Adsorption of Arsenite and Arsenate in Variable Charge Soils of New Zealand

Mahimairaja, S[1*] and Bolan, N.S[2]

[1]Dept. of Environmental Science, Tamil Nadu Agricultural University, Coimbatore – 641003, India
[2]Centre for Environmental Risk Assessment and Remediation, University of South Australia, Mawson Lakes, SA 5095, Australia

** Corresponding author: E Mail: rajasmahimai@yahoo.co.in*

Abstract

The chemical species and their physico-chemical reactions in soils determine the chemistry and biotoxicity of arsenic (As) in soils. Therefore, in the current study, the adsorption of arsenite - As(III), and arsenate – As(V) in selected soils of New Zealand that differ in their charge components was examined. The adsorption kinetics showed that irrespective of soil types, the adsorption of As(III) continued upto 48 hrs, although more than 90% occurred within 24 hrs. In contrast, the adsorption of As(V) was initially rapid (> 80% within 30 min) and continued afterwards at a slow rate upto 48 hrs. The results of batch experiments have shown that the sorption data for both As(III) and As(V) were adequately described by the Freundlich equation. Marked differences were observed among the soils. In general, soils with allophonic clay mineral and high CEC adsorbed more As than soils with mica / illite minerals and low CEC. The phosphate addition markedly reduced [20 to 43% in As(III); 13 to 54% in As(V)] the adsorption, particularly at lower concentration of As. ***(Keywords:*** *arsenite: arsenate: adsorption: isotherms: bioavailability: cation exchange capacity)*

Introduction

Arsenic (As) is a toxic metalloid which enters terrestrial and aquatic ecosystems through both natural (geological) processes and anthropogenic (industrial and agricultural) activities (Adriano, 2001). Indiscriminate disposal of domestic (sewage) and industrial (timber, tannery, paints and electroplating, etc.) wastes, excessive use of As-based pesticides and mining activities have resulted widespread As-contamination of soils and water ecosystem in many parts of the world. Arsenic contamination in soil and water has become a sensitive environmental issue due to its adverse effect on human and animal health (Mahimairaja *et al*., 2005). The extensive As-contamination of ground waters in Bangladesh and West Bengal is of geological origin (Alam and Sattar, 2000; Smith *et al*., 1999) and has

been considered of calamitous proportion because significant segment of the population is at high risk, with untold number already suffering from irreversible effects of As poisoning.

The chemistry and bioavailability of As in soils and aquatic ecosystems is strongly influenced by its speciation and physico-chemical reactions like adsorption and desorption. No other single factor indicates more about the probable fate of a metal(loid) than its resultant distribution between the soil solution phase and soil solid phase. Despite the considerable research on As in soils, data on As adsorption particularly for variable charge soils of New Zealand still limited. Such data may help to develop the remediation strategies for As-contaminated soils. Therefore, the adsorption of As(III) and As(V) in selected soils of New Zealand that varied in their variable charge components was examined. Remediation based on *in situ* immobilization by soil amendments is becoming increasingly popular because of high rate of success. Phosphate ions induce the mobilizations of As, thereby increasing its bioavailability. Large quantities of phosphate (P) fertilizers are used in New Zealand pasture soils. Hence, the effect of P fertilizers on the adsorption and mobilization of As(III) and As (V) in soils was also examined.

Materials and Methods

Batch experiments

A series of laboratory batch experiments were conducted to examine the adsorption of different species of As viz., As(III) and As(V) in New Zealand soils (Egmont, Manawatu, Tokomoru, Ramiha, and Blenheim soils) that differ in chemical characteristics (Table 1). Firstly, the adsorption at a range of equilibrium period (0.5, 1, 2, 5, 8, 12, 24, 36 and 48 hrs) was examined at a single input concentration of 100 mg L^{-1}. It was found that sorption equilibrium was achieved within 24 hrs. The adsorption isotherms for As(III) and As(V) were obtained by batch studies at concentrations ranged between 0 and 100 mg L^{-1} using $NaAsO_2$ for As(III) and $Na_2HAsO_4.7H_2O$ for As(V) with 0.03M $NaNO_3$ as the matrix electrolyte. The soils were mixed with the As solutions in polypropylene tube at a soil: solution ratio of 1:20 by shaking on an end-over-end shaker for 24 hrs at 20±2^oC. The concentrations of As(III) and

As(V) remaining in the solution were measured using a Graphite Furnace Atomic Absorption Spectrophotometer (GFAAS). Differences in the initial and the equilibrium solution concentrations were computed to determine the amount of As(III) and As(V) sorbed per unit mass of soil.

