Soil pH and free Fe/Al oxides control As availability and fractionation in representative Taiwan soils contaminated by As

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Abstract
A large area of agricultural soils mostly growing rice in Guandu Plain, Taipei was contaminated by arsenic (As). Rice produced in the As-contaminated area was safe for consumers even total As in soils reached as high as 535 mg/kg. Results of As fractionation in soils in this area indicated that As availability in soils were very low and supposed that this may be explained by high contents of amorphous materials in soils. To further prove this hypothesis and find out the major soil properties affecting As availability in representative Taiwan soils contaminated by As, this study apply As solution in 9 different soil samples with various characteristics and investigate the dynamics of As fractionation in soils under two cultivation systems, paddy fields or upland. We found that As transferred to non-labile fractions with time and the relative portions of As fractions were quite stable after 90 days of incubation in both cultivation systems. The ageing effect is more apparent in paddy fields condition compared with dry land condition. This study concluded that soil pH and free Fe/Al oxides are the major soil properties affecting As availability and fractionation in the representative Taiwan soils contaminated by As.

Key Words
Arsenic, contamination, fractionation, amorphous materials, cultivation systems, Guandu Plain.

Introduction
Arsenic is a contaminant of public concern since it is highly toxic and carcinogenic. It may be accumulated in plants and eventually be transferred to humans through the food chain (Rahman *et al.* 2008). According to a survey conducted in 2006, more than 60 hectares of soils located in Guandu Plain, Taipei, were contaminated by arsenic (≧60 mg/kg). The maximum As concentration in topsoil (0-15 cm) reached 535 mg/kg in this area. The contamination source of arsenic in this area may came from the soil parent material, andesite, and the hot spring water of Thermal Valley located around 5 km northeast away from Guandu Plain. The hot spring water flowed out and mixed with the stream water which was used as irrigation water for the As-contaminated area of the Guandu Plain.

The food safety of rice produced in this area was investigated (Su *et al.* 2008). It was found that the arsenic concentrations in rice grain were all below 0.5 mg/kg DW, no matter how high the arsenic concentration in soil was. No relationship or trend was found between total arsenic concentration in soil and in brown rice. It was concluded that the rice cultivated in the Guandu Plain is safe for consumers. Another study that conducted arsenic fractionation in 13 soil samples collected from Guandu Plain showed that the non-specifically-bound As in soils, which is related to bioavailability, is extremely low in this area (<1% of total As) and the amorphous hydrous Fe and Al oxide-bound As was the major fraction in soils (>50% of total As). A hypothesis was proposed that the amorphous materials in soils may play a central role in limiting the availability of arsenic in the soils (Su and Chen, 2008). To prove the hypothesis and find out the major soil properties affecting As availability in representative Taiwan soils, this study apply As solution in soil samples collected from 9 representative soil series in Taiwan and investigate the dynamics of As fractionation in soils with time under two cultivation systems, paddy fields condition or dry land condition.

Methods
Soil samples collection
According to the reports of previous soil survey in Taiwan, around 20 kilograms of 9 soil samples were collected from agricultural topsoil (0-20 cm) belong to the following soil series representative in Taiwan: Chengchung (Cf) and Annei (An), weathered from sandstone and shale; Erhlin (Eh) and Liuchieh (Lc), weathered from clay slate; Shanhua (Sk) and Linfengying (Lh), weathered from Taiwan clay; Pinchen (Pc) and Chentsoliao (CCe), weathered from red earth; Kuantu (TKt), weathered from andesite (Table 1). The collected soil samples were air-dried, ground, 2 mm sieved, and stored in plastic bottles for further laboratory analysis.

Soil sample analysis
The soil pH (soil:water = 1:1), organic carbon (Walkley-Black method), particle-size analysis (hydrometer method), amorphous Fe, Al, and Mn (acid ammonium oxalate in darkness method), free Fe, Al, and Mn (citrate-bicarbonate-dithionite method), available P (Bray-1 method), and total As (digested by HNO_3/H_2O_2) were analyzed.

Soil spiked by As solution
The solution of $Na_2HAsO_4 \bullet 7H_2O$ was added in one kilogram of each soil samples to reach As load of 60 mg/kg, the soil regulation standard in Taiwan, and incubated for 300 days in two cultivation systems. The cultivation system of paddy fields was simulated by immersing soil with water for 90 days and then maintained soil water content at 70% of water holding capacity (WHC) of soil samples for 60 days. Repeat the same cycle again for the whole period of 300 days incubation. The cultivation system of upland was simulated by maintaining soil water content at 70% of WHC of soil samples for 300 days. Spiked soil samples were stored on indoor bench.

Soil sequential extraction procedures
Arsenic fractionation in soil samples on the 15th, 90th, 150th, and 300th days of incubation were conducted by sequential extraction procedures (SEPs) proposed by Wenzel *et al.* (2001). Five As fractions were operationally defined by authors as: (1) non-specifically-bound As (extracted by $(NH_4)_2SO_4$); (2) specifically-bound As (extracted by $(NH_4)H_2PO_4$); (3) amorphous hydrous Fe and Al oxide- bound As (extracted by NH_4-oxalate buffer); (4) crystalline hydrous Fe and Al oxide-bound As (extracted by NH_4-oxalate buffer + ascorbic acid); and (5) the residual As (digested by HNO_3/H_2O_2).

Results
The characteristics of 9 collected soil samples varied widely and total As concentrations in soils were all below 20 mg/kg (Table 1). After As solution application, total As concentrations in soil samples reached the expected value and ranged from 61.1 mg/kg to 76.3 mg/kg. The accuracy of SEPs was tested by comparing the sum of five As fractions in soil samples on the 15th day of incubation against the total As concentrations independently analyzed in a single acid digest. The recovery ranged from 93% to 137%.

Table 1. Characteristics of 9 soil samples.

Soil sample	pH	Organic C (%)	Total As (mg/kg)		Bray-1 P (mg/kg)	Sand (g/kg)	Silt (g/kg)	Clay (g/kg)
			Original	Spiked				
Chengchung (Cf)	6.84	0.817	6.60	62.9	38.4	281	566	153
Annei (An)	6.72	1.22	12.8	72.3	12.6	104	546	350
Erhlin (Eh)	6.39	1.23	9.82	65.7	23.8	245	483	272
Liuchieh (Lc)	6.23	1.38	10.9	62.0	11.0	238	507	255
Shanhua (Sk)	7.09	1.33	8.58	76.3	69.9	291	408	301
Linfengying (Lh)	6.23	3.28	11.8	61.1	66.4	72	434	494
Pinchen (Pc)	4.67	0.915	9.54	66.9	3.98	80	384	536
Chentsoliao (CCe)	4.86	0.809	8.91	72.8	66.9	226	334	440
Kuantu (TKt)	5.35	1.92	19.1	73.3	51.9	283	316	401

Table 1. (continued)

Soil sample	Free Fe (g/kg)	Amor. Fe (g/kg)	Free Al (g/kg)	Amor. Al (g/kg)	Free Mn (g/kg)	Amor. Mn (g/kg)	Parent materials
Chengchung (Cf)	5.06	2.95	0.421	0.471	0.043	0.036	sandstone & shale
Annei (An)	11.7	5.80	0.896	0.832	0.384	0.400	sandstone & shale
Erhlin (Eh)	9.61	4.69	0.462	0.432	0.103	0.092	clay slate
Liuchieh (Lc)	12.6	3.78	0.600	0.497	0.186	0.194	clay slate
Shanhua (Sk)	11.5	4.02	0.915	0.582	0.209	0.210	Taiwan clay
Linfengying (Lh)	16.5	3.61	1.54	0.844	0.239	0.251	Taiwan clay
Pinchen (Pc)	26.4	1.91	5.86	2.17	0.047	0.019	red earth
Chentsoliao (CCe)	22.8	1.77	2.51	1.16	0.248	0.263	red earth
Kuantu (TKt)	19.8	7.49	1.57	1.80	0.144	0.130	andesite

Amor.: Amorphous.

Arsenic in all soil samples transferred from labile fractions (fraction (1) and (2)) to non-labile fractions (fraction (3) to (5)) with time and this ageing effect was more apparent in paddy fields condition compared with dry land condition (Fig. 1). The relative portions of As fractions were quite stable and did not change very much after 90 days of incubation in both cultivation systems. The specifically-bound As and the amorphous hydrous Fe and Al oxide-bound As were the major fractions in most soil samples, however, for Pc, CCe, and TKt soil samples, more As existed as non-labile fractions.

All the 9 soil samples can be divided into 2 groups according to relative portions of labile As fractions. Group 1 includes the first 6 soil samples collected from soil series of Cf, An, Eh, Lc, Sk, and Lh. The other 3 soil samples collected from soil series of Pc, CCe, and TKt were categorized as Group 2. The relative portions of labile As fractions in Group 2 was around 60% of those in Group 1 after 90 days incubation in both cultivation systems. This indicated that soils belong to Group 2 can effectively reduce environmental risks of As contamination in soils. Compared with Group 1, soil samples in Group 2 contained high amounts of free Fe, free Al, and amorphous Al and the soil pH were all lower than 5.5. This can be interpreted by the facts that Fe/Al oxides in soils had high sorption capacity of As and net surface charge of soil colloids tend to be positive at lower pH, which facilitates the sorption of As by soil colloids because As existed as oxyanions in soils. Compared with the other two soil samples in Group 2, the soil sample of TKt collected from Guandu Plain had apparently higher amounts of amorphous Fe. This supported the hypothesis that the amorphous materials in soils of Guandu Plain play an important role in limiting the availability of As in the soils. From this study we further found that low pH and high amounts of free Fe/Al in soils of Guandu Plain also inhibited As availability in highly As-contaminated soils.

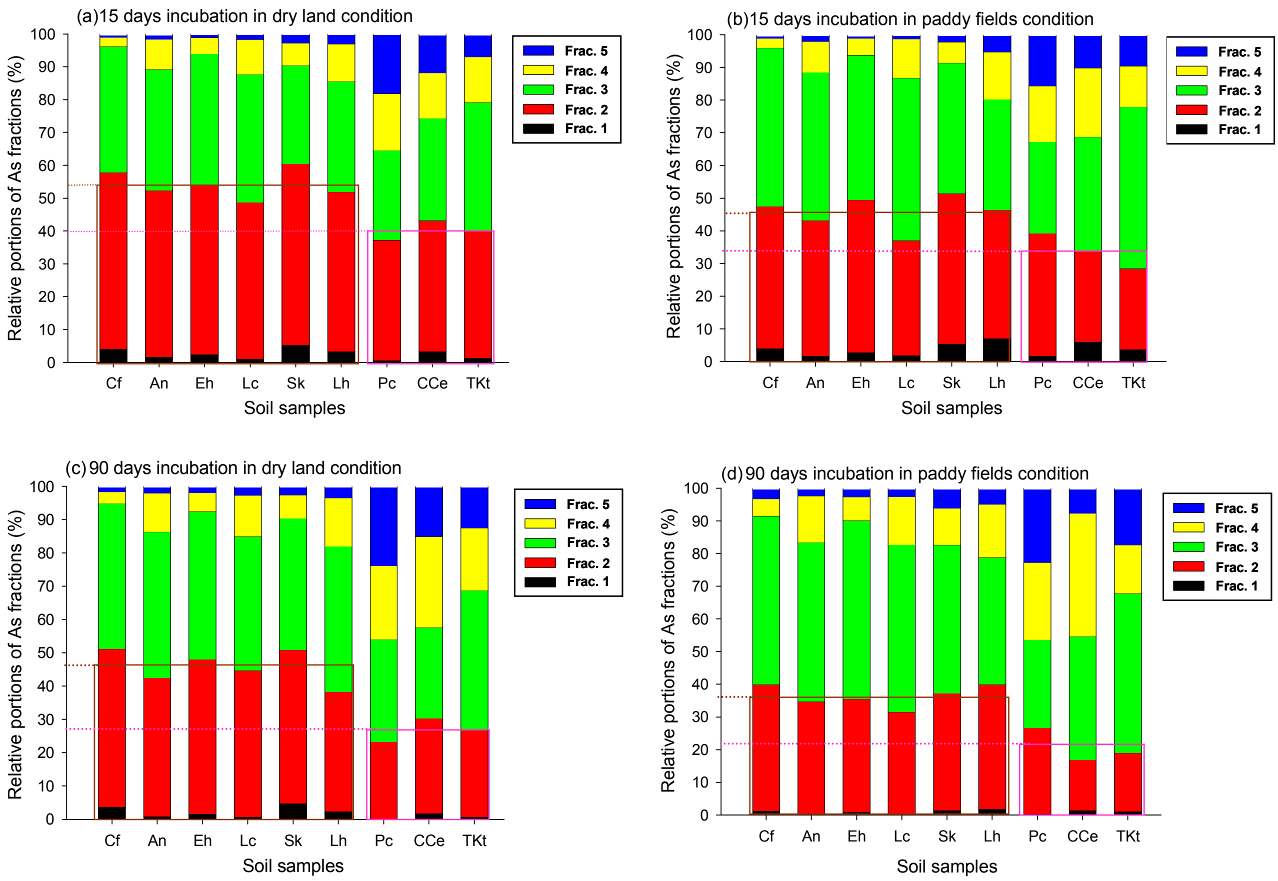

Figure 1. The distributions of As fractions in 9 soil samples after spiking on 15th and 90th day of incubation in dry land and paddy fields condition. The first 6 soil samples (Cf, An, Eh, Lc, Sk, and Lh) are categorized as Group 1 and the latter 3 soil samples (Pc, CCe, and TKt) are categorized as Group 2 based on the relative portions of labile As fractions (fraction 1 and fraction 2).

The Pearson correlation coefficients between the measured soil properties and relative portions of As fractions in soils on the 90th day of incubation showed that the distribution of As fractions in soils was mainly related to soil pH and free Fe/Al (Table 2). This study indicated that the impacts of As-contaminated soils on crop production and agro-ecosystems should not be assessed only by total As in soils because soils with lower pH and higher contents of free Fe/Al oxides can effectively reduce the availability of As in soils. From the results of this study, we supposed that acidic soils (pH < 5.5) containing free Fe + free Al higher than 20 g/kg can be categorized as Group 2. Soils belong to Group 2 had higher capacity to endure As contamination and reduce environmental risks.

Table 2. Pearson's correlation coefficients between soil properties and As fractions in two cultivation systems.

Param-eters	pH	O.C.	Total As	Bray-1 P	Free Fe	Amor. Fe	Free Al	Amor. Al	Sand	Silt	Clay
D.-F. 1	0.65	0.01	-0.53	0.63	-0.57	-0.18	-0.46	-0.59	0.46	0.19	-0.47
D.-F. 2	0.92**	-0.09	-0.45	-0.05	-0.95**	0.09	-0.81**	-0.94**	0.37	0.79*	-0.85**
D.-F. 3	0.77*	0.43	0.25	-0.08	-0.76*	0.65	-0.73*	-0.54	0.12	0.61	-0.53
D.-F. 4	-0.91**	0.01	0.30	0.11	0.94**	-0.25	0.70*	0.75*	-0.34	-0.75*	0.80**
D.-F. 5	-0.93**	-0.23	0.14	-0.11	0.92**	-0.33	0.93**	0.92**	-0.29	-0.71*	0.72*
P.-F. 1	0.21	0.54	-0.01	0.95**	-0.13	0.01	-0.36	-0.28	0.21	-0.27	0.05
P.-F. 2	0.83**	0.22	-0.44	-0.14	-0.74*	-0.04	-0.44	-0.66*	-0.15	0.79*	-0.46
P.-F. 3	0.68*	-0.05	0.13	-0.06	-0.83**	0.58	-0.92**	-0.71*	0.62	0.54	-0.84**
P.-F. 4	-0.78*	-0.14	0.01	0.20	0.81**	-0.47	0.61	0.52	-0.29	-0.64	0.68*
P.-F. 5	-0.77*	-0.06	0.36	-0.11	0.80**	-0.04	0.84**	0.96**	-0.20	-0.69*	0.65

D.-F.: Dry land-Fraction; P.-F.: Paddy fields-Fraction; O.C.: Organic Carbon; Amor.: Amorphous; *: significant at $\alpha = 0.05$; **: significant at $\alpha = 0.01$.

Conclusion

After spiking soil samples with As solution to the level of soil regulation standard enacted in Taiwan, the dynamics of As fractions in soils from 9 common soil series under simulated paddy fields or dry land conditions showed that As transferred to non-labile fractions with time and this trend is more apparent in paddy fields condition. Soil pH and free Fe/Al oxides are the major soil properties affecting As availability and fractionation in the representative Taiwan soils contaminated by As. Soils weathered from red soil and andesite are acidic (pH < 5.5) and containing high amounts of free Fe/Al (> 20 g/kg) can effectively reduce As availability if contaminated by As. Further studies are required to quantify the influence of soil pH and free Fe/Al oxides on environmental risks caused by As-contaminated soils.

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