and this would be an added advantage of this treatment in addition to the expected decrease in Pb bioavailability. Concentrations of Pb in Swiss chard (a well known heavy metal accumulator) were far below the maximum permissible level for leafy vegetables in both for no compost and compost added treatments (Table 3). Compost addition reduced the Pb concentrations in Swiss chard ~44 to 49% compared to the no compost treatment. Cleaning method appeared to have some influence on the potential Pb transfer from plants to consumers. Discussions on effects of compost treatments on soil pH, EC, PBET will also be presented. Relationships between plant Pb uptake and extractable Pb will be developed.

Table 2. Lead concentrations in soils, determined by 4M HNO_3 digestion, after compost treatments. Analysis performed on ICP-AES.

Main plot Treatment	Subplot treatment (plant type)	Total Pb concentration (mg/kg)
Compost	Swiss Chard	81.2 ± 4.2†
	Sweet Potato	101.6 ± 16.3
	Tomato	96.5 ± 10.8
No compost	Swiss Chard	95.3 ± 12.6
	Sweet Potato	130.3 ± 10.3
	Tomato	123.1 ± 21.1

† ±standard error of three field replicates

Table 3. Concentration of Pb in Swiss chard (μg/kg, dry weight basis). Analysis performed on GF-AAS.

Main plot treatment	Cleaning method†	Pb concentration (μg/kg)
Compost	Kitchen	311.92 ± 69.67‡
	Lab	259.27 ± 21.83
No compost	Kitchen	523.67 ± 138.43
	Lab	392.87 ± 82.15

† Two cleaning methods was applied to the harvested plant material
‡±standard error of three field replicates

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Human health problems related to trace element deficiencies in soil

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Abstract
Human health problems related to deficiency of essential trace elements are discussed. The most extensive problems, affecting one billion people or more worldwide, are associated with inadequate supply of iodine, selenium, and/or zinc. These problems are commonly occurring in, but not limited to, developing countries, and may fortify effects of other health-related problems such as famine and infectious diseases. Future developments in food production to meet the needs of an increasing world population should not neglect the content of essential trace elements in the products.

Key Words
Trace element deficiency, human health, developing countries, iodine, zinc, selenium.

Introduction
Soils can adversely affect human health in several ways. The organism can be affected directly by soil ingestion or inhalation of soil particles, or by contact through wounds. Moreover the soils may contain chemical elements and substances, either naturally or through pollution, that are toxic to humans and animals by excessive intake. On the other hand, many soils may contain too small quantities of essential elements in plant-available form to provide adequate supply to plants, animals, and in the end, man (Deckers and Steinnes 2004). For every essential element there exists a range of safe and adequate human intake. Any supply in excess of this may be toxic. On the other hand intake below this range is likely to cause deficiency problems and in extreme cases death. This range of optimal intake varies among the essential elements and may be considerably narrower for some elements than for others. There is a vast literature on soil pollution with toxic substances and the risk to human health. The most severe case worldwide is probably the excessive lead contamination of urban soils mainly from leaded petrol, which has been shown to significantly affect children´s blood lead levels (Mielke *et al.* 1997). Still problems related to deficiencies in mineral elements are even more widespread and affecting perhaps as much as one third of the population in the world. These problems are generally most abundant in developing countries where people depend largely on locally grown food, often in combination with a general food shortage. Such problems may be expected to continue and even become more serious in a world where a rapidly increasing population depends on food produced on a steadily decreasing agricultural area.

The major mineral elements needed by living organisms, namely sodium, magnesium, phosphorus, sulfur, and chlorine, rarely represent any deficiency problem in humans. However, man and his livestock also depends on a number of elements present in the body only in trace concentrations but still being absolutely necessary for the fulfillment of essential functions in the body. If these elements are not supplied in sufficient amounts through food and drinking water, serious health problems may become evident. This paper, therefore, is concentrated on the essential trace elements. Deficiency problems related to trace elements are also relatively common in agricultural crops. Only exceptionally are these elements added to commercial fertilizers. A soil deficient in one or more essential trace elements may not only reduce the yield of agricultural crops growing on it but also lead to less transfer of the elements to humans or livestock. Trace elements essential to plants but not to humans or animals may thus indirectly affect human health either directly or through the livestock.

Trace element deficiency problems
The elements present only in trace concentrations in the human body but still having a well-defined biochemical function are chromium, cobalt, copper, iodine, iron, manganese, molybdenum, selenium, and zinc. The same elements are also essential to mammals, including most domestic animals. Human health problems related to trace element deficiencies are particularly widespread for iodine, selenium, and zinc, and this paper is therefore focused on those three elements.

Iodine

The span between low and high iodine soils is very large, from about 15 mg/kg in organic-rich soils near the coast (Låg and Steinnes 1976) to less than 1 mg/kg in areas far inland. The major mechanism of iodine transfer from ocean to land reflects preferential volatilization of seawater iodine into the atmosphere (Fuge 2005) and the most likely source seems to be the release of volatile methyl iodide by marine organisms (Yoshida and Muramatsu 1995). The relative role of wet and dry deposition of iodine on land surfaces is not clear (Fuge 2005) and little is known with regard to the quantities of marine iodine carried to areas remote from the sea. Iodine has long been known as an essential element for humans and mammals, where it is a component of the thyroid hormone thyroxene. Insufficient supply of iodine may lead to a series of iodine deficiency disorders (IDD), the most common of which is endemic goiter. Iodine deficiency during pre-natal development and the first year of life can result in endemic creatinism, a disease which causes stunted growth and general development along with brain damage. This brain damage may occur even when there is no obvious physical effect, and probably represents the most widespread current geomedical problem on Earth with as much as 1.6 billion people at risk (Dissanayake 2005). The areas of the world currently most affected by IDD are largely located in developing countries of Africa, Asia, and Latin America (Fuge 2005), mainly in areas located far from the ocean. Even in some affluent countries of Western Europe however it has been suggested that as much as 50-100 million people may be at risk (Delange 1994).

Selenium

Selenium concentrations in soils show extreme geographical variations. This along with a narrow range of safe and adequate intake means that problems have been identified in humans and livestock both in relation to selenium deficiency and excess. In USA there are large areas in the Great Plains where selenium-rich soils are present and some plants may reach levels toxic to livestock. On the other hand the selenium-deficiency related disorder white muscle disease in animals has been commonly observed in several states of the northeast as well as the northwest of USA (Muth and Allaway 1963). China is another country where soils show extremely variable selenium contents geographically (Fordyce 2005), and where significant problems inn humans are evident both in low-selenium and high-selenium districts. Geographically widespread endemic diseases such as Kashin-Beck disease, an endemic osteoarthropathy resulting in chronic arthritis and deformity of the joints, and Keshan disease, a cardiomyopathy whereby the heart muscle is damaged, were both associated with selenium deficiency (Tan and Hou 1989). Rice appeared to concentrate Se more efficiently from the soil in these areas than other local food crops, and people on a rich rice diet showed less selenium deficiency symptoms that people with other eating habits. Recently selenium supplementation to the affected populations has reduced these health problems substantially. It has been indicated that certain iodine deficiency and selenium deficiency problems in humans may be interconnected (Kohrle 1999, Fordyce 2005).

Also in the developed countries the selenium status varies considerably among different populations, depending on the composition of the diet. Around 1970 the incidence of cardiovascular disease in Finland was among the highest in the world, and it was hypothesized that low selenium might be one of the reasons. A large-scale experiment adding selenium to fertilizer was therefore initiated. This led to increased selenium content in bread grain as well as milk, and eventually an increase of serum selenium concentration in the population to the level assumed to be optimal (Hartikainen 2005). Låg and Steinnes (1974; 1978) found that selenium in forest soils of Norway decreased regularly with distance from the ocean from around 1.0 mg/kg near the coast to <0.2 mg/kg in areas shielded from marine influence, suggesting that the marine environment might be a significant source of selenium to coastal terrestrial areas. This seemed surprising considering the extremely low content of selenium in seawater (0.1 µg/L). Cooke and Bruland (1987) however, studying the chemical speciation of dissolved selenium in surface water, observed the formation of volatile organo-selenium compounds, mainly dimethyl selenide, $(CH_3)_2Se$, and hypothesized that out-gassing of dimethyl selenide may be an important removal mechanism for dissolved selenium from aquatic systems. Thus, in a similar way as for iodine, it may seem that biologically driven transport from the ocean to continental areas naturally low in selenium may be a significant factor alleviating selenium deficiency problems.

Zinc

Zinc is an essential trace element required by all living organisms because of its critical roles both as a structural component of proteins and as a cofactor in enzyme catalysis (Leigh Ackland and Michalczyk 2006). According to Alloway (2005) zinc deficiency is the most widespread essential trace element deficiency in the world, perhaps affecting as much as one third of the world´s human population. Large areas of the world have soils that are unable to supply staple crops, such as rice, maize, and wheat, with sufficient zinc. In several countries large proportions of the arable soils are affected by zinc deficiency, such as in India where around 45% of soils are deficient in zinc (Singh 2001). Zinc deficiency in humans was first observed and reported among rural inhabitants of the Middle East in the early 1960's (Nauss and Newberne 1982). Dietary zinc deficiencies are also found in industrialized countries such as USA (Nauss and Newberne 1982) and Sweden (Abdulla *et al.* 1982). Moderate zinc deficiency has been cited as a major etiological factor in the adolescent nutritional dwarfism syndrome in the Middle East, the cardinal features of which are severe delay of sexual maturation and dwarfism (Hambidge *et al.* 1987). Recently it was suggested that fetal Zn deficiency contributes to the pathogenesis in adults (Maret and Sandstead 2008).

Concerns for the future

Regional differences in chromium, copper, iron, iodine, selenium, and zinc in the human diet occur both in developed and developing countries, but their effects are usually more evident in the latter, largely because of malnutrition and reliance on local food products (Oliver 1997). Moreover effects of infectious diseases are likely to be more serious in a population already suffering from imbalances in the diet. The total extent of problems related to trace element deficiencies in developing countries is potentially very large, and further work is required in order to identify the full scale of these problems and eventually solve them. However, the main problem in the 21st century related to human nutrition is obviously the still rapidly increasing population worldwide. At the same time the area of agricultural land is decreasing, due to factors such as urbanization, desertification, and increased soil erosion. During the last few decades the global human population growth has been outpaced by a dramatic increase in amount of food produced per area of land, facilitated by the use of high-yielding crop varieties, chemical fertilizers and pesticides, irrigation, and mechanization (Matson *et al.* 1997). The strong agricultural intensification however has also had several negative effects worldwide (Foley *et al.* 2005), and the production potential of existing agricultural land has been affected by reduced soil fertility in many areas. This development may also have depleted the soil with respect to plant-available forms of essential trace elements. In order to secure the food supply to the next generations it may be necessary to change land-management strategies e.g. by increasing agricultural production per unit land area, per unit fertilizer input, and per unit water consumed. This could be possible e.g. by changing the diversity of crop species and further genetic improvement of key species. There are reasons to believe that the success of such food production changes may be measured mainly in quantitative terms, i.e. in produced tons or calories. It appears important however that the quality of the product, i.e. the distribution of essential nutrients, be given appropriate weight. This also includes the essential trace elements discussed in the present paper, and appears to be particularly important in future projects related to improvement of food production in developing countries.

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Melioidosis case clusters in a tropical urban setting: Association with soil type and geomorphology

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Abstract
Geospatial analysis of the distribution of clinical cases of melioidosis, an often fatal tropical disease, in the Townsville region indicated case clustering in distinct geomorphic settings and characteristic soil associations. Two significant clusters were identified. Cluster 1 is associated with piedmont slopes adjacent to granitic hill and mountain slopes. The soils developed on colluvium are typically Kandosols with dark grey-brown loamy sand to silty loam A horizon, grading into dark red or yellow sandy clay loam to sandy clay subsoils. Cluster 2 is associated with Pleistocene floodplains, levees and channel-fill. The duplex soils typically grade from acidic to alkaline at depth. These soils are poorly draining due to a shallow impermeable B horizon in Sodosols. It is postulated that the two geomorphic positions and soil types are predisposed to soil wetness following periods of intense rainfall. Cluster 1 is located where large amounts of runoff are received from the adjacent granitic hill, whereas Cluster 2 associates with poorly drained soils at the lower edges of poorly drained alluvial plains. This preliminary study has generated the hypothesis that melioidosis distribution in the Townsville region is controlled by environmental factors, specifically soil type, geomorphic position and drainage. A detailed multidisciplinary field-based study investigating soil physico-chemical features, field isolates of *Burkholderia pseudomallei*, and epidemiological considerations is now underway to test this hypothesis.

