Arsenic and lead contaminated rice soils in the Guandu Plain, Northern Taiwan

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Abstract

This study aimed to investigate the species of As and Pb (beudantite) residues presented in the seriously contaminated agricultural rice soils in the Guandu Plain. Two pedons in the Guandu Palin agricultural soils, each pedon separated into five horizons (each of 20 cm) were collected for this study. Soil samples were air-dried, ground and passed through 2 mm sieves, and subjected to soil physical and chemical analysis, X-ray diffraction (XRD) analysis and sequential fractionation. Soil samples were packed into a columns for leaching with simulated acid rain. Bulk and clay fraction samples were digested with aqua regia solution to determine As and Pb contents. The XRD analysis indicated beudantite particles were present in clay fractions, showing high concentrations of As and Pb, because of the careless irrigation with water which was introduced from Huang Gang Creek hot springs about 50 to 100 years ago. The spring waters in the Beitou Thermal Valley contain high concentrations of As and Pb. There are only low concentrations of As and Pb that can be leached out with simulated acid rains (i.e., pH 2 and 4), even for 40 pore volumes in leaching experiments. Thus, the remediation of As and Pb in this agricultural rice paddy soils still merits further study.

Key Words

Agricultural paddy soils, beudantite, hot springs, sequential extraction.

Introduction

Taiwan was a colony of the Japanese Government from 1895 to 1945. At that time, farmers occasionally irrigated the Guandu agricultural rice soils during the drought seasons (personal communications with local senior farmers) from Huang Gang Creek, being unaware of the presence of arsenic (As), lead (Pb) and sulfate (SO_4) contaminants in the spring waters. The irrigated water in the Huang Gang Creek originated from Beitou Thermal Valley (i.e., outcrop size about 0.35 hectare, ha) of hot spring waters. It was lucky that there was no black foot diseases occurred in this region because of the strong smell of hot spring waters. From previous soil survey, the As and Pb contaminated soils in the Guandu rice soils occupy about 842 ha, and serious As (i.e., As concentrations are higher than 60 mg/kg) contaminated of rice soils in the Guandu Plain occupy about 128 ha. This study aimed to investigate the species of As and Pb (beudantite) residues present in the seriously contaminated agricultural rice soils in the Guandu Plain.

Methods

Soil sampling

Two pedons of agricultural rice soils were sampled from Guandu Plain. Two sites (pedons 1 and 2) were located in the range of latitudes 25°7’40.87’’N and 121°29’47.37’’E (pedon 1), and 25°7’35’35.26’’N and 121°29’46.19’’E (pedon 2), respectively, of the subtropical region. These two soil profiles have five depth (20 cm) intervals which were analyzed to determine whether chemical and mineralogical differences existed with depth. The soils can be classified as clay loam, mixed, thermic, Typic or Umbric Albaqualfs (Soil Survey Staff 2006).

Chemical and physical properties of soil test

Soil pH was determined on 1:1 soil to water suspensions using a pH meter. Organic carbon and total nitrogen concentrations were determined on a Perkin-Elmer CHN Analyser. For cation-exchange capacity (CEC) determination, 10 g of air dried soil sample was equilibrated with NH_4-acetate (pH = 7.0) solution and washed with 10% NaCl solution. The NH_4 concentration was determined by the Kjeldahl method (Rhoades 1982). Soil bulk density and particle density were determined using the core and density bottle methods (Blake and Hartge 1986). 0.25 mg of bulk soil and clay fraction was digested with aqua regia solutions, As and Pb concentrations were determined by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES, Perkin-Elmer, Model Optima 2000DV).

