

Adsorption and leaching of aromatic arsenicals in Japanese agricultural soils

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Abstract

We investigated the adsorption and mobility of aromatic arsenicals (AAs) in two types of Japanese agricultural soils through the batch and column leaching experiments. AAs were composed of both phenyl or methyl group and arsenate. The amounts of adsorbed AAs onto both Fluvisols, sandy loam, and Andosol, light clay, increased in the order of phenylarsonic acid (PAA) > methylphenylarsinic acid (MPAA) > diphenylarsinic acid (DPAA) > methylphenylarsine oxide (MDPAO) = dimethylphenylarsine oxide (DMPAO). The adsorbed amounts of all AAs onto Andosols, which had relatively high amorphous minerals and organic carbon, were higher than those of Fluvisols. The adsorbability of AAs on soils increased with the increasing a portion of arsenate of AAs. The mobility in Fluvisol was in the orders of DMPAO (30cm) > MDPAO(25cm) > MPAA(20cm) > DPAA(15cm) = PAA(15cm). The mobility in Andosol was in the orders of DMPAO (15cm)=MDPAO(15cm) > DPAA(10cm) > MPAA(5cm) = PAA(5cm). The mobility of MDPAO and DMPAO in soils was higher than that of PAA and MPAA, and all AAs's mobility in Andosols was lower than that in Fluvisols. Consequently, the mobility of AAs in soils decreased with increasing the adsorbability of AAs on soils.

Key Words

Chemisorption, Freundlich equation, hydrophobic bonding, ligand exchange, variable-charge minerals.

Introduction

Diphenylarsinic acid (DPAA) and methylphenylarsinic acid (MPAA) were detected in paddy rice grown in Kamisu-town, Ibaraki Prefecture, Japan in 2004. It is necessary to evaluate the risk to the human of these aromatic arsenicals (AAs) through the soil, water, and farm product. Recently, Arao *et al.* (2009) investigated the uptake of AAs from agricultural soils by rice with compared to the results from AAs-added solution culture experiment, and they reported that MPAA and DPAA were methylated not in the rice plant but in the soil under flooded conditions. However, there has been little research on the behavior of AAs in the agricultural soils and farm products. The objectives of this study were to understand the basis of the adsorption characteristics of AAs in soils and to evaluate the mobility of AAs in agricultural fields.

Materials and methods

Chemicals

Analytical grade AAs as shown by Figure.1 were used in this study. Standard stock solution of AAs (100 mg/L) was prepared in 0.02 mol/L sodium hydroxide or 10% ethanol, and diluted with ultra-pure water.

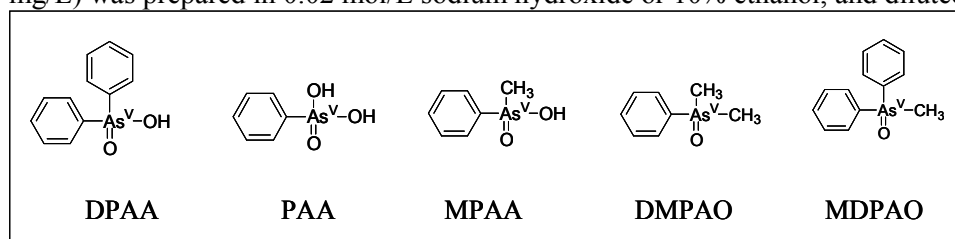


Figure 1. Chemical structure of AAs in this study. DPAA: diphenylarsinic acid; PAA: phenylarsonic acid; MPAA: methylphenylarsinic acid; DMPAO: dimethylphenylarsine oxide; MDPAO : methylphenylarsine oxide

Soil samples

Two types of non-contaminated soils were collected from the surface (top15 cm) in fields in Japan (Kamisu and Tsukuba, Ibaraki Pref.). Soil samples were air-dried, and were then passed through a 2 mm sieve. Soil pH, particle size distribution, cation exchange capacity (CEC), carbon and nitrogen contents, acid oxalate extractable Fe, Al, and Si contents, 1M HCl soluble and total arsenic (As), and phosphate adsorption coefficients were measured.

Adsorption experiment

Adsorption experiments were carried out in a 12-mL glass tube at 25 ± 2 °C according to the method of OECD Guideline for the Testing of Chemicals 106 (OECD 2000). Two grams of soil was put into the glass tube, and 10 mL of AAs solution, such as DPAA, PAA, MPAA, MDPAO, and DMPAO, was added to each soil sample at the soil to solution ratio of 1:5. The final concentration of arsenic (As) in each solution was set to 0, 100, 300, 1000, 3000, and 10000 $\mu\text{g/L}$ including 0.01 mol/L CaCl_2 . Each glass tube was shaken for 24 hours at 25 ± 2 °C. After centrifuged at 3000 rpm for 20 min, the supernatant was filtered with a 0.2 μm membrane filter. The solution was diluted with ultra-pure water, and As in the solution was determined by inductively coupled plasma-optical emission spectrometry (ICP-OES).

Column leaching experiment

DPAA, PAA, MPAA, MDPAO, and DMPAO, were added to the soil according to the method of OECD Guideline for the Testing of Chemicals 312 (OECD 2004). Soil was filled to become 30cm of soil layer thickness with seven fractional columns (5cm in diameter, 5cm in height, and no active alumina). Soil column was filled in 0.01 mol/L CaCl_2 solution during a day. After then, the AAs solution was added to surface water (each AAs was 1 mg As, and total As was 5mg), and 0.01 mol/L CaCl_2 solution flowed at the rate of 0.136 mL/min for 48 hours (corresponded to precipitation 200mm/2day). The percolating water during the experiment was collected using the fraction collector every hour, and As concentration in the percolating water was measured by ICP-OES. The soil column after leaching experiment was divided into 6 sections of soil. AAs were extracted from these soils according to the methods of Baba *et al.* (2008).

Results and discussion

Physico-chemical properties of soils

Physico-chemical properties of soils (Kamisu and Tsukuba) are summarized in Table 1 and Table 2. Tsukuba soil had relatively high organic matter (74.3 g/kg) and clay content (38.5 %), and cation exchange capacity (CEC) (37.9 cmol_c/kg) in comparison to Kamisu soil (Table 1). Tsukuba soil had also high oxalate-extractable Fe, Al, and Si contents, while low oxalate-extractable Fe, Al, and Si contents characterized Kamisu soil (Table 2). Therefore, high amorphous Fe, Al and Si contents of Tsukuba soil will increase the soil surface area, which will potentially reduce the bioavailability of AAs. According to Soil taxonomy (Soil Survey Staff 1998) and WRB (FAO, ISRIC, and ISSS 1998), Kamisu soil was classified as Typic Udifluvents or Eutric Fluvisols, and Tsukuba soil was Typic Fluvudands or Haplic Andosols, respectively.

Table 1. Physico-chemical properties of soil samples.*

Sample	Hor. Depth (cm)	Particle size distribution			Texture	pH		CEC ($\text{cmol}_c \text{ kg}^{-1}$)	Total			
		Sand (%)	Silt (%)	Clay (%)		H ₂ O	KCl		C (g kg^{-1})	N (g kg^{-1})	CN ratio	
Kamisu	Ap	0-15	78.9	9.1	12.0	SL**	5.8	5.2	14.0	9.8	0.8	12.1
Tsukuba	Ap	0-15	26.4	35.1	38.5	LiC	5.8	5.0	37.9	74.3	4.8	15.5

*, oven-dry basis, **, SL: sandy loam, LiC: light clay

Table 2. Physico-chemical properties of soil samples (continued).*

Sample	Oxalate extractable				As		Phosphate abs. coeff.*** ($\text{g P}_2\text{O}_5 \text{ kg}^{-1}$)	Soil classification	
	Fe (g kg^{-1})	Al (g kg^{-1})	Si (g kg^{-1})	Al+1/2Fe (g kg^{-1})	1M HCl (g kg^{-1})	Total (g kg^{-1})		WRB (1998)	USDA system (1998)
Kamisu	7.0	1.8	1.5	5.3	0.55	6.2	7.1	Eutric Fluvisols	Typic Udifluvents
Tsukuba	19.0	43.7	17.0	53.2	1.05	12.1	21.7	Haplic Andosols	Typic Fluvudands