Key Words
Melioidosis, soil type, GIS, disease cluster, environment

Introduction
Melioidosis is a potentially fatal bacterial infection endemic across northern Australia, southeast Asia and other parts of the tropics (Currie *et al.* 2008). The causative organism is the soil borne bacterium *Burkholderia pseudomallei*. Clinical manifestations of melioidosis range from localised infection to its most acute form of rapidly fatal fulminant sepsis. Despite the initiation of intensive therapy, mortality remains at 21% in patients with melioidosis in Australia (Currie *et al.* 2000). Contact with soil or contaminated water is believed to be a precursor to disease onset and cases occur mainly in association with periods of heavy rain during the wet season, in northern Australia between January and May (Thomas *et al.* 1979; Currie and Jacups 2003; Cheng *et al.* 2005).

Melioidosis is an environmental disease (Inglis *et al.* 2001). Biogeochemical factors will determine the geographic distribution of *Burkholderia pseudomallei* in its environmental setting. Pathogenicity, exposure and acquisition modes and human physiological response will determine disease distribution and presentation. Significant progress in understanding the human response to exposure to *Burkholderia pseudomallei* is being made (Wiersinga *et al.* 2006), but our understanding of the environmental conditions that determine the geographic range of the bacteria, and hence areas of risk for human activity, is limited (see Inglis and Sagripanti 2006; Palasatien *et al.* 2008).

Within North Queensland, the city of Townsville and its suburbs are overrepresented in cases of melioidosis (Malczewski *et al.* 2005). Anecdotal evidence suggested that the distribution of melioidosis cases based on residential addresses clustered in particular suburbs. A pilot project (Corkeron *et al.* 2009) sought to test this idea and identify any potential environmental features geospatially associated with clusters. The aim of this study was to test whether regional environmental parameters such as geological substrate, soil type, geomorphology and drainage correlate to case clusters in Townsville.

Methodology
This study utilised a GIS framework (ArcMap 9.3; ESRI Inc. Redland, Ca) to integrate regional data sources

including elevation, geology, local soil classifications, drainage systems, roads, Australian Bureau of Statistics population census data and cadastral data. A 12-year melioidosis case distribution database from the Townsville region (based on residential addresses) was linked to the cadastral layer. Soil data and distribution was derived from previous soil mapping and soils reports on the Townsville region (Murtha, 1975; 1982).

Results

Within ArcGIS the case distribution was compared against the general urban population distribution using Ripley's K-function. Two significant case clusters were identified (Clusters 1 and 2, Table 1) and a third minor cluster noted (Cluster 3, Table 1). Geospatial comparison of case distribution with soil and geomorphic features allowed identification of key landscape units associated with case distribution (Figure 1). Cluster 1 is associated with the soils formed in the colluvium from the granite out crop at Castle Hill and Mount Stuart. This cluster is identified in the 'piedmont slope and uplands' landscape unit. Cluster 2 is associated with Pleistocene alluvial soils and identified in the 'older alluvial plain, fan and channel infill' landscape unit. Within this cluster, several cases are associated with 'younger alluvial terraces and channel infill'. Cluster 3, with 12 cases, is associated with 'beach ridges and littoral' landscape unit.

Table 1. Key environmental parameters associated with disease clusters.

Parameter	Cluster 1	Cluster 2	Cluster 3
No. of cases	18 (27.7%)	35 (53.8%)	12 (18.5%)
Landscape Unit/ Geomorphology	Piedmont slopes and colluvial fans derived from granitic hills.	Both Holocene and Pleistocene alluvial plains, terraces, levees, in-filled channels and meanders.	Frontal beach ridges, swales and salt pans.
Geology	Castle Hill Granite. Biotite leucogranite, microgranite; minor granophyre, granodiorite.	Stratified alluvial clay, silt, sand and gravel	Siliceous and calcareous sand, some carbonate nodules
Soil types	Mostly Kandosols. Dark grey-brown loamy sand to silty loam A horizon, grading into dark red or yellow sandy clay loam to sandy clay subsoils. Some Kurosols, light grey brown sandy loam A horizon with abrupt change to mottled brown-yellow heavy clay B horizon.	Pleistocene alluvium mainly Sodosols. Abrupt texture contrast between sandy or silty loam A horizon and sodic clay B horizon. Mottling and redoximorphic features common in B horizon. Frequent Kandosols in recent alluvium, sandy loam A horizon grading to sandy loam and clay loam.	Rudosols and Tenosols, mostly as beach ridges. Minimal pedological development. Loose pale brown loamy sand grading into light brown or yellowish brown loose single grain sand. Occasional Sodosols in swales between ridges, associated with salt pans.
pH and drainage	Acid topsoil and subsoil. Fair drainage, but high risk of short-term water logging after heavy rainfall due to landscape position at base of Castle Hill. Higher risk of water logging for Kurosols.	Acidic A horizons, and alkaline, sodic subsoils, poor drainage due to shallow, impermeable B horizon in Sodosols, frequent seasonal water logging. Kandosols are acid throughout, lack impermeable B horizon, high soil moisture due to proximity to river.	No detailed soil information available. Drainage from ridges is good, but poor in Sodosol swales and saltpans.
Elevation and proximity to drainage	Hilly and mountainous elevation from ~300-600m asl. Cases confined to elevations from 40m to ~ 10 m asl. Localised gully drainage; colluvium and soil development localised to break of slope, mostly on lower slopes.	Low elevation across coastal plain; ~ 25 m asl in headwaters and ~ 5 m asl in lower reaches. Proximity to streams and creeks; soil associations (defined by Murtha, 1972) occur parallel to modern drainage. Pleistocene soil associations are commonly adjacent to modern streams and creeks. The modern fluvial system dominating the Townsville flood plain is geomorphically consistent with the ancient fluvial system.	Less than ~5 m asl. Dune systems sporadically cut by meandering mangrove creeks. In undeveloped areas, swales may be inundated by king tides and flood events.

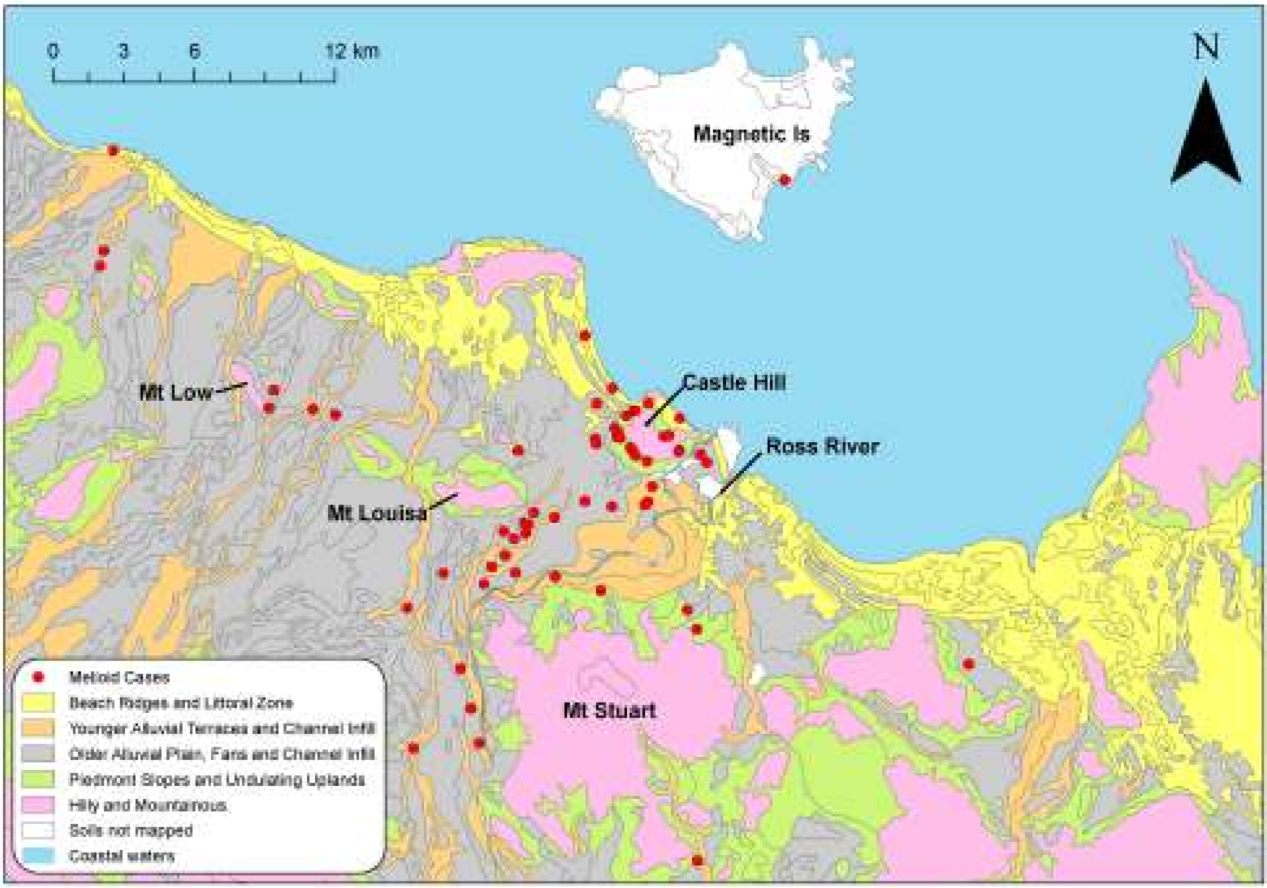

Figure 1. Case distribution in the Townsville region and distribution of associated landscape units (see Table 1 for descriptions). Adapted from Corkeron *et al.* (2010).

Discussion and Conclusions

The cases in Cluster 1 primarily occur on piedmont slopes (3-15%) of colluvium derived from the granitic Castle Hill. The soils are prone to erosion, and gullies dissecting the soils are common. A complex association of soil types has formed in this landscape unit, but the most frequent soils are mildly acidic gradational soil types (Kandosol) and less frequent Kurosols. These soils, commonly developed on the break of slope, likely experience transient waterlogging when large amounts of runoff are received from the adjacent granitic hill during the wet season.

The majority of cases in Cluster 2 are associated with soils with a clay-rich B horizon (sandy clay-heavy clay texture) within 40-50 cm of the surface. Most common of these clayey soils are Sodosols (25 out of 35 cases), texture contrast soils with an alkaline B horizon and a coarser textured mildly acidic A horizon. They have formed in Pleistocene floodplain, levees and channel infill. These soils are prone to waterlogging, as shown by the common mottling and redoximorphic features of the B horizons. Minor cases are associated with Kandosols, which occur in the recent alluvium, mainly as terraces, levees and channel infill. These typically have sandy clay loam A horizons grading to sandy loam and clay loam. Considering the environmental preferences of the pathogen (acidic, high soil moisture; Palasatien *et al.* 2008), this suggests that the pathogen is most likely to occur in the acidic, coarse A horizons of clay-rich soils which are prone to water logging, i.e. in the top 30-40 cm of the soils.

Cluster 3, comprising 12 cases, occurs in areas mapped as beach ridges and littoral zone. Soils on the ridges have been classified as Rudosols and Tenosols, poorly developed soils formed in siliceous and calcareous sands of marine origin. While the sandy Rudosols and Tenosols occuring on the beach ridges are well-drained, this is not the case for the Sodosols which are found in some of the swales and salt pans between beach ridges. These swales may represent localised areas of waterlogging. However, Corkeron *et al.* (2010) noted that 6 of these cases in this cluster are from nursing home addresses, probably reflecting human risk factors over environmental factors as drivers for disease acquisition.

This study demonstrates a geospatial relationship between disease distribution and identifiable soil and geomorphic features, as well as underlying geology, presumably a significant control on clay composition in overlying soils. This association supports the hypothesis that soil is the environmental reservoir of *B. pseudomallei.* Whereas an association between *B. pseudomallei* and particular soil properties in the North Queensland area was first reported in 1979 (Thomas *et al.* 1979), the precise ecological niche of *B.pseudomallei* is unclear. In the Northern Territory there is a demonstrated association between environmental isolates and the presence of grasses, disturbed soil, acid pH, livestock usage and soil texture (Kaestli *et al.* 2009). In endemic areas in Thailand, sandy soils, soil pH, depth of at least 30cm, moisture content of >10%, higher total nitrogen and oxygen demand, all predispose to finding the organism in soil (Palasatien *et al.* 2008).

Future research will extend this project to a field-based program in Townsville to delineate geomorphic features in detail, and fully characterise soil types within a geomorphic framework. A microbiological analysis integrated with the soil study will attempt to isolate *B. pseudomallei* at soil sampling sites, and at variable depths within the soil profile. Thus, the distribution of the causative organism in the environmental reservoir can be directly correlated with soil properties and case distribution. Resolution of the physico-chemical parameters that characterise soils with positive bacterial isolates may clarify processes of pathogen-soil interaction, providing a foundation for understanding the ecology of the pathogen within its environment.