XRD analyses

Organic matter was removed by 30% H_2O_2 and heating on a hot plate. For improved identification of soil clay minerals by X-ray diffraction (XRD) analysis in soil clays, the soil samples were treated or not treated with dithionite-citrate-bicarbonate (DCB) and heating at 80°C, to remove or not remove free sesquioxides, respectively (Mehra and Jackson 1960). The silt was separated from the sand by wet-sieving (53 µm sieve) (Gee and Bauer 1986). The deferrated soil clays were saturated with Mg and K, and mounted as slurries on glass slides for XRD analysis (Jackson 1979). The Mg-saturated clays were examined at 25°C before and after glycerol solvation. The K-saturated clays were examined at 25°C and after heating at 105°, 250°, 350°, 450° and 550°C for 2 h.The oriented clay mineral aggregates were examined with an X-ray diffractometer (Rigaku Geigerflex) with CuKα radiation at 35 kV and 15 mA, recorded in the range of 3-50 °2θ. The beudantite samples collected from the bank of the Huang Gang Creek were also subjected to powder XRD analysis.

Soil column leached with simulated acid rains

In order to simulate the long-term effect on the Guandu soils leached by the acid deposition, to assess the influence of acidity on retention of Pb and As, soil column samples were artificially leached with simulated acid rain. We selected the pH 2 and 4 of simulated acid rains of 7,450 and 45 µeq/L (i.e., SO_4^{2-} concentrations) of sulfuric acids solutions for the soil column leaching experiments. An acrylic column of soil of 10 cm length (internal diameter of 2.54 cm) was collected from 0-20 cm and 20-40 cm of soil samples (i.e., 32.5 gm) placed into each 5 cm of soil column, then a simulated acid rain solution was introduced. The bulk density of soils in a column was 1.30 g/cm^3. Flow velocity observed from average saturated hydraulic conductivity of soils was 1.0 cm/h. Detailed procedures are described by King *et al.* (2006) and Liu *et al.* (2006).

Sequential fractionations of soil As and Pb

Bulk soil samples were air dried and with sequential fractionated for their As and Pb components, using the modified method of Wenzel *et al.* (2001); Yocubal and Akyol (2008). One gram of oven dried soil sample with 25 mL of extracting solution. The soil samples were fractionated by following sequential extractions: (1) 50 mM [$(NH_4)_2SO_4$] solution, at 20°C shaken for 4 h (nonspecific bound. easily exchangeable); (2) 50 mM [$(NH_4)_2H_2PO_4$] solution, at 20°C shaken for 16 h (strongly bound inner-sphere complexes); (3) 1 M, pH 5 of NaOAc/HOAc buffer solution shaking at 20°C for 6 h (bound to carbonate); (4) pH 6 of 100 mM $NH_2OH{\cdot}HCl$ + 1 M NH_4OAc solution shaking 30 min (bound to Mn oxyhydroxides). (5) pH 3.25, 200 mM of NH_4-oxalate buffer solution shaking 4 h in the dark at 20°C, wash step with pH 3.25, 200 mM NH_4-oxalate buffer solution, shaking at 20°C for 10 min. (bound to amorphous Fe and Al oxyhydroxides). (6) 15 mL, 30% H_2O_2 and 3 mL, 20 mM HNO_3 at 85°C shaking for 2 h, and 5 mL, 3.2 M NaOAC solution, shaking at 85°C for 3 h (Tessier *et al.* 1979) (bound to sulfides and organic matter). For total Pb and As analysis samples are digested with aqua regia solution in a microwave (total fractions) (US-EPA 2007).

Results

Chemical and physical properties of soil tested

Mean soil pHs range from 5.1 to 7.1 (Table 1). Organic carbon, total nitrogen contents and C/N ratios are in the range from 0.35 to 2.72, 0.04 to 0.19, and 9.10 to 32.91%, respectively. Organic carbon and total nitrogen contents decrease with increasing soil depth. The range of CEC is from 11.38 to 22.54 cmol$_{(+)}$/kg. Exchangeable K^+, Na^+, Ca^{2+}, Mg^{2+} and base saturation are in the range from 0.19 to 1.57, 0.78 to 1.46, 5.74 to 11.06, 1.82 to 2.94 cmol /kg, and 42.3 to 98.4%, respectively. These pedons are close to the Chilung watershed with high groundwater tables, containing high exchangeable cations. Soil textures are clay, clay loam and silt clay loam. Mean As and Pb concentrations in bulk soil and clay fraction show that the As concentrated in surface soil and Pb is concentrated in the 60-80 and 80-100 cm layers, indicating the leaching of Pb to deeper soil horizons. However, arsenic movement in pedons is related to the fluctuation of underground water tables and soil redox potentials.