***, phosphate absorption coefficient

Adsorption experiment

The amounts of adsorbed AAs onto both Fluvisol (Kamisu) and Andosol (Tsukuba) increased in the order of PAA>MPAA>DPAA>MDPAO=DMPAO (Figure 2a, b). Moreover, all of AAs were strongly adsorbed onto Andosols compared with Fluvisols. Adsorption isotherms can be fitted using Freundlich equation. PAA, MPAA, and DPAA, which have hydroxyl group in those structural formulas, were seemed to be mainly adsorbed onto the surface hydroxyl groups at layer silicate edges, on oxyhydroxides of iron and aluminium, and on noncrystalline aluminosilicates. These AAs were chemisorbed by variable-charge minerals to make

inner-sphere complexes by ligand exchange reaction as well as phosphate sorption (Obihara and Russell 1972; Nanzyo and Watanabe 1981). In addition, a part of the structures in these AAs might be adsorbed onto soil organic matter with both phenyl and methyl group by the hydrophobic bonding. On the other hand, both DMPAO and MDPAO, which have no hydroxyl group, would be mainly adsorbed onto soil organic matter by the hydrophobic bonding only. Judging from these results, an adsorption of AAs, which have hydroxyl group, by ligand exchange reaction, might be stronger than that of AAs, which have no hydroxyl group, by the hydrophobic bonding.

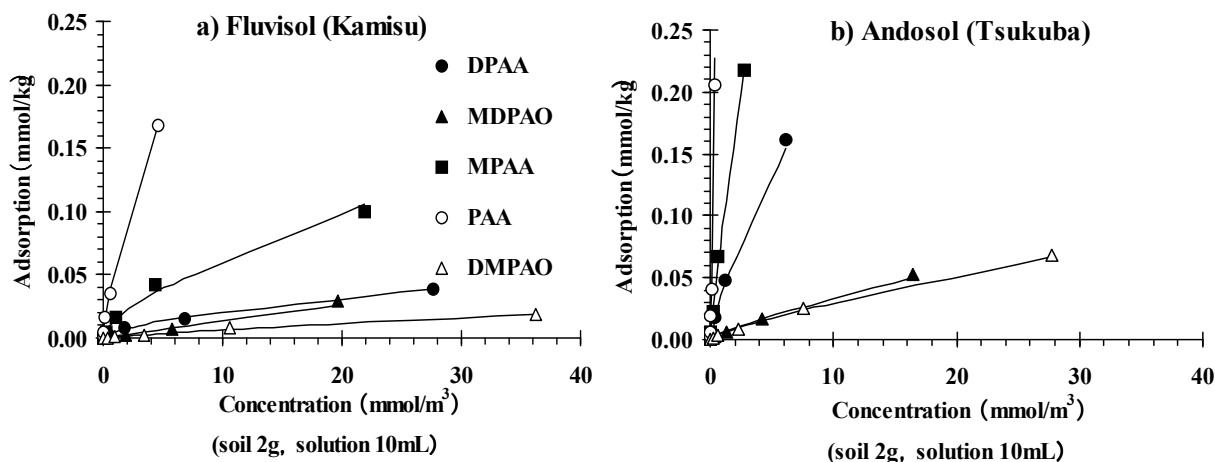


Figure 2. Adsorption isotherms of aromatic arsenicals (AAs) on Japanese agricultural soils. a) Fluvisol (Kamisu) and b) Andosol (Tsukuba).

Column leaching experiment

Figure 3 shows AAs distribution of soil column two days after leaching experiments. It was clear that the mobility of AAs in Andosol was lower than that in Fluvisol (Figure 3a, b). The mobility in Fluvisol (0.5% or more of the total AAs was detected) was in the orders of DMPAO(30cm) > MDPAO(25cm) > MPAA(20cm) > DPAA(15cm) = PAA(15cm). The mobility in Andosol was in the orders of DMPAO(15cm) = MDPAO(15cm) > DPAA(10cm) > MPAA(5cm) = PAA(5cm) (Table 3). Any AAs could not be detected in the percolating water during two days (data not shown). Both PAA and MPAA were retained at the surface of both soils because PAA and MPAA were seemed to be tightly adsorbed onto variable-charge minerals in the soil by ligand exchange reaction as well as the results of adsorption experiment. On the other hand, both DMPAO and MDPAO can move down relatively because these chemicals would be less adsorbed than PAA and MPAA. Therefore, it was confirmed that these results of adsorption experiment were corresponded to those of soil column leaching experiment.

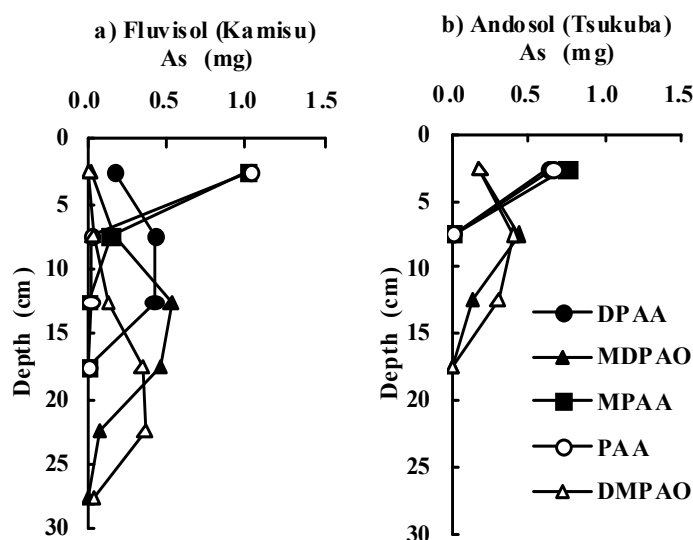


Figure 3. Aromatic arsenicals (AAs) distribution of soil column two days after leaching test. a) Fluvisol (Kamisu) and b) Andosol (Tsukuba).

Table 3. Aromatic arsenicals (AAs) distribution of soil column two days after leaching test on Fluvisol (Kamisu) and Andosol (Tsukuba).

Depth (cm)	Fluvisol (Kamisu)					Andosol (Tsukuba)				
	Distribution (%)					Distribution (%)				
	DPAA	MDPAO	PAA	MPAA	DMPAO	DPAA	MDPAO	PAA	MPAA	DMPAO
0-5	16.4	1.8	96.1	86.1	1.2	97.8	23.8	100	100	20.9
5-10	41.8	13.6	2.4	12.3	3.9	2.2	58.6	n.d.	n.d.	45.1
10-15	41.5	41.6	1.6	0.7	14.2	n.d.	17.5	n.d.	n.d.	34.0
15-20	0.4	36.4	n.d.	0.9	37.4	n.d.	n.d.	n.d.	n.d.	n.d.
20-25	n.d.	6.6	n.d.	n.d.	39.3	n.d.	n.d.	n.d.	n.d.	n.d.
25-30	n.d.	n.d.	n.d.	n.d.	4.0	n.d.	n.d.	n.d.	n.d.	n.d.

*n.d.:not detected

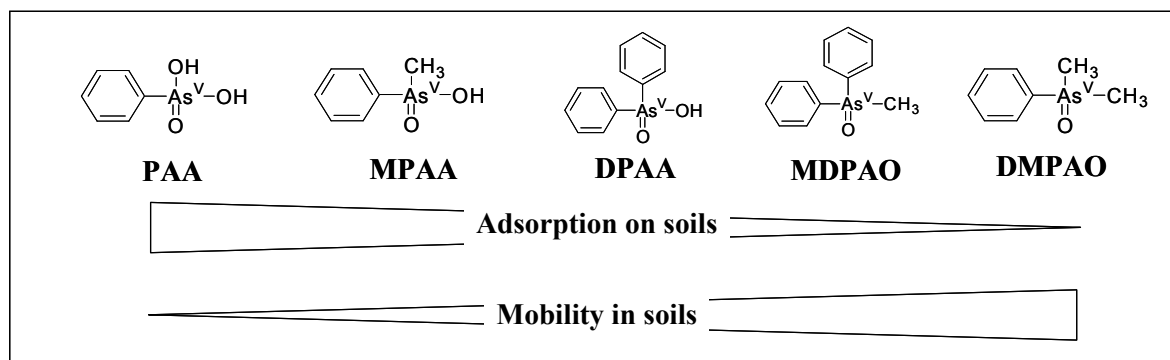


Figure 4. Relationship between adsorption and mobility of aromatic arsenicals (AAs) on soils.

Conclusion

The adsorption characteristics and mobility of AAs were summarized by Figure 4. The adsorption mechanism of PAA, MPAA and DPAA onto soils might be different from that of MDPAO and DMPAO due to the difference in these AAs's structural formulas. However, all AAs were strongly adsorbed onto Andosols compared with Fluvisols. The mobility of MDPAO and DMPAO in acid soils with low clay and oxide content like Fluvisols was higher than that of PAA and MPAA. Judging from the viewpoint of the long-term fate, it is possible that both MDPAO and DMPAO in Fluvisols move down to ground water.

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