Whereas understanding the environmental aspect *B. pseudomallei* lifecycle is essential to understanding the pathogenesis of melioidosis, linking disease distribution to environmental controls is complicated by predisposing human health factors and socioeconomic influences. For this reason, an epidemiological analysis of case characteristics as recorded by the Tropical Public Health Unit in Townsville will also be undertaken and synthesised with the environmental findings. The multidisciplinary approach in this case-study will provide findings and a research template applicable to other melioidosis endemic sites in Australia and developing tropical countries such as Thailand and Papua New Guinea, where health burden is not well supported by health resources.

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Nitrate Situation in Some Vegetables and the Necessity of Crop Production via Organic Farming

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Abstract
Nitrate is potentially harmful regardless of the source. Commonly, vegetables are considered as one of the resources causing the nitrate to enter the body. The object of this research was to determine the amounts of nitrate in cucumber, carrot, lettuce, tomato and potato in the greengroceries at southwest region in Shiraz city (South of Iran). Samples were collected from seven different places in April, May and June 2008. After the sample preparation, the amounts of nitrate were measured. Finally, the concentration of nitrate in samples was compared with the World Health Organization (WHO) standards. The results showed that the amounts of nitrate in many of sampled vegetables are higher than accepted standards. April is a critical time for nitrate accumulation in harvested vegetables. Cucumber, potato and tomato had much more nitrate than the standards. It can be concluded that for healthy crop production a move to organic farming is a necessity for governments and farmers.

Key Words
Vegetables, Nitrate Levels, Biofertilizers, Shiraz.

Introduction
Globally, human nitrogen production has increased rapidly since 1950 and currently exceeds nitrogen fixed by natural sources by about 30% (Fields 2004). Nitrogen is the nutrient applied in the largest quantities for lawn and garden care and crop production. Fertilizer is the largest contributor to anthropogenic nitrogen worldwide. In addition to fertilizer, nitrogen occurs naturally in the soil in organic forms from decaying plant and animal residues.

Nitrate is essentially harmless. However, certain kinds of bacteria in the digestive tract change the nitrate into nitrite, a much more harmful substance. Human exposure to nitrates and nitrites results primarily from dietary ingestion, particularly from vegetables and cured meats.

A potential cancer risk from nitrate (and nitrite) in water and food has been reported. A study in humans showed that nitrate in vegetable matrices and from other sources, such as drinking-water, is almost totally bioavailable. The bioavailability of nitrate from spinach, lettuce and beetroot was high and not significantly different from that of nitrate in drinking-water (Lambers *et al*. 2000). After ingestion, nitrate is readily absorbed from the upper gastrointestinal tract. Up to 25% is actively excreted in saliva, where about 20% is converted to nitrite by bacteria in the mouth (Spiegelhalter *et al*. 1976). This conversion can occur at other sites including the distal small intestine and the colon.

A possibility exists that nitrate can react with amines or amides in the body to form nitrosamine which is known to cause cancer. Nitrate must be converted to nitrite before nitrosamine can be formed.
When nitrate levels in drinking water are below the current regulatory standard, the large majority of individual's nitrate intake is from vegetables rather than water (ECETOC 1988). The half-life of nitrate in the body is over 8 hours, which means that after a meal containing spinach, lettuce or another source of nitrate, the levels in the blood will be elevated for about 40 hours (McKnight *et al.* 1997).
The aims of this investigation were study of the nitrate levels in supplied vegetable crops in some stores and comparisons of obtained data with standards.

Methods

This investigation carried out with vegetables including cucumber, carrot, lettuce, tomato and potato in southwest of Shiraz city (South of Iran). Samples were collected in three times (April, May and June 2008) from seven greengrocery stores. After washing with tap water and distilled water, moisture contents of samples were determined at 60 °C. Dried samples were powdered with grinder and 0.5gr of powdered samples were poured in 50ml of distilled water mixed and shake for 30 minutes. The mixture was filtered by paper filter. Then 0.1gr of MgO and 0.1gr of Devardo Alloy added to 5ml of filtered extract and shake for 30 minutes. Eventually, the amounts of nitrate were measured by Kjeldahl method. The total means of obtained data for each vegetable were compared with World Health Organization standards (WHO 1976).

Results

The means of nitrate content in vegetables shown in table 1 for three events. Data shown in column 2, 3 and 4 are the means of 7 measurements and data shown in column 5 are the means of 21 measurements.

Table 1. The means of nitrate in different vegetables (mg/kg of fresh weight).

Vegetable	April 2008	May 2008	June 2008	Total mean	WHO standard
Cucumber	1021	794	203	673	150
Carrot	539	454	99	364	415
Lettuce	1873	804	637	1105	2001
Tomato	1272	799	754	942	300
Potato	1091	702	178	657	250

The whole of sampled vegetables except lettuce contain nitrate higher than WHO standards in April and May, but in June, only cucumber and tomato had higher nitrates than WHO standards.

According to table 1, it is obvious that the amounts of nitrate in many of sampled vegetables are higher than accepted standards. For example, the nitrate content in cucumber was 1021 mg/Kg in April. This shows the nitrate content in cucumber was 5.8 times higher than standard (WHO 1976). The same calculations for potato and tomato show 3.4 and 3.2 times compared to standards. The amounts of nitrate in studied vegetables decreased with time. It seems that April is a critical time for producers and consumers. Total mean comparisons show that almost sampled vegetables (except lettuce) have nitrate higher than standards. Vegetables are the major source of the daily intake of nitrate by human beings, supplying about 72–94% of the total intake. Part of this nitrate-N is converted to nitrite and N-nitroso compounds that have detrimental effects on human health (Gupta *et al*. 2008).
Some vegetable species such as lettuce, spinach, beetroot, celery, eggplant, beet, banana, strawberry, tomatoes and peas are known to accumulate high concentration of nitrate under heavy fertilization (Gupta *et al*. 2008). Being a rich source of nutrients and antioxidants, leafy vegetables occupy an important place in the human diet. However, attention should be paid to fertilization managements. Probably, abuse application of nitrogen fertilizers i.e. use of higher amounts of urea than the needs of plants is responsible for this crisis. It is suggested that remove of chemical fertilizers subsides and obligate the farmers for soil testing. Nitrate fertilizer applied shortly before harvest causes the greatest increase in nitrate levels and should be avoided. In addition, lack of precision in harvest time can be as the second factors. Attention to organic farming via application of green manures, animal manures, composts, biofertilizers and conservation tillage could be mitigating the present problems.

Conclusion

Management practices such as proper fertilizer application follow the soil testing and deleting the chemical fertilizers subsides and use of organic materials and biofertilizers to reduce the risk of nitrate accumulation help keep the produced crops safe.

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Selenium concentration in soil of Iran

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Abstract
Selenium (Se) plays a key role in the maintenance of normal health in human population. This micronutrient is a crucial nutrient for human health. Se enters the food chain through plants and its concentration in foods is determined by a number of geological and geographical factors. The content of Se in food depends on the Se content of the soil where plants are grown or animals are raised. Since no precise report has been drawn up on Se status for soil and water in different regions of Iran, this research measured soil Se in selected areas of North, South, and Center of Iran (from east to west) for continuing complementary research in the future. Sampling was performed in 51 locations. 17 samples of surface cultivated soil (at depth between 0-20 cm) were collected in each area. Upon preliminary preparation of samples at a research laboratory, the Se rate was measured with ICP-OES Model Varian Vista-MPX. The results of this study demonstrate that some parameters such as rainfall conditions in sampling time, rainfall condition in the days before sampling, the elevation above sea level of sampling points, spraying poison condition, and irrigation methods such as underground water, subterranean, dry farming had significant effects on soil Se rates.

Key Words
Selenium, soil, Iran, rainfall situation, pesticide used, type of irrigation.

Introduction
Selenium (Se) is a trace element that depending on its concentration, it is both toxic and an essential part of nutrition. Se, as an essential part of nutrition was first reported in 1957 by Schwarz and Foltz, who called it factor 3 (Schwarz and Foltz 1957). Factor 3 is an operational name given to an incompletely characterized selenium-containing natural product that, in minute amounts, prevents liver damage in rats due to deficiency of vitamin E. Se is an essential trace element that is an integral part of many proteins, with catalytic and structural function. The antioxidant properties of some selenoproteins, such as glutathione peroxidase, may be particularly important in carcinogenesis and heart disease. The content of Se in food depends on the Se content of the soil where the plants grown or animals are raised. In accordance with the outcomes generated by several surveys, it has been specified that, Se deficiency resulting from Se relates to the high risk of diseases such as cancer, cardiomyopathy, myocardial deaths, arthritis rheumatoid, as well as the lesions affected on failure-to-thrive (F.T.T.) (Rayman 2000; Clark *et al.* 1996; Willett *et al.* 1983; Alissa *et al.* 2003; Bergqvist *et al.* 2003; Altekin *et al.* 2005; Kosar *et al.* 2006). The aim of this study was to measure Soil Se concentration in some areas on North, South, and Center (from east to west) of Iran for the first time.

Materials and methods
Sampling was performed on north, south, and central (from east to west) regions of Iran. Using map of Iran and specifying length of sampling route, dimensions were computed 850 km northward; 2000 km southward, and 2350 km toward the central region, approximately. Consequently, the taken samples were determined in northern region at an approximate distance of 50 km; in southern region at an approximate distance of 118 km and in central region at an approximate distance of 138 km.

In every selected area in North, South, and Central of Iran, 17 samples of surface soil (at a depth of 0-20 cm) samples were collected at the points indicated in Figure 1. In this study, cultivated soil was collected. A questionnaire related to geographical and regional special particulars such as rainfall situation, pesticide used, types of irrigation, and elevation of sampling points were used and filled. Samples are kept in special sampling vessels, refrigerated, and sent to the research laboratory of Faculty of Science, Faculty of Chemistry, Tehran University to determine Se rate. Upon preliminary preparation using Aqua Regia digestion method for soil samples, the Se rates were measured with ICP-OES Model Varian Vista-MPX. The results were statistically analyzed through SPSS Ver. 11 to determine the relations between Se concentrations and the data collected by questionnaire.

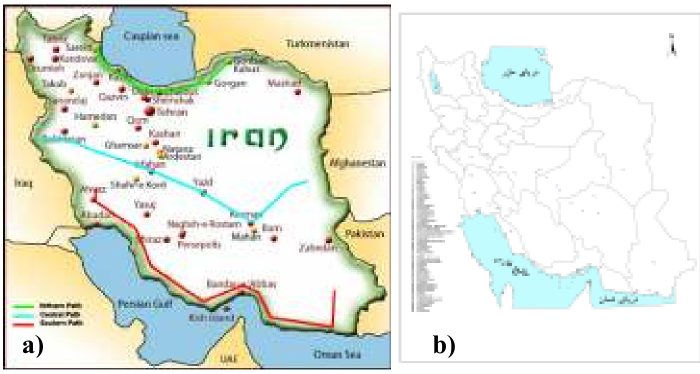

Figure 1. Soil Selenim sampling paths(a) and points(b) of Iran.

Results

Results demonstrated that, there are a statistical significant difference between the mean of soil Se in the different selected areas of North, South, and Center of Iran (Sd = 0.08)(PV <0.0001). The highest mean of total soil Se in north of Iran was seen in Astara – Abassabad areas with (0.28 ppm Se), Ramsar, and Gonbadkavos (0.27 and 0.25 ppm Se) respectively, and the lowest mean soil Se was belonging to Sari and Kord Koy (0.04 and 0.05 ppm Se) respectively (Figure 2). The highest total soil Se in South of Iran was seen in Behbahan with (0.41 ppm Se) and Omidiye and Chahbahar (0.39 and 0.39 ppm Se) and the lowest total soil Se were belonging to Bandare Khamir and Jahloo Kenare (0.15 and 0.16 ppm Se respectively) (Figure 3). The highest total soil Se in center of Iran was seen in Yazd with (0.45 ppm Se) and Shabab and Kerman (0.36 ppm Se) and the lowest mean soil Se were belonging to Nay Band and Daran with (0.11 and 0.12 ppm Se, respectively) (Figure 4).

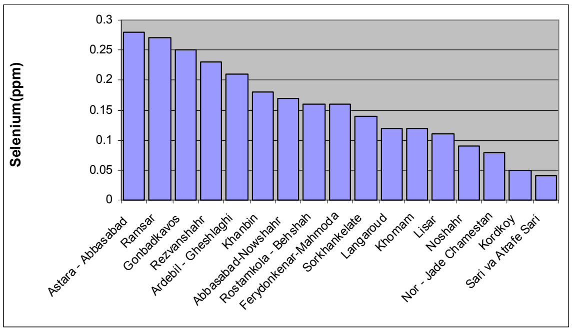

Figure 2. Mean of total soil Se in selected areas of North of Iran (2006-2007).