Table 1. Some important characteristics of soils used in the study

Soil	pH (H_2O 1:2.5)	Organic carbon (g kg^{-1})	P retention (%)	CEC (cmol $kg^{-1)}$	Dominant clay mineral
1. Egmont (*Typic Dystrandept*)	5.21	78.5	83	26.2	Allophane
2. Manawatu (*Dystric Fluventic*)	6.01	29.1	33	7.6	Mica / illite
3. Ramiha (*Typic Dystrandept*)	4.79	56.2	79	22.4	Allophane
4.Tokomaru (*Typic Fragiaqualf*)	5.32	34.3	51	11.2	Mica/illite
5. Blenheim (*Typic Fragiaqualf*)	5.80	32.4	12	6.5	Mica / illite

The sorption data were fitted to Freundlich isotherm (Eq 1) and Langmuir isotherm (Eq 2):

$$(x/m) = K_f \, Ce^n \qquad \text{(Eq 1)}$$

where, (x/m) is amount of As adsorbed (mg kg^{-1}), K_f is Freundlich distribution coefficient, is the equilibrium solution concentration (mg L^{-1}), and the '*n*' is equilibrium constant (dimensionless).

$$Y = (MbC) / (1 + (bC)) \qquad \text{(Eq 2)}$$

Where Y = amount adsorbed (mg kg^{-1}), C = equilibrium solution (mg L^{-1}), and b is the Langmuir constant, related to adsorption energy.

To describe the adsorption kinetics, the zero-, first-, second-, and third-order reactions, the parabolic diffusion, and the Elovich equations (Table 2) were tested for goodness of fit by least-squares regression analysis. The equation that best described the

adsorption of As(III) and As(V) by these soils was determined by computing a standard error of estimate (SE) using the following equation:

$$SE = [\Sigma (q_t - q^*_t)^2 / (n-2)]^{(1/2)} \quad \text{(Eq3)}$$

Where q_t and q^*_t are the measured and calculated sorbed As in soil at time *t*, and *n* is the number of time points for measurements. The standard error of estimate is considered to be the best measure of the agreement of the calculated values with the observed values (Steel and Torrie, 1960).

Table 2. Various kinetic models used

Model	Equation	Parameters
Zero-order reaction	$q_t = q_o + k_o t$	k_o, zero-order rate constant (mg As kg^{-1})
First-order reaction	$1n\ q_t = 1n\ q_o + k_1 t$	k_1, first-order rate constant (1/s)
Second-order reaction	$1/q_t = 1/q_o - k_2 t$	k_2, second-order rate constant [(mg As $kg^{-1})^{-1}$]
Third-order reaction	$1/q_t^2 = 1/q_o^2 - k_3 t$	k_3, third-order rate constant (mg As $kg^{-1})^{-2}S^{-2}$]
Parabolic diffusion	$Q = \alpha + k_d \sqrt{t}$	k_d, diffusion rate constant (mg As $kg^{-1})^{0.5}$]
Elovich-type equation	$q_t = q_o + (1/\beta)\ 1n\ (\alpha\ \beta) + (1/\beta)\ 1n\ t$	α , initial As sorption rate (mg As $kg^{-1}h^{-1}$), and β, As desorption constant (mg As $kg^{-1})^{-1}$]

q_t and q_o are the amount of As sorbed (mg As kg^{-1}) at time zero and t, respectively.