X-ray diffraction

The powder XRD pattern of beudantite which was collected from the bank of Huang Gang Creek showed many peaks which coincide with JCPDS 19-689. This XRD pattern also contain several peak of quartz (JCPDS 33-1161) (Figure 1A) and a 7.1 Å kaolinite peak. Oriented XRD pattern of the DCB treated clay samples (i.e., pedon 1, 60-80 cm), indicted vermiculite which was characterized by the 14.1 Å reflection for Mg-saturated clay at 25°C, collapsing to

Table 1. Chemical and physical properties of soil tested.

Pedon	Soil depth	pH	Organic C	Total N	C/N	CEC	Base Saturation	Sand	Clay	Texture
	(cm)		(----------%---------)		ratio	cmol $_{(+)}$/kg	(%)	(-----%-----)		
1	0-20	5.1	2.48	0.19	13.38	21.33±4.51	52.0	40	30	CL
	20-40	6.0	1.28	0.11	12.21	17.84±2.46	78.1	22	34	C
	40-60	6.2	1.39	0.09	15.39	16.08±1.61	98.4	30	28	C
	60-80	5.7	0.77	0.08	10.25	13.17±4.32	77.4	38	28	CL
	80-100	5.6	0.91	0.10	9.10	20.91±6.38	78.2	26	32	C
2	0-20	6.1	2.72	0.19	14.68	22.54±1.63	42.3	48	26	SCL
	20-40	6.4	1.22	0.05	24.62	22.79±3.39	45.3	44	26	SCL
	40-60	7.1	0.35	0.03	12.02	11.38±1.15	82.2	66	16	SL
	60-80	6.7	1.25	0.04	28.85	19.57±6.55	58.7	40	24	CL
	80-100	6.4	1.25	0.04	32.91	12.89±3.34	86.7	44	22	CL

10.1 Å when the K-saturated clay was heated at 110°C. The 7.1 Å of kaolinite at 25°C of the K-saturated clay was not observed after heating the K-saturated clay at 550°C (Figure 1B). The reflection at 10.1 Å of illite for K-saturated clay was present when clay heated at temperatures from 110° to 550°C. Semi-quantitative of clay mineralogy shows the following trends: vermiculite > kaolinite > illite > mixed layered clays in all pedons. After the clays were treated with DCB procedures to remove the free sesquioxides, clay fractions show significant beudantite reflections (i.e., 2.82, 2.97, 2.56, 2.37 and 1.98 Å) (Figure 1B). XRD analysis clearly shows that the beudantite exists in the soil profile of rice field in the Guandu Plain. These XRD patterns provided the further evidence that As and Pb (i.e., fine particle size of beudantite existing in water suspensions and soil clay fractions) present in soil profiles.