According to the WHO classification (< 0.05 ppm total soil Se = deficiency), the rate of soil Se in 2 areas in North of Iran (Sari and surburbs, Kord Koy, 0.04, 0.05 ppm total soil Se respectively) were at the range of low or deficient. But in according to the Tan's classification, the rates of soil Se in 10 regions of total 51 soil samples in North and Center of Iran were less than < 0.15 ppm Se, and are thus low or deficient in Se. Most of the soil samples (n = 32) in North, South, and Center of Iran (62%) were classified in moderate values of

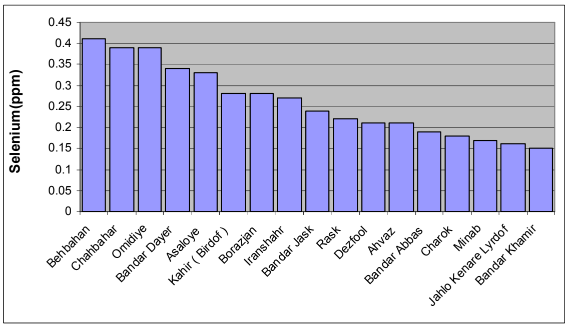

Figure 3. Mean of total soil Se in selected areas on the South of Iran (2006-2007).

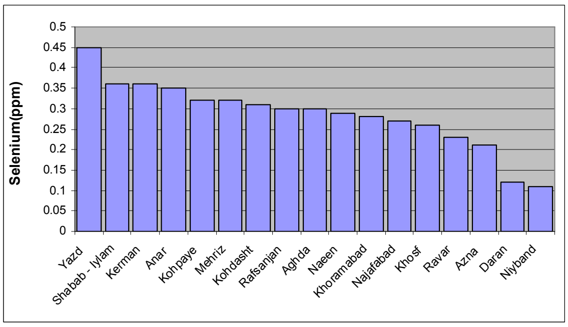

Figure 4. Mean of total soil Se in selected areas of Center of Iran (2006-2007).

total Se in the soils (0.175-0.40 mg/kg total soil Se). The total soil sample of 11 areas have low Se rates (< 0.15 ppm soil Se, (21.56%) and in the six areas the amount of total soil Se were be low and deficiency (11%) but total soil Se in Yazd, in Center, and Behbahan in South of Iran were 0.45 and 0.41 ppm which categorized in high Se rate (> 0.40 ppm Se)(Tan *et al.* 1994). A total soil Se content exceeding 0.5 ppm could be regarded as potentially toxic (Kubota and Allaway 1972; Pureves 1985). There are statistical significant difference between soil Se rate in North, South and Center of Iran and rainfall status in selected areas (PV <0.001). In high rainfall areas = (0.18 ± 0.019 ppm Se). In low rainfall areas = (0.28 ± 0.016 ppm Se). Between the total mean rate of soil Se and the kind of irrigation, there was a significant statistical difference. To this case, in the areas which were cultivated by dry farming, the mean rate of soil Se was more than the regions that irrigated by underground water, subterranean. There are statistical significant differences between the mean soil Se rate in North, South, and Center of Iran, and the height of region from the sea level, that is the areas which had (200–1000 meter height from the sea level) the highest total mean soil Se rate (0.30 ppm Se) in comparison with the regions that had lower total mean soil Se rate (0.16 ppm Se) with elevations under the sea level. There were statistical significant difference between the mean rate of soil Se and the use of spray poison: the mean soil Se rate in the areas that spray poison, at least once a year was higher than the regions where spraying poison has never been performed (P<0.021).

Discussion

Se is a trace element used in proteins, in the form of the twenty-first naturally occurring amino acid (selenocysteine) (Science News 2008). The major determinant of Se status in humans is the level of available Se in the soil, where plants are grown or animals are raised. (Rayman *et al.* 2000; Combs *et al.* 2001). Most Se ingested by animals and humans comes from the soil, through plants. Levels of Se available in soils are highly variable globally. Areas that are notably low in Se include parts of China, Siberia, Central Africa, Eastern Europe, and New Zealand (Combs *et al.* 2001). Although large areas have not yet been mapped for Se, it is apparent that many people have too little Se to support maximum selenoenzyme expression (Rayman 2002). In this study, for the first time it was found that, there were significant difference among the total soil Se rate in selected areas of North, South, and Center of Iran. The highest total soil Se was found in central regions of Iran, and the lowest amount was found in the north of Iran. Se in many European countries is relatively low due to the low soil Se concentrations or poor bioavailability of soil Se in a great part of Europe (Bugel *et al.* 2008).

Comparison of the rates of total soil Se levels in three parts (North, South, and Center) of Iran showed that, the lowest level was in the North regions of the country. Bioavailability of Se may have fallen in the areas subject to acid rain or excessive artificial fertilization of soils, in which, both of them reduce plant absorption of the mineral (BMJ 1997). Findings were in accordance to the results of above research. As it has demonstrated, there were the statistical significant differences between the soil Se rate in North, South, and Center of Iran and rainfall status in selected areas (PV <0.001). In high rainfall areas = (0.18 ± 0.019 ppm Se). In low rainfall areas = (0.28 ± 0.016 ppm Se). Also, this study showed that, in some areas in North of Iran, where the soil was poor in Se. For this reason there is a need to do more researches in these regions. Finland is the first country decided to increase the Se content of Finnish feed and food by the addition of sodium selenate to fertilizers, at a concentration of 16 or 6 mg/kg for cereal and grassland crops, respectively (Koivistoinen and Huttunen 1986). Total average water Se level in all of selected areas in North, South, and Center from east to west of Iran was less than 0.010 ppm. WHO's Guidelines for drinking water quality - the international reference point for Standard Setting and drinking water safety- set up in Geneva, in 1993, demonstrated that Se can be normally found in fresh water/surface water/ ground water is less 0.01 mg/L Therefore, Se in water samples was in a standard setting (Lenntech 1998). WHO set the health-based guideline for Se in drinking water at 10 μg/L (WHO 2004, 2006).

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Sinister soils and risky rhizospheres: The ecology of melioidosis and other soil-borne infections

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Abstract
The danger of soil borne human infection is not only seasonal. It has a patchy distribution over a huge geographic range, causing problems with accurate risk modelling. Infections resulting from environmental exposure are caused by organisms that can persist in the soil for a long time either as spores or by relying on an internal nutrient store. There is a remarkable lack of hard data on the occurrence of soil borne human diseases. Melioidosis is a soil-borne disease of surprises. In its most severe form, it presents as a systemic bloodstream infection with or without pneumonia. The microbial ecology of soil is complex and probably has a bearing of bacterial survival, growth and therefore the risk of subsequent human disease following soil contact. Given the ability of some disease-causing bacteria to persist for long periods in soil, it is clear that some soils must be regarded as a potential health hazard. It would be sensible to combine bacteriological risk and soil health index analysis in a hypothesis-driven surveillance programme.

Key Words
Risk modeling, seed borne, uncertainty, tropical environments

Introduction

"*I will show you fear in a handful of dust*."

TS Eliot, The Waste Land, 1922.

Not that long ago a driver bogged his 4x4 near to Katherine in the Northern Territory, Australia. He managed to get going again after a bit of heavy digging, but within 48 hours he was dead; slain by a little-known bacterial infection that lies dormant in the soil of northern Australia. His is not the only story of sudden death from soil-borne infection in recent times. Every year the *Northern Territory News* carries reports of deaths and intensive care admissions due to soil disease. Public health authorities warn people of the risks yet, despite these warnings the deaths continue. The danger of soil borne infection is not only seasonal. It has a patchy distribution over a huge geographic range, causing problems with accurate risk modelling.

Dishing the Dirt
The above infection is known as melioidosis and is caused by the Gram negative bacterial species *Burkholderia pseudomallei*. It is not the only soil-borne infection. A short list includes anthrax (*Bacillus anthracis*), a variant of Legionnaires' Diseases (*Legionella longbeachae*), gas gangrene (*Clostridium perfringens*), tetanus (*Clostridium tetani*) and Nocardiosis (*Nocardia* species) (Table 1). The details of atypical Legionella infection have yet to be worked out but *L. longbeachae* generally causes pneumonia after the use of garden products such as potting mix (1). The other conditions listed are caused by infections linked to farm animals. Interestingly, these infections are rarely if ever contracted by man-to-man transmission. They are all infections of environmental exposure and are all caused by infective agents that can persist in the soil for a long time either as spores or by relying on an internal nutrient store. These bacteria are tougher than the ones that cause more common infections.

Sweeping the Dirt Under the Table
There is a remarkable lack of hard data on the occurrence of soil borne human diseases. Where, when, how often and under what circumstances these infections occur is often a matter of conjecture because they are not normally communicable diseases. They do not cause outbreaks in the classic sense of the word and therefore do not attract the attention of public health authorities. That is, unless they have the potential for use as a biological weapon, as is the case with *B. pseudomallei*, the cause of melioidosis. This bacterial species has gained notoriety in the last decade because it is on the Centers for Disease Control wanted list as

a potential weapon agent (2), having attracted the attention of the Soviet Union during the Cold War. There is no good evidence that is has been used in this capacity, but more tellingly there have been several clusters of cases with fatalities. Two of these case-clusters occurred in northern Australia; one in the West Kimberley and one in the Northern Territory (3, 4). All Australian jurisdictions in the tropics now include melioidosis on their list of notifiable diseases. Unfortunately, the rest of Australia has yet to catch up. Melioidosis is not notifiable in New South Wales, Victoria, the Australian Capital Territory, South Australia and Tasmania where sporadic, travel-associated infection goes without further comment.

An Unusual Infection

Melioidosis is a disease of surprises. In its most severe form, it presents as a systemic bloodstream infection with or without pneumonia (5). Death occurs rapidly unless intravenous antibiotic treatment is commenced without delay, and may not be averted even when the right antibiotics are used from the start. This septicaemia can relapse after a few days or weeks of antibiotic therapy, necessitating a prolonged course of oral antibiotic treatment to eradicate residual, dormant infection. But melioidosis can also present after a long, disease-free interval of up to six decade following initial environmental exposure. In between septicaemia and asymptomatic, dormant infection lie localised, abscess-like foci which can erupt at any time into a full-blown bloodstream infection. Patients with melioidosis therefore die in spite of the correct antibiotics or they can survive, having been right to the brink of hopeless multi-organ system failure (6). Most of the severe cases occur in people with underlying medical conditions such as diabetes, renal failure and alcoholic liver disease, but not all fatalities occur in these vulnerable people.

Table 1. Selected human bacterial infections associated with soil exposure

Infection	Bacterial cause	Distribution	Exposure
Anthrax	*Bacillus anthracis*	with domestic livestock & wildlife worldwide	skin inoculation, inhalation
Botulism	*Clostridium botulinum*	With domestic livestock worldwide	ingestion
Gas gangrene	*Clostridium perfringens*	with livestock worldwide	dermal inoculation
Infective diarrhoea	*Salmonella, Shigella, Campylobacter, E.coli*	worldwide	ingestion of faecal-soil mix
Legionnaires' Disease	*Legionella longbeachae*	patchy, sporadic including W & S Australia	inhalation
Leptospirosis	*Leptospira icterohaemorrhagiae*	Widespread in tropics & temperate zones	Mucosal surface exposure to urine-soil mix
Melioidosis	*Burkholderia pseudomallei*	tropics esp. N Australia & SE Asia	inhalation, dermal inoculation
Nocardiosis	*Nocardia* species	Patchy, sporadic	Dermal inoculation, inhalation
Tularaemia	*Francisella tularensis*	N America, Scandinavia	Inhalation, skin inoculation
Tetanus	*Clostridium tetani*	with livestock & other animals worldwide	dermal inoculation into deep soft tissues

Geographic Distribution

The sporadic nature of melioidosis and its link with environmental exposure allows us to draw a map of the endemic area; broadly speaking in the tropical north of Australia where annual rainfall is greater than 800mm. This appears to be an infection of warm, wet summers, as confirmed by detailed analysis in Darwin. Beyond Australia, melioidosis is found in many parts of the tropics, particularly in Southeast Asia where rice farmers are at high risk of infection. Environmental studies have shown that *Burkholderia pseudomallei* is sporadically distributed in our region and can be found in a variety of types of worked soil, including rice, rubber and banana plantations and close to urban centres (7,8) (Figure 1).

Seed and Soil

Understanding of the distribution of *B. pseudomallei* in the rhizosphere is far from complete. Where present, it is usually located between 5cm and 60cm depth and has a preference for waterlogged and clay soils (9). Recent prospective sampling on a mine site in WA suggested a predilection for transitional soil environments in an area of re-vegetation (10). Crushed rock on the excavation site, mine tailings and also pristine bush were either no- or low yield for *B. pseudomallei*. These results are consistent with finding other *Burkholderia* species in forest environments where soil has been altered by forest management (11). It is interesting that a rural location in southwestern Australia where cases of melioidosis occurred in goats and the human community yielded *B. pseudomallei* from environmental samples during the case cluster (12), but not after established restoration of native vegetation and avoidance of chemical fertilization with substances that can be used by *Burkholderia* species as growth substrates. The microbial ecology of soil is complex and probably has a bearing of bacterial survival, growth and therefore the risk of subsequent human disease following soil contact. We discovered that *B. pseudomallei* could survive inside free-living amoebae of a type that are commonly found in soil and surface water (13). More recently we showed that these bacteria can also survive in mycorrhizal fungi and can be transferred from generation to generation in this protected environment (14). These interactions between bacteria and more complex microorganisms have been used to improve the yield of *B. pseudomallei* from surveillance soil samples (15). The observation raises the question of whether fungal spores or amoebic cysts can act as a vehicle for airborne spread of these disease-causing bacteria.

Figure 1. Rice fields in Malaysia; a suitable worked soil habitat for proliferation of *B. pseudomallei*.

Healthy Soils?

Given the ability of some disease-causing bacteria to persist for long periods in soil, it is clear that some soils must be regarded as a potential health hazard. Effective laboratory methods for field studies are still in their infancy, but a molecular microbiology approach shows some promise (15). Backed up by GIS mapping of known high-risk locations, it may be possible to develop a predictive approach in future, but with the caveat that the areas of interest are large and the knowledge gaps are large. An alternative or possibly complementary approach is to attempt a definition of bacteriologically healthy soil, to include qualitative and quantitative bacteriological analysis. Very little work has been done on this in tropical Australia as yet because it has previously been given a low priority. Now that the increasing rainfall patterns in the northwest have been recognized and an expansion of agriculture in the Kimberley is planned, it is a good time to revisit the issue. Surely it would be sensible to combine bacteriological risk and soil health index analysis in a hypothesis-driven surveillance programme? A failure to act at this stage may lose an opportunity to both plan for sustainability of arable production and minimize human disease risk in the East Kimberley.

Wider Issues
These are not trivial issues. There may only be a handful of cases of melioidosis in the Kimberley each year, but that number reflects a small population base. It is still one of the highest incidence locations for the disease in the region. Multiply the population, increase a receptive soil environment by expanding productive agriculture and add steadily increasing annual rainfall and periodic cyclones, and you can see why the epidemiologists expect to see an increase in melioidosis cases. This is only one soil borne disease we believe to be impacted by climate change and other anthropogenic drivers (16). It is likely that these determinants of soil borne disease will also impact subtly on the epidemiology of the other infections considered here, though the precise outcomes are difficult to predict without better surveillance data. This is likely to be a subject of intense study in years to come.

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The Influence of Soil on Public Health

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Abstract
Soil is the most complicated biomaterial on the planet due to complex soil architecture and billions of soil microbes with extreme biotic diversity. Soil is potentially a source of human pathogens, which can be defined as geo-indigenous, geo-transportable, or geo-treatable. Such pathogens cumulatively can and do result in multiple human fatalities annually. A striking example is Helminths, with current infections worldwide estimated to be around two billion. However, soil can also be a source of antibiotics and other natural products that enhance human health. Soil-borne antibiotics are used to treat human infections, but can also result in antibiotic-resistant bacteria. Natural products isolated from soil resulted in 60% of new cancer drugs between the period 1983-1994. Soils are also crucial to human health through their impact on human nutrition. Finally, from a global perspective, soils are vital to the future well-being of nations through their impact on climate change and global warming. A critical review of soil with respect to public health leads to the conclusion that overall soil is a public health saviour. The value of soil using a systems approach is estimated to be $20 trillion, and is by far the most valuable ecosystem in the world

Key Words
Soil, pathogens, antibiotics, natural products, carbon sequestration.

Introduction
Soil is usually thought of as dirt by the layman or material that you walk on, or something that gets all over you. When we move to the higher echelon of science, researchers usually think of soil from the agronomic aspect, or perhaps in terms of its environmental influences. What is generally not recognized is that soil can have both direct and indirect influences on public health, and that these effects can be beneficial or harmful. In this paper we discuss whether or not soil is a public health threat or saviour.

Soil as a public health threat or saviour
Soil as the earth's veneer
Soil takes thousands of years to develop and can be as thin as 1 meter or as thick as 30 meters. This fragile veneer is the most complicated biomaterial on the planet, and is vital for human life as we know it (Young and Crawford 2004). Abiotic soil constituents such as sand, silt, clay and organic colloids control the chemical transformations that occur via surface mediated reactions. Conversely trillions of soil microorganism control biochemical transformations within soil. Soil microbes can also infect humans causing disease, or be a source of toxins. Microbes can also be a source of natural products that benefit human health.

Table 1. Direct influences of soil on public health.

Antibiotic resistant microbes within soil	Soil microbial production of antibiotics, e.g., Streptomycin
Soil toxins, e.g., aflotoxin	Natural products, e.g., paclitaxel
Plant pathogens, e.g., *Fusarium*	Soil microbes enhancing plant growth, e.g., *Pseudomonas*

As seen in Table 1 soil can directly influence public health in a positive or detrimental manner. Soils can be a source of various types of pathogens (Table 2). Soils can even be a potential source of death as in the case of geoindigenous pathogens (Table 3) or provide substances that save lives as in the case of the anti-cancer agent paclitaxel (Table 4).

Table 2. Soils and human pathogens.

Geo-indigenous soil pathogens
• Human pathogens native to soils that can metabolize and reproduce
Geo-transposable soil pathogens
• Soil enhanced transport of pathogens via water or dust
Geo-treatable soil pathogens
• Inactivation of introduced pathogens by soil

Adapted from Pepper *et al.* 2009.

Table 3. Human geo-indigenous soil pathogens.

Type of organism	Affliction	Incidence in soil
Human virus	NA	Never indigenous-no host
Bacteria *Bacillus anthracis* *Legionella* spp.	 Anthrax Legionnaire's disease	Routinely found in most soils Found in soil composts and potting soil
Fungi *Coccidiodes immitis* *Histoplasma capsulatum*	 Valley Fever Respiratory infections	 Highly prevalent in SW United States Prevalent in Midwest and southern United States
Protozoa *Naegleria fowleri*	 Brain encephalitis	 Found in soil and water

Adapted from Pepper *et al.* 2009.

Table 4. Impact of natural products on human health.

Item	Extent %	Reference
Prescription drugs	40	Strobel and Daisey 2003
New chemical products registered by U.S. Food and Drug Administration	49	Brewer 2000
Approved drugs between 1989 and 1995	60	Grabley and Thiericke 1999
Approved cancer drugs between 1983 and 1994	60	Concepcion *et al.* 2001
Approved antibacterial agents between 1983 and 1994	78	Conception *et al.* 2001

Adapted from Pepper *et al.* 2009.

On balance however, the overall direct impacts of soil on public health are beneficial, as evidenced by food itself which is grown in soil and sustains the world's population. Soil is also a large reservoir of natural products and antibiotics that save millions of lives.

Soils can also affect public health indirectly through their effect on climate change. Specifically global climate change is now predicted to result in catastrophic events including tsunamis, flooding, droughts, and changes in the regions of the world that become inflicted with microbial infectious disease. Soils constitute the single largest terrestrial carbon stock, with more than three times that in vegetation and function as both a source and a sink of carbon dioxide (CO_2) Managing soils to increase soil organic carbon (SOC) storage and remove CO_2 from the atmosphere provides a significant, immediately available, low-cost option for mitigating GHG emissions (Paustian *et al.* 1998; Lal 2004). Improved crop and soil management strategies have the technical potential to sequester as much as 200 Tg CO_2/yr in the US (~15% of US emissions) (CAST 2004) and 5000 Tg CO_2/yr, globally (IPCC 2007). Overall, amount of C stored in soils is a function of biological, chemical, and physical parameters (Rice and Angle 2004). .

Conclusions

A critical review of soil with respect to public health leads to the conclusion that soil is a public health saviour. The number of soilborne geo-indigenous human pathogens is far less the number of pathogens that are introduced into soil and subsequently inactivated. More importantly, soils possibly impact human health and welfare in other profound ways. Sickness and ill health are routinely treated with natural products obtained from soils, such as antibiotics, anti-cancer drugs, insult mimics, and immunosuppressive drugs. In addition, soils provide food and nutrition for humans and animals alike. Attempts have recently been made to estimate the value of ecosystems using the “global unified metamodel of the biosphere” (GUMBO). Using this systems approach, soil was estimated to have a global value of $20 trillion, and is by far the most valuable ecosystems in the world (Boumans *et al.* 2002). However, in light of the enormous beneficial influences of soil on public health, even this dollar value is likely to underestimate the true value of soil by several orders of magnitude. Indeed, life on Earth without earth would be impossible.

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Trace-metal concentrations in African dust: Effects of long-distance transport and implications for human health

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Abstract
The Sahara and Sahel lose billions of tons of eroded mineral soils annually to the Americas and Caribbean, Europe and Asia via atmospheric transport. African dust was collected from a dust source region (Mali, West Africa) and from downwind sites in the Caribbean [Trinidad-Tobago (TT) and U.S. Virgin Islands (VI)] and analysed for 32 trace-elements. Elemental composition of African dust samples was similar to that of average upper continental crust (UCC), with some enrichment or depletion of specific trace-elements. Pb enrichment was observed only in dust and dry deposition samples from the source region and was most likely from local use of leaded gasoline. Dust particles transported long-distances (VI and TT) exhibited increased enrichment of Mo and minor depletion of other elements relative to source region samples. This suggests that processes occurring during long-distance transport of dust produce enrichment/depletion of specific elements. Bioaccessibility of trace-metals in samples was tested in simulated human fluids (gastric and lung) and was found to be greater in downwind than source region samples, for some metals (e.g., As). The large surface to volume ratio of the dust particles (<2.5 μm) at downwind sites may be a factor.

Key Words
African dust, human health, trace-element enrichment, long-distance transport, metal bioaccessibility.

Introduction
The African dust system is the largest in the world, annually exporting billions of tons of eroded mineral soils to the Caribbean and Americas, Europe and Asia via atmospheric transport. Dust from Africa is a known source of nutrients and co-factors to downwind organisms and ecosystems, both terrestrial (e.g., the Amazon Basin, Swap *et al.* 1992) and marine (e.g., Jickells 1999). During long-distance transport, larger particles are removed via gravitational settling such that the air mass becomes enriched in fine particles (<2.5 μm aerodynamic diameter) as they are transported to the Caribbean and beyond. The resulting small particles are a cause for concern because fine particles are respirable and have been associated with increased incidence of cardiovascular and pulmonary disease and mortality. As part of a larger study investigating the effects of African dust air mass composition (trace elements and anthropogenic contaminants such as pesticides, polycyclic aromatic hydrocarbons, and polychlorinated biphenyls) on human health and downwind ecosystems such as coral reefs (Garrison *et al.* 2003), samples of African desert dust were collected in a dust source region and at downwind sites and analysed for trace-element concentrations and enrichment. Bioaccessibility of dust-borne metals in simulated lung and gastric fluids was also investigated.

Methods
Sites
A. Source region:
1. dust - Emetteur Kati, Mali (12.69°N, 8.02°E; 555 m elevation; 2-15 April 2008; n = 8)
2. dry deposition - Bamako, Mali (12.65 °N, 8.03 °E; 385 m; 19 Mar-15 May 2002, Apr 2003; n = 3).

B. Downwind sites:
1. SE Caribbean: Flagstaff Hill, Tobago (11.33°N, 60.54°W; 329 m; 27 May-22 June 2008; n = 5)
2. NE Caribbean: St. Croix, Virgin Islands (17.75°N, 64.59°W; 27 m; 20 Jun-24 Aug 2008; n = 5)

Field sampling
Samples of total suspended particles were collected using high-volume brushless motors (110v/12 amp or 220v/6amp) to pull 200 – 1000 m^3 air through pre-baked (600C, 8 hrs) and pre-weighed 90 mm quartz-microfiber filters (QM/A) in Teflon filter holders. Flow rates were determined using a Gilmont #6 calibrated flowmeter. Field blanks were collected during each sampling period at each site. Samples and blanks were placed in individual sealable plastic bags and frozen until analysis. Air samples at downwind sites were collected only when: the wind direction was from the east to southeast; the Navy Aerosol Analysis and

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Prediction System model indicated African dust; and when Saharan dust was observed in the atmosphere. The presence of Saharan dust was confirmed in the field by: 1) the presence of reddish-brown particles on filters; 2) high Fe content of particles; and, with further confirmation after trace-element analysis by 3) La-Sc-Th ratios within the range of African dust (Muhs *et al.* 2007).