Effect of phosphate on adsorption

The effect of phosphorous (P) fertilizers on the adsorption and mobilization of As(III) and As(V) in soils was examined. Duplicated soil samples were incubated with P (KH_2PO_4) at a rate equivalent to 50 kg P ha^{-1} for 3 days. Then the samples were equilibrated on an end-over-end shaker for 24 hrs at 20±2°C in polypropylene tubes with 20 ml of 0.03M $NaNO_3$ solution containing varying amounts (0, 1, 5, 10, 25, 50 and 100 mg L^{-1}) of both As(III) and As(V). The equilibrium concentrations were measured using FAAS and the amount adsorbed calculated.

Results and Discussion

Adsorption kinetics

The adsorption experiment showed that irrespective of soil types, the adsorption of As(III) continued upto 48 hrs, although more than 90% occurred within 24 hrs. In contrast, the adsorption of As(V) was initially rapid (>80% occurred within 30 minutes), particularly, in Egmont and Ramiha soils and continued afterwards at a slow rate upto 48 hrs. An initial fast process per unit time followed by slower and finally a steady-state condition generally characterized the sorption patterns. The amount of As sorbed by these soils was poorly described by the zero-, first-, second-, and third order reactions. With increasing order of reaction from zero to third, the coefficient of determinants (R^2) and the standard error of estimate (SE) of the dependant variable decreased for As(III) (Table 3). Whereas for As(V) the SE appeared to have increased and there was only a small increase in coefficient of determinants. The parabolic diffusion equation described As sorption for the five soils much better than did the zero-, first-, second-, and third order reactions (Table 4).

Table 3. Range and means of coefficients of determinations (R^2) and standard error of estimate (SE) of the various kinetics equation used for As(III)

Equation	R^2		SE	
	Range	Mean	Range	Mean
Zero-order reaction	0.483 – 0.803	0.634	11.3 – 21.4	14.4
First-order reaction	0.429 – 0.723	0.588	2.1 – 18.8	11.6
Second-order reaction	0.367 – 0.628	0.525	9.9 – 16.5	11.9
Third-order reaction	0.301 – 0.522	0.448	9.3 – 13.8	11.2
Parabolic diffusion	0.686 – 0.922	0.794	4.8 – 14.1	8.3
Elovich-type	0.849 – 0.929	0.892	0.7 – 5.1	2.1

The relatively highest R^2 (0.892 for As(III), 0.727 for As(V)) and combined with the relatively lowest SE (2.1 for As(III), and 3.78 for As(V)) over the whole time range indicated that the As sorption in these soils was better described by Elovichian kinetics.

Table 4. Range and means of coefficients of determinations (R^2) and standard error of estimate (SE) of the various kinetics equation used for As(V)

Equation	R^2		SE	
	Range	Mean	Range	Mean
Zero-order reaction	0.081- 0.676	0.489	0.1 – 58.5	18.8
First-order reaction	0.081 – 0.676	0.475	0.1 – 28.3	12.8
Second-order reaction	0.081 – 0.676	0.454	0.4 – 86.2	21.2
Third-order reaction	0.081 – 0.676	0.428	6.2 – 79.1	20.9
Parabolic diffusion	0.195 – 0.786	0.647	0.1 – 51.3	14.1
Elovich-type	0.132 – 0.931	0.727	0.1 – 15.2	3.78

Adsorption isotherms

The sorption data for both As(III) and As(V) were adequately described by the Freundlich equation (Eq 1), as indicated by high correlation coefficients (R^2) (Table 5). The As-adsorption isotherm obtained for the six soils are depicted in Figure 1 to 5. The distribution coefficient (K_f), a measure of adsorption capacity, varied from 28.3 to 448.7 for As(III) and 239 to 557.2 for As(V). Marked differences were observed in the adsorption capacity among the soils for both As(III) and As(V). In general, in all soils except Blenheim, the K_f were higher for As(V) than As(III), indicating higher adsorption capacity of these soils for As(V).