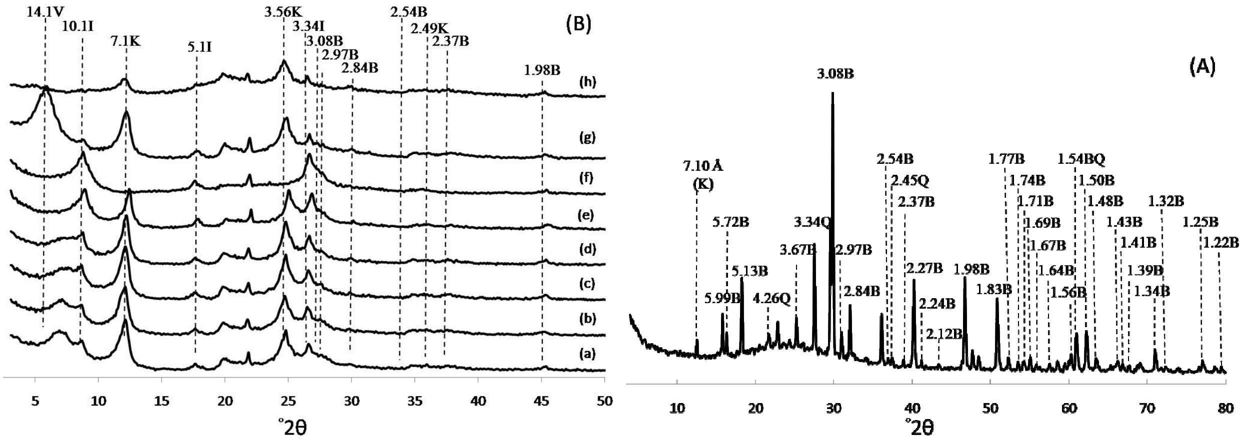

Figure 1. Powder X-ray diffractograms of (A) beudantite collected from the bank of Huang Gang Creek and (D) oriented XRD pattern of DCB treated with clays fractions (60-80 cm), K-saturated clay at (a) 25°, (b) 105°, (c) 250°, (d) 350°, (e) 450°, (f) 550°C, and Mg-saturated clay at (g) 25° C and (h) glycerol solvation. B: beudantite, Go: goethite, I: illite, K: kaolinite, Q: quartz, V: vermiculite.

Soil columns leached with simulated acid rains

Figure 2 shows the accumulation of As in leachates. Accumulation of As in leachates are 0.489 and 0.394 mg (i.e., total amounts of As in soil column is 17.51 mg), which correspond to 2.8 and 2.2% for pH 2 and 4 simulated acid rain leaching after 40 pore volumes. Thus, only low amounts of Pb were leached out. It is indicated that the soil beudantite is not readily leached out by simulated acid rain. Thus, beudantite cannot completely leach out of Guandu Plain rice soils over many years of cultivation of rice. Beudantite still remained in soil profiles.

Sequential extractions

Most of the Pb and As are present in the residual fractions after sequential fractionations. High percentages of As remain in soil profiles possibly bound to amorphous, Fe and Al oxyhydroxides and residual minerals. Pb concentrations show a similar trend except for the 60-80 and 80-100 cm soil horizons.

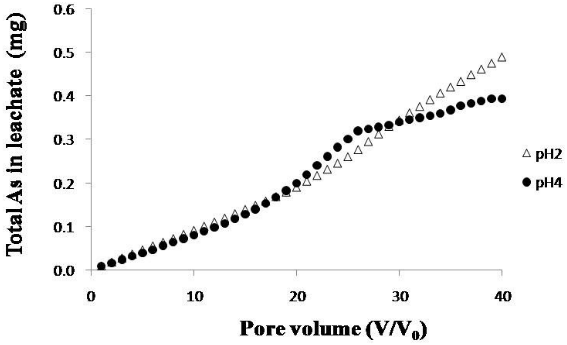

Figure 2. Soil columns leached with simulated acid rains accumulated As after 40 pore volumes of leaching experiments.

Conclusions

Chemical, physical, EDS and XRD analyses indicate that beudanite particles are present in the Guandu agricultural rice soils. As and Pb contaminate the rice soils because of the careless introduction of irrigation waters from the Huang Gang Creek of the Beitou Thermal Valley under the colony of the Japanese Government, from 1985 to 1945 during drought seasons. The spring waters contain high concentrations of As and Pb. Beudantite has not been completely leached out even though the Guandu Plain rice soils have passed through many years of rice production. High concentrations of As and Pb remain in soil profiles as residual minerals as indicated by sequential fractionation. Thus, the remediation of As and Pb from the Guandu agricultural rice soils remains an important research subject and merits further study.

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