Laboratory and data analysis

Samples and field blanks were analyzed for 32 elements using inductively coupled-plasma mass spectrometry (Briggs and Meier 2002), instrumental neutron activation analysis and/or graphite-furnace atomic-absorption spectrometry. Because sampler enclosures were made of aluminium sheeting, Al concentrations in samples were not reliable. Trace-element enrichment factors were determined by normalizing sample concentrations to average Upper Continental Crust (UCC) values of Wedepohl (1995). Downwind sample (TT and VI) concentrations were also compared to local (TT and VI) soils as a check for local contamination.

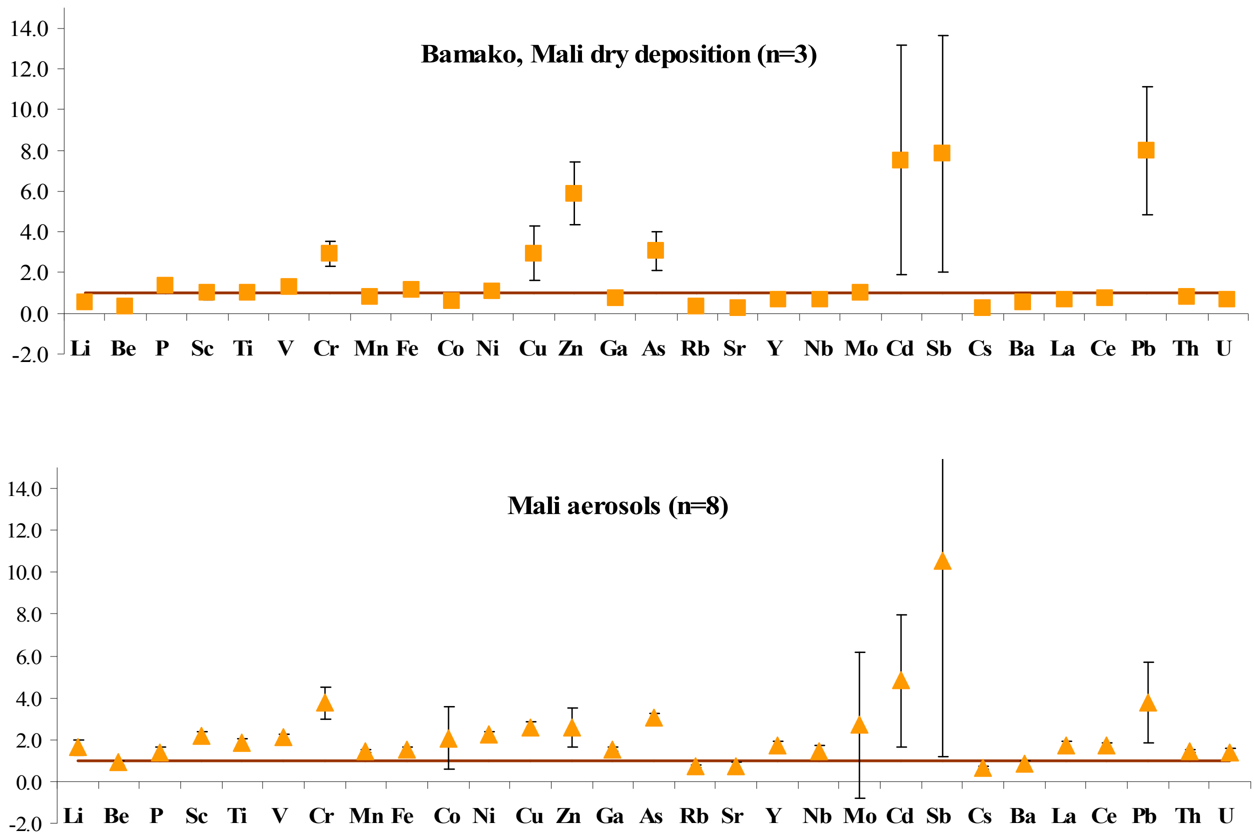

Figure 1. Enrichment of trace-metals in African dust and dry deposition samples from the dust source region relative to average upper continental crust composition (orange line; Wedepohl 1995). Enrichment factor shown on y-axis; error bars represent one standard deviation.

Results

Concentrations of 32 elements analyzed in dust samples collected from the dust source region (Mali) and from downwind sites (TT and VI) in the Caribbean were generally found to be similar to average UCC composition (i.e., enrichment factor close to 1) but some elements exhibited evidence of depletion or enrichment (Figures 1 and 2). These findings are in general agreement with other studies (e.g., Schütz and Rahn 1982; Castillo *et al.* 2008; Trapp *et al.* 2008). Only source region dust and dry deposition samples were found to be enriched in Pb, with local/regional use of leaded fuel the most likely source. The enrichment of Cd and Zn in dry deposition samples from the Niger River Valley in Bamako, Mali (Figure 1) was similar to that reported in dust aerosol samples collected in Barbados (Trapp *et al.* 2008) and considerably lower than values associated with pollution sources such as tire dust (Ozaki *et al.* 2004; Bermili *et al.* 2006). Sb enrichment was most pronounced in Mali samples but within reported values for desert dust (Schütz and Rahn 1982). Dust particles transported long-distances (VI and TT samples) showed greater enrichment of Mo and minor depletion of other trace-elements (Li, Ti, La, Ce, Th, U) relative to source region aerosols (Figures 1 and 2). The enrichment/depletion patterns in Tobago and VI samples (Figure 2) were most likely the result of chemical and physical processes during long distance transport, the distance transported, and the resulting fine particle size of dust at downwind sites. Mo enrichment has been reported to be greatest in the finest particle fraction (0.3-1.5 µm; Castillo *et al.* 2008). Bioaccessibility of dust trace-elements in simulated human fluids (gastric and lung) was found to be greater in downwind than source region samples, for a few elements (e.g., As; Morman *et al.* 2009). Total As concentrations in fluids showed > 40% bioaccessibility in most samples (Morman *et al.* 2009). The relatively small size of particles (high surface area to volume ratio) at downwind sites may be a factor in increased bioaccessibility.

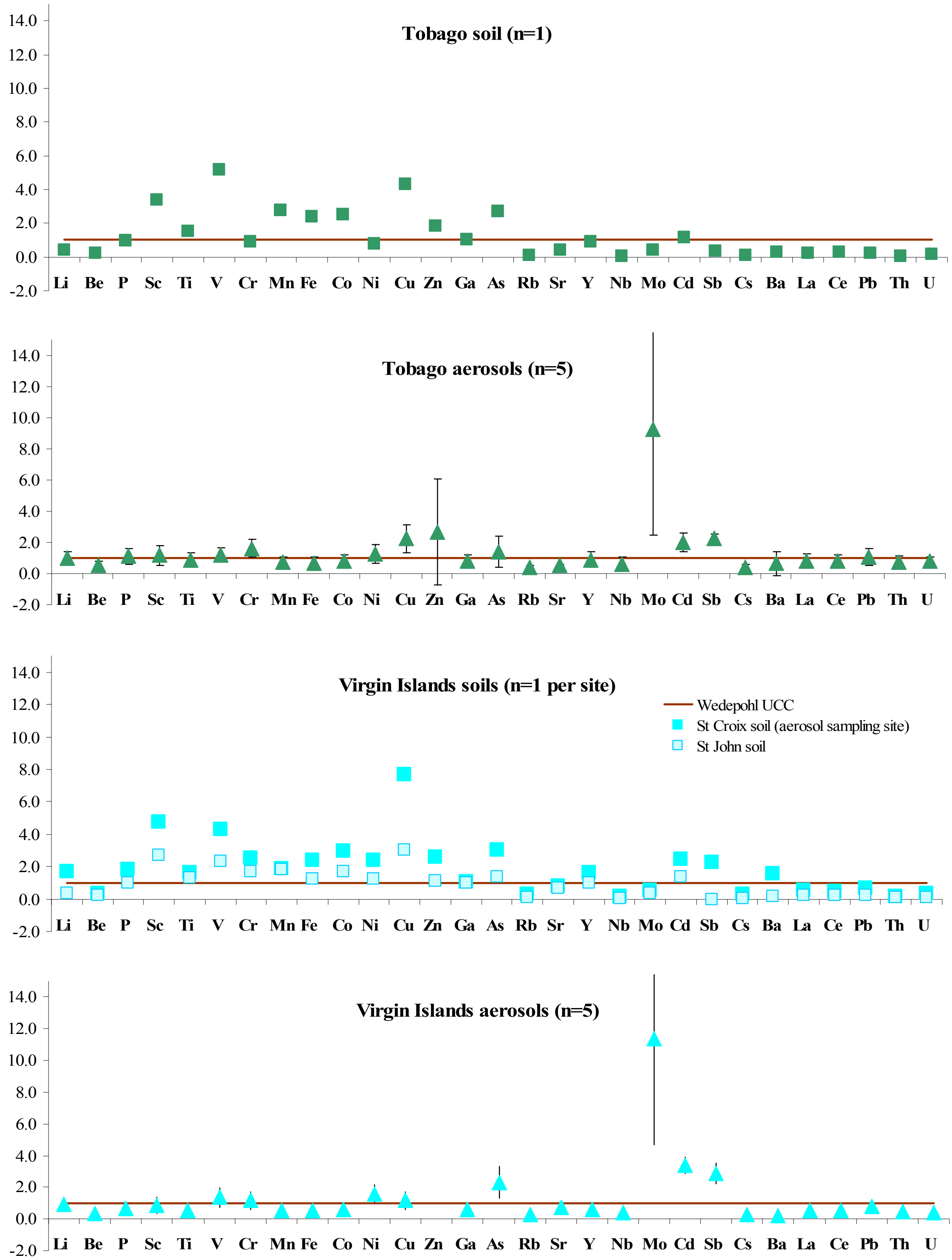

Figure 2. Enrichment of trace-metals in African dust and in soils at downwind sites to average upper continental crust composition (orange line; Wedepohl 1995). Enrichment factor shown on y-axis; error bars represent one standard deviation.

Conclusion

Trace-element concentrations in African dust collected from the source region (Mali) and from downwind sites in the Caribbean were similar to UCC composition. Minor enrichment/depletion of some trace elements was found but concentrations did not exceed those known to be toxic to humans and other animals. Dust and dry deposition samples from the dust source region were enriched in Pb, most likely due to use of leaded gasoline in the region during the sampling periods. Enrichment/depletion of trace elements in dust from downwind sites was most likely a function of chemical and physical processes during long-distance transport and distance transported. Of greatest concern are the possible effects of African dust-associated trace-elements that act as cofactors (e.g., Fe, Zn) or are known xenobiotics (As and Pb) on human health as well as microbial communities, organisms, and ecosystem processes at dust source and downwind locations. Investigation of bioaccessibility and biomobility of African dust–associated xenobiotics such as As should be the first priority.

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Uptake of cadmium by lettuce in tropical contaminated soils

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Abstract
Cadmium (Cd) is one of several metals that have come under suspicion in recent years as environmental contaminants potentially harmful to human health. The objective of this study was to evaluate the availability of Cd in soil and its distribution in root, stem and leaf of lettuce plants grown in a soil contaminated with Cd. The experiment was conducted under greenhouse conditions in Piracicaba-SP. Lettuce plants (two plants/pot) were cultivated in pots filled with 3/dm^3 of Oxisol samples using a randomized block design in a factorial scheme (5 x 2) with three replicates. The treatments consisted of: 0.0; 0.5; 1.3; 3.0 and 6.0 mg/dm^3 rates of Cd (as $CdCl_2$), based on the guideline established by the Environmental Agency of the State of Sao Paulo, Brazil - Cetesb. The external loading of Cd increased available Cd in soil as estimated by three extractors: DTPA, Mehlich-1 and $CaCl_2$. The concentration of Cd accumulated in different parts of plants was positively related to available Cd in the soil and to Cd application rates. The current “prevention” values of soil contamination for Cd proposed by Cetesb were somewhat restrictive but may still result in Cd concentration in the edible part of lettuce above the permitted value by food legislation.

Key Words
Lactuca sativa L., Cd availability, food safety, soil pollution, trace-element

Introduction
Cadmium is a heavy metal naturally present in soils. It may be added to the soil as a contaminant in fertilizers, manure, sewage sludge and from aerial deposition. The amount of cadmium contributed from each source varies with location due to differences in soil types, management practices and exposure to pollution sources, but the level of Cd in soil appears to be increasing over time (Kabata-Pendias and Mukherjee 2007). Cadmium is of concern to human health because it is easily transferred to human beings through food chain. Cadmium has no essential biological functions and highly toxic to plants and animals. Human dietary intake of Cd from vegetables is primarily dependent on the concentration of Cd in the edible part and not necessarily on the uptake of Cd by the whole plant (Yang *et al.* 2004). To evaluate the soil quality, Brazilian environmental protection agencies used generic Cd values found in bibliographic references; these values are often obtained under different conditions from those found in the tropical regions, and thus may lead to erroneous hazard estimates. The objective of this study was to evaluate the availability of Cd in soil and its distribution in root, stem and leaf of lettuce plants grown in the Cd contaminated soil.

Methods
A greenhouse experiment was carried out from November 2008 to March 2009 in Piracicaba, State of São Paulo, Brazil. Lettuce (*Lactuca sativa* L.) cv. Elisa da Sakata was used as test plant. The experimental design was randomized complete blocks in a factorial scheme 5 x 2 (five rates of Cd and two soils) with three replications, totaling 30 experimental units. Each experimental unit consisted of a pot filled with 3/dm^3 of two Oxisols (Typic Haplustox and Rhodic Hapludox), with chemical and physical attributes presented in Table 1. The treatments consisted of: 0.0; 0.5, 1.3; 3.0 and 6.0 mg Cd/dm^3 soil, based on the guideline established by Cetesb (2005), added as $CdCl_2.H_2O$. The soils with and without Cd loading were incubated at room temperature for 60 days with soil moisture maintained at 60% water holding capacity. Adequate amounts of $CaCO_3$ and $MgCO_3$ (Ca:Mg ratio of 3:1) were added to increase soil base saturation (BS = 80%) (Trani *et al.* 1997). Only the Typic Haplustox was fertilized (basal application and side-dressing) according to Malavolta (1980). Two lettuce plants were grown per pot and harvested on the 40th day after emergence. Root, stem and leaf were separately harvested and washed two to three times with tap water and once with deionized water before being oven dried at 65 °C for 72 hr. The dry matter yields of each plant part were recorded, and oven dried plant tissues were ground in a Wiley mill, and submitted to nitric-perchloric

digestion according to Malavolta *et al*. (1997) for determination of Cd by inductively coupled plasma mass spectroscopy (ICP-MS). Immediately before plant transplanting soil samples from each pot were collected and analyzed for available Cd by using 0.1 mol L^{-1} $CaCl_2$ (Houba *et al.* 2000), DTPA (pH 7.3) (Abreu *et al.* 2001) and Mehlich-1 (Embrapa 1997). Data were submitted to analysis of variance and polynomial regression, using the SAS system of analysis (SAS Institute 2002). Correlation coefficients were determined between the Cd concentration in soil and Cd accumulated in leaf.

Table 1. Chemical[A] and physical[B] attributes of the soils (0-20 cm depth) used in the experiment.

Attributes	Rhodic Hapludox	Typic Haplustox
pH $CaCl_2$ 0.01 M	5.7	4.1
Organic matter (g/dm^3)	51	26
P (mg/dm^3)	103	5
K ($mmol_c/dm^3$)	10.3	0.7
Ca^{+2} ($mmol_c/dm^3$)	62	6
Mg^{+2} ($mmol_c/dm^3$)	18	4
Al^{+3} ($mmol_c/dm^3$)	2	7
H+Al ($mmol_c/dm^3$)	25	42
Sum of bases ($mmol_c/dm^3$)	90.3	10.7
CEC ($mmol_c/dm^3$)	115,3	52.7
Base saturation (%)	78	20
Al saturation (%)	2	40
B (mg/dm^3)	0.65	0.11
Cu^{+2} (mg/dm^3)	2,2	0.5
Fe^{+2} (mg/dm^3)	32	71
Mn^{+2} (mg/dm^3)	47.2	3.7
Zn^{+2} (mg/dm^3)	9.5	0.7
Cd^{+2} (mg/dm^3)	<0.01	0.01
Particle size (%)		
Sand (> 0.05 mm)	41	64
Silt (> 0.002 and < 0.05mm)	14	16
Clay (< 0.002 mm)	45	20

CEC = cation exchange capacity. [A]Raij *et al*. (2001). [B]Embrapa (1997).

Results

Extractable Cd estimated by the three extraction procedures increased significantly with increasing rate of external Cd loading (Figure 1a, b, c). The relationship between extractable Cd and Cd loading rates followed a linear model for both soils. Among the three extractants, DTPA and Mehlich-1 extracted similar amount of labile Cd in soils, and the 0.1 mol L^{-1} $CaCl_2$ extraction provided the least amount of labile Cd with a relatively smaller correlation coefficient for one soil (Figure 1c). Therefore, it may not be as good as the other two extraction methods for estimation of available Cd in the clayey tropical soils. Similar results were also reported by Trombeta *et al.* (2009). The concentrations of Cd in root, stem or leaf were linearly or quadratically correlated with external loading rate of Cd (R^2>0.99, p<0.01) (Figure 2a, b, c). Except for root Cd concentration in the Rhodic Hapludox, the relationship between Cd concentration in root, stem or leaf lettuce and Cd application rate fitted a quadratic model. These findings are in agreement with previous reports by Moustakas *et al.* (2001). Leaf Cd concentrations were 16.3 and 35.5 mg/kg at the Cd loading rate of 1.3 mg/dm^3 (alert value) and 45.5 and 76.0 mg/kg at the Cd loading rate of 3.0 mg/dm^3 (intervention value) respectively, for Rhodic Hapludox and Typic Haplustox soil. In general, fresh lettuce contains up to 97% water, the leaf Cd concentrations on the fresh weight basis varied between 0.48 and 2.28 mg/kg and the high end is above critical level of 1.0 mg/kg fresh weight (Anvisa, 1965) or 0.66-3.0 mg/kg on the dry weight basis (Kabata-Pendias and Pendias 2001).

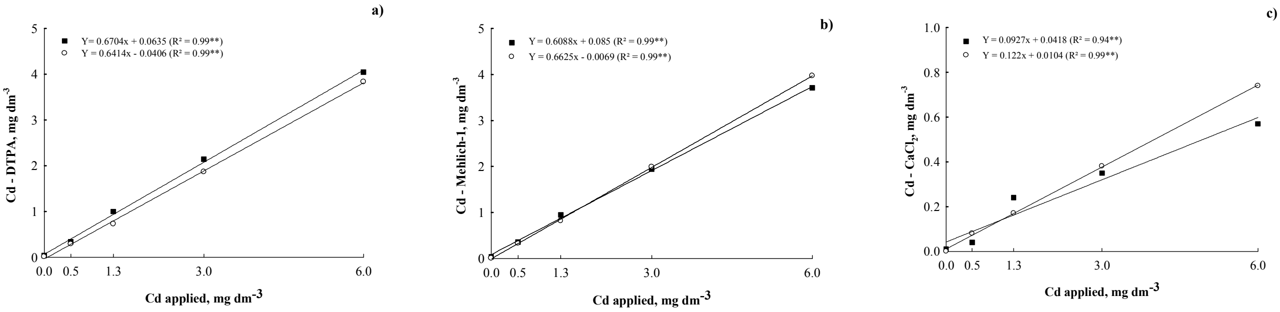

Figure 1. Cadmium concentration in soil extracted by DTPA (a), Mehlich-1 (b) and $CaCl_2$ (c) in function to soil types (■ Rhodic Hapludox; ○ Typic Haplustox), and rates of Cd applied. ** – significant at *p < 0.01*.

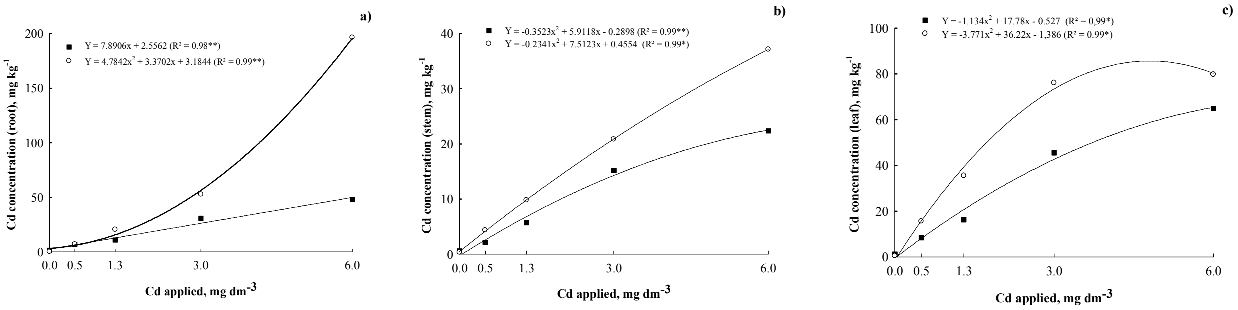

Figure 2. Cadmium concentration in root (a), stem (b) and leaf (c) of lettuce in function to soil types (■ Rhodic Hapludox; ○ Typic Haplustox), and rates of Cd applied. **, * – significant at $p < 0.01$ and $p < 0.05$ respectively.

These results indicate that when available Cd in the soils reached 3.0 mg/dm^3, the concentration of Cd in the lettuce leaf will be high enough to cause risks to human health. Australia has adopted maximum permissible concentrations for Cd in various foods, including 0.05 mg Cd kg^{-1} fresh weight for potatoes (McLaughlin *et al*. 1994). Lettuce is a bioindicator plant of heavy metals because it has the capacity to accumulate high concentrations of metals (Alloway 1995). Lettuce, spinach, celery, and cabbage tended to accumulate high concentrations of Cd, whereas potato tubers, maize, French beans, and peas accumulated relatively small amounts of Cd (Davis and Carlton-Smith 1980). The World Health Organization set a maximum provisional tolerable intake limit of 60 to 70 µg Cd per day for an adult (World Health Organization 1973), and the Codex Alimentarius Commission of FAO/WHO is discussing a limit of 0.1 mg Cd kg^{-1} for cereal grains and oilseeds traded on international markets. However, even small amounts in foods can have a significant effect in the long term because Cd accumulates in the body. There was a positive correlation between leaf Cd accumulation of lettuce and extractable Cd in the soils estimated by each of the three procedures (Figure 3).

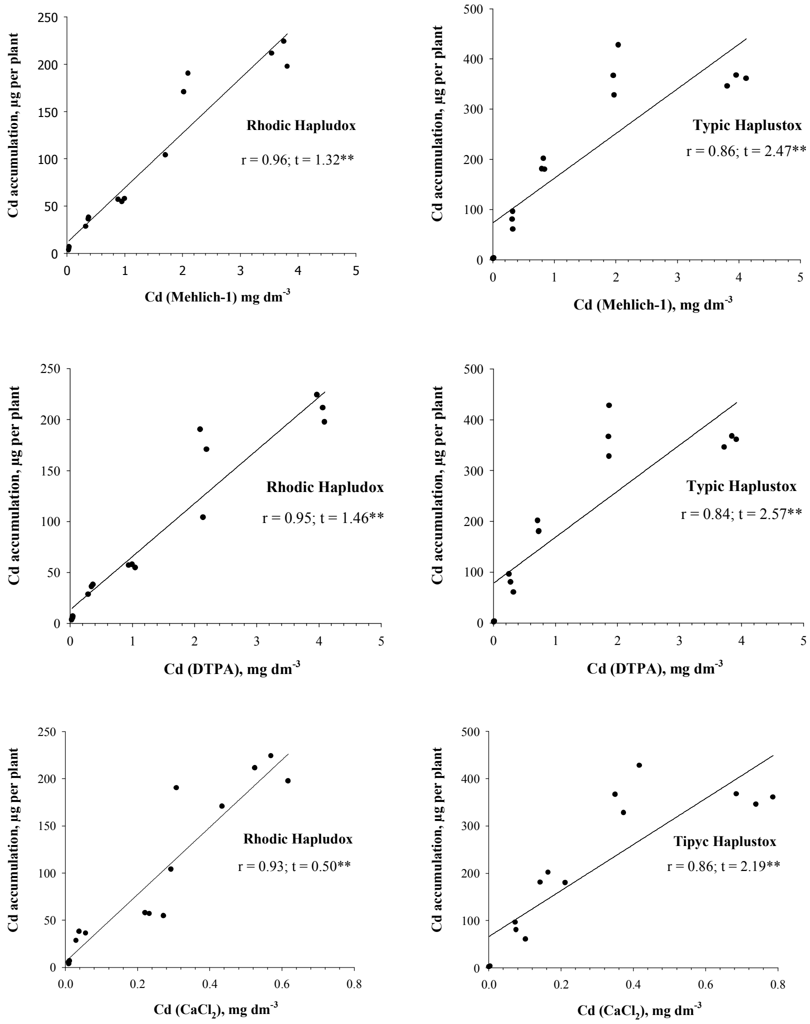

Figure 3. Correlation between leaf Cd accumulation of lettuce and extractable Cd in the soils estimated by Mehlich-1, DTPA and $CaCl_2$. ** – significant at $p < 0.01$.

Conclusion

The external loading of Cd linearly increased available Cd in soils and subsequently Cd concentrations in the root, stem and leaf of lettuce grown in both Oxisols. DTPA, Mehlich-1 and $CaCl_2$ were effective for the determination of available Cd in the tropical soils. The concentrations of Cd in root, stem, and leaf of lettuce plants were significantly increased with an increase in soil available Cd or external Cd loading rate. The current “prevention” values of soil contamination for Cd, proposed by Cetesb, were somewhat restrictive but may still result in Cd concentration in the edible parts of lettuce above the permitted level established by food legislation.

Acknowledgment

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Human and ecological risk assessment of contaminated sites – Key knowledge gaps

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Abstract
Since the inception of the Industrial Revolution, human activities have substantially accelerated the cycling of contaminants in the environment. This has resulted in a large number of contaminated sites worldwide. Environmental legislation dealing with risk assessment and remediation has been traditionally based on total contaminant concentrations. The main cause for this pragmatic approach has been related to knowledge gaps in human and ecological risk assessment. Here we discuss a number of important gaps, namely contaminant bioavailability, mixed contaminant ecotoxicology and emerging contaminants. The concept of bioavailability has gained significant acceptance but its implementation into the terrestrial regulatory framework is still hindered by the limited availability of validated methodologies. While in the case of lead and arsenic human risk assessment the state-of-the-art is such that bioavailability-based risk assessment will be incorporated in the near future into legislation, the situation for other inorganic and organic contaminants is still far from being resolved. The second key knowledge gap is related to mixture of contaminants. While contaminant mixtures represent the norm in real case scenarios, environmental legislations are generally based on individual contaminants. These knowledge gaps also apply to the area of emerging contaminants that in itself is challenging in terms of human and ecological risk assessment.

Key words
Bioavailability, emerging contaminants, human and ecological risk assessment, mixed contaminants, remediation

Introduction
Over the past 150 years, urban development, industrial, agricultural, military, mining and medical activities have generated large quantities of hazardous wastes that have resulted in environmental contamination issues. Thousands of organic and inorganic contaminants enter the soil environment as a result of these activities, with physical, chemical and biological processes including sorption to soil surfaces, diffusion into nanopores and mineral particles, partitioning into organic material, volatilization, degradation (biotic and abiotic), transformation etc. influencing their fate and potential hazard. While it is difficult to quantify, it has been estimated that the number of contaminated sites in Australia is approximately 100,000 with an estimated remediation / management cost of $5-8 billion. These values are small compared to the number of contaminated sites and estimated remediation costs in Europe and the US. Due to the toxic, mutagenic, teratogenic and carcinogenic properties of many environmental pollutants, there is great concern regarding the presence of these substances in the environment. While the cost to society of exposure to environmental contaminants is difficult to calculate, in the US alone, it has been estimated that the cost of cancer resulting from environmental pollutant exposure in 2008 was in excess $13.7 billion (ACS 2009).

As a result of the potential risk to human and environmental health from the exposure to these contaminants, remediation of contaminated land has become an increasing priority. The major objective of any remediation process is to reduce the actual or potential environmental threat and reduce unacceptable risks to man, animals and the environment to acceptable levels. Strategies to either manage and/or remediate contaminated sites have developed largely from application of stringent regulatory measures set up to safeguard ecosystem function as well as to minimize the potential adverse effects of contaminants on environmental and human health. While our understanding of contaminant fate and transport is ever increasing, knowledge gaps still exist which may impact remediation requirements and the associated resources and expense. Key knowledge gaps for environmental risk assessment include:

1. Contaminant bioavailability
2. Mixed contaminants
3. Emerging contaminants

Contaminant bioavailability
This area of research has attracted considerable investment in the last few decades. Bioavailability assessment in the context of environmental risk is a considerable task as contaminant bioavailability is not only controlled by the chemical-physical processes occurring in the soil but also by the variability in biological response between different animal, plant and microbial species. In the context of human health risk assessment and remediation decisions, contaminant bioavailability is fundamental in determining acceptable endpoints and potential clean up options. Bioavailability controls the amount of the contaminant, obtained via ingestion, inhalation or dermal pathways, that reaches systemic circulation. As a result, to enhance risk assessment and remediation decisions, fundamental knowledge is required on how to assess contaminant bioavailability, the impact of physicochemical parameters on bioavailability and how this information can be used to better quantify exposure for human health risk assessment. While it is assumed that contaminant bioavailability may vary depending on a variety of environmental parameters, its determination in the context of human health risk assessment is lacking for the majority of contaminants.

A major constraint in the assessment of contaminant bioavailability is the associated costs. Although *in vivo* studies utilizing appropriate animal models are an appropriate method for determination of contaminant bioavailability for inclusion in human health exposure assessment, the time required for *in vivo* studies, the expense of animal trials and ethical issues preclude their use as routine bioavailability assessment tools. As a result, rapid, inexpensive *in vitro* methods simulating gastrointestinal conditions in the human stomach have been developed as surrogate bioavailability assays. These assays determine contaminant concentrations that are solubilised following gastrointestinal extraction and are therefore available for absorption into systemic circulation (bioaccessible fraction). *In vitro* assays have the potential to overcome the time and expense limitations of in vivo studies thereby providing a surrogate measurement of bioavailability that is quick and inexpensive compared to animal models (Ruby *et al.* 1996; Basta *et al.* 2001). However, before these assays can act as a surrogate measurement for contaminant bioavailability, the correlation between *in vivo* bioavailability and in vitro bioaccessibility is a mandatory prerequisite for both regulatory and scientific acceptance. While *in vivo-in vitro* correlations have been determined for inorganic contaminants (Figure 1) such as arsenic (Rodriguez *et al.* 1999; Basta *et al.* 2001; Juhasz *et al.* 2007; Juhasz *et al.* 2009a) and lead (Schroder *et al.* 2001; Drexler and Bratton, 2007; Juhasz *et al.* 2009b), a dearth of information is available on the assessment of organic contaminant bioavailability for refining exposure for human health risk assessment. The development of validated tools for quantifying contaminant bioavailability is an ongoing research priority as outcomes will reduce the uncertainty associated with exposure assessment which will refine risk calculations.

It should also be noted that human health risk assessment for contaminated soil based on bioavailability poses some challenges in terms of future liability. In fact, bioaccessibility measurements are based on an assessment at a specific time and environmental conditions. Changes in these conditions over time may enhance or reduce bioaccessibility in ways that are difficult to predict. A consequence of this is that, if bioaccessibility is used as a driver and as an assessment of remediation, the longevity of a remediation treatment must also be considered in terms of bioaccessibility in the medium to long term. In other words, because of the dynamic nature of bioaccessibility, remedial actions driven by a bioaccessibility may require long-term monitoring.

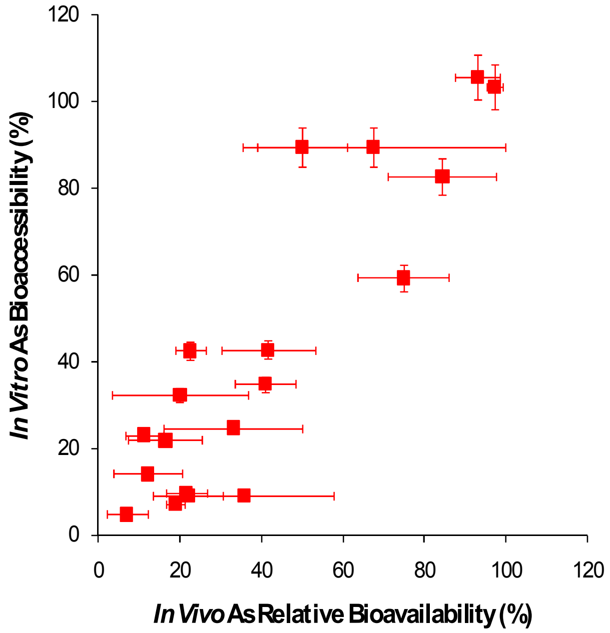

Figure 1. Relationship between arsenic relative bioavailability, determined using an *in vivo* swine assay and *in vitro* arsenic bioaccessibility using the gastric phase of the SBRC assay (SBRC-G). Arsenic relative bioavailability (%) = 0.99 x SRBC-G + 1.66, r2 = 0.75; Pearson correlation = 0.87 (Juhasz *et al.* 2009a).

Mixed contaminants

At the majority of contaminated sites, pollutants are present as mixtures. This is due to both geogenic and anthropogenic processes. In the case of heavy metals and metalloids, specific mineralogical associations can be found in nature and are due to chemical and physical similarities of various elements. For instance, zinc ores also contain significant amounts of lead and cadmium while arsenic is often associated with gold or copper ores. Consequently, mining and smelting operations almost always result in multi-element contamination. Other common sources of contamination, such as the use of pesticides, the disposal of sewage sludge, animal manures and slurry, and waste-derived products (e.g. composts) on land, also results in the release into the environment of a complex mixture of organic and inorganic contaminants. Consequently, both human and ecological receptors are exposed to contaminant mixtures. However, toxicological research is dominated by studies of single contaminant exposure rather than assessing mixture toxicity. This approach neglects mixture effects that could reduce or enhance contaminant toxicity due to antagonistic or synergistic processes. In the environment it is often the case that many contaminants may be present at concentrations close or below their individual no observed effect concentrations (NOEC), yet in a mixture they may contribute to substantial effects (Altenburger *et al.* 2003). Also, the presence of toxicant mixtures in the field has been identified as one of the key factors causing differences between laboratory and field based toxicity data (Weltje 1998).

At the legislative level, the need to incorporate mixture interaction in the regulatory framework has been recognised by regulating authorities but the process of incorporation of mixture toxicity in regulations has been hindered by the paucity of studies available, especially for the terrestrial environment. This translates into regulations that focus on the effects of individual chemicals where mixture effects are considered only indirectly via safety/assessment factors, which are often contentious. The development of scientifically-based regulations can only be achieved when the relevant information is available. However, work focusing on mixture toxicity in the terrestrial environment has been fragmented and the information available is scarce and inconsistent especially in the case of plant and microbial toxicity. Possibly the main reason is related to the fact that information regarding mixture toxicity requires a very large number of observations. However, various approaches for testing this type of interactions have been proposed that allow extraction of the relevant information while substantially decreasing the amount of data required.

Emerging contaminants

The widespread occurrence of newly identified contaminants such as polybrominated diphenyl ethers (PBDEs), perfluorinated chemicals (PFOS, PFOA etc.), illicit drugs, personal care products, antiviral agents, nanoparticles etc. in the environment is of growing concern. While information regarding their fate, transport and human/ecological effects is starting to emerge, limited data is available which could be used for regulatory guidance. For example, PBDEs and perfluorinated chemicals are a class of industrial chemicals widely used in various industrial applications including as fire retardants, are highly resistant to degradation, bioaccumulative and have behavioral properties similar to persistent organic pollutants (e.g. PCBs, DDT). Human exposure to PBDEs is reflected by the considerable increase in the concentration of PBDEs in breast milk. Birnbaum and Staskal (2004) reported that PBDEs in breast milk of North American women increased from <1 µg/l to 200 µg/l over a 25 year period while Meironyté *et al.* (1999) reported a 60-fold increase in the concentration of PBDEs in Swedish woman breast milk between 1972 and 1997. While international efforts have documented the accumulation of PBDEs in humans, regulatory guidance on these compounds is lacking. In Australia, recent research revealed the presence of PBDEs in carpet dusts and soil from several peri-urban localities. Greater than 65% of soil and sediment samples (n = 60) collected from industrial, recreational and waste dumps in Adelaide (South Australian) contained PBDEs including BDE- 7, 17, 28, 47, 77, 100, 119, 99, 85, 154, 153, 138, 183, 196, 197, 207, 206 and 209. The concentrations of ∑PBDEs in samples ranged from 320 to 1050 ng/g while at point sources, ∑PBDEs ranged from 230 to 3470 ng/g. This study illustrated that the use of PBDEs at point sources (e.g. plastic industries) may lead to contamination of nearby environments, however, their potential impact on environmental health is largely unknown. A major challenge associated with emerging contaminants, such as PBDEs, include the evaluation of their health risks given limited knowledge on the toxicity and environmental behaviour of these chemicals.

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