Table 5. Freundlich equation describing the adsorption of As(III) and As(V) in soils

Soils	As(III)		As(V)	
	Equation	R^2	Equation	R^2
Egmont	$x/m=144.2\ Ce^{1.40}$	0.891	$x/m=557.2\ Ce^{1.22}$	0.992
Manawatu	$x/m=28.3Ce^{0.47}$	0.969	$x/m=339.6\ Ce^{1.04}$	0.909
Ramiha	$x/m=448.7\ Ce^{1.07}$	0.943	$x/m=492.0\ Ce^{1.32}$	0.978
Tokomaru	$x/m=285.7\ Ce^{1.42}$	0.957	$x/m=479.7\ Ce^{1.07}$	0.916
Blenheim	$x/m=397.2\ Ce^{0.64}$	0.921	$x/m=239.0\ Ce^{0.63}$	0.951

* $(x/m) = K_f Ce^n$

The Egmont, Ramiha and Tokomaru soils adsorbed higher amounts of As(V) and As(III) than did Manawatu and Blenheim soils. The difference in adsorption is mainly due to variability in soil characteristics. It is evident that the soils with allophonic clay mineral adsorbed higher amounts of As than soils with mica / illite clay minerals. The large amounts of organic carbon and high cation exchange capacity and phosphorus retention in Egmont and Ramiha soils also might have enhanced the adsorption (Bolan *et al*., 2003). The adsorption and retention of As by soils determine its persistence, reactions, movement, transformation and ecological effects (toxicity). As in the case of most other metal(loid)s and non-metals, the first reaction to occur in soils is adsorption onto soil particles. Numerous studies have dealt with As sorption onto specific minerals and uncontaminated soils. Ferrous oxides/hydroxides are most commonly involved in the adsorption of As in both acidic and alkaline soils. Carbonate minerals adsorb As in calcareous soils. In acidic soils, Mn oxides and biogenic particles play a dominant role in the adsorption of As (Oscarson *et al*., 1981; Arai *et al*., 2003). Arsenic is known to have high affinity for oxide surfaces, and several biogeochemical factors are found to play a major role on adsorption. Soil particle size, organic matter, type and nature of constituent minerals, pH, redox potential, and competing ions have all been shown to influence As adsorption (Smith *et al*., 1999; Chiu and Hering, 2000).

Effect of phosphate

In general, phosphate addition resulted in a decrease (20 to 43% in As(III); 13 to 54% in As(V)) in As-adsorption, particularly, at lower levels of As addition (Table 6). In Egmont and Ramiha soils (with high P fixing capacity) the adsorption of both As(III) and As(V) decreased markedly due to P addition, particularly at low concentration of As. Whereas, at higher levels of As, the addition of P resulted relatively higher adsorption of both As(III) and As(V). In Manawatu soil (with low P fixing capacity) P addition resulted consistently higher adsorption at all levels of As(III).

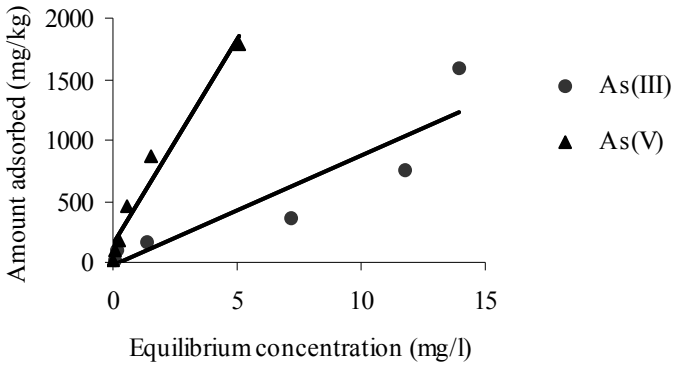

Figure 1. Arsenic adsorption isotherm for Egmont soil

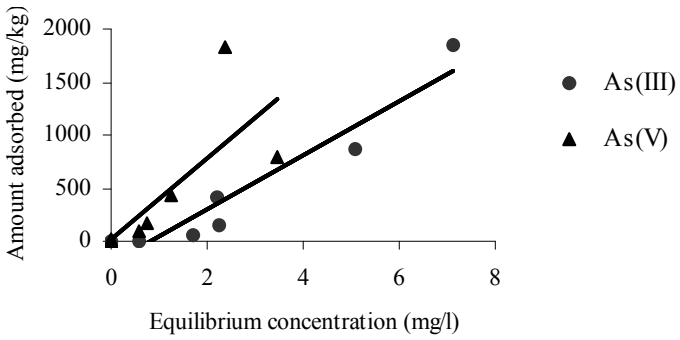

Figure 2. Arsenic adsorption isotherm for Manawatu soil

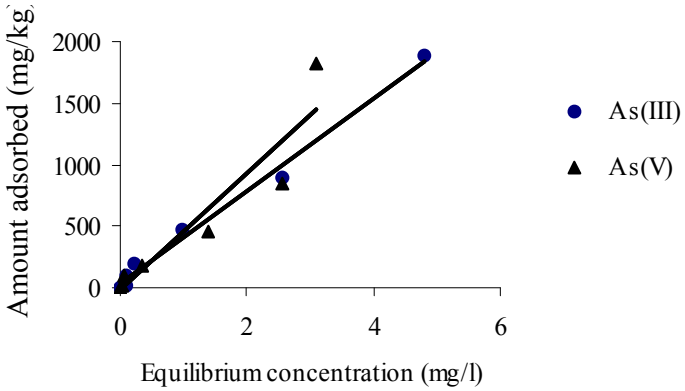

Figure 3. Arsenic adsorption isotherm for Ramiha soil

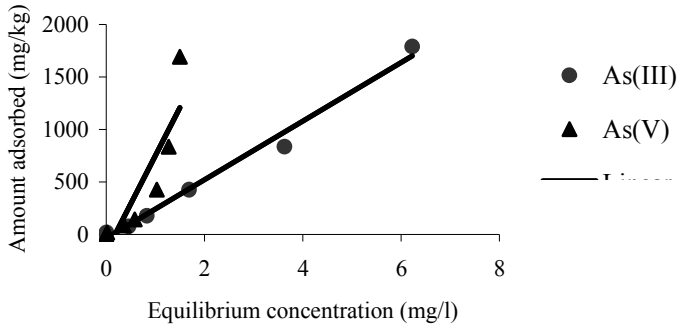

Figure 4. Arsenic adsorption isotherm for Tokomaru soil

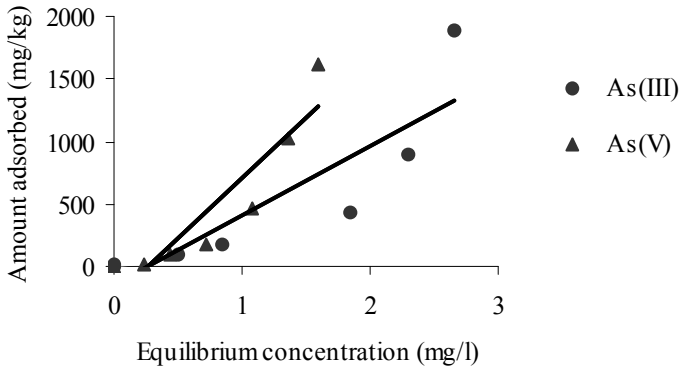

Figure 5. Arsenic adsorption isotherm for Blenheim soil

Similar effect was also observed on As(V) adsorption but only at higher levels of As (Table 6). In general, except in Blenheim soil, P addition markedly increased the adsorption of both As(III) and As(V). The decrease in adsorption could possibly be due to competitive effect of phosphate ions for exchange sites. However, at higher concentrations As(III) and As(V) might have replaced the phosphate ions from the exchange sites and strongly adsorbed. The effect of P addition on As-adsorption was dependent on soil type. One effect of P addition is to increase the soil's surface negative charge thereby reducing As-adsorption. Both As and P are Group V_A elements and thus have similar electron configurations and

chemical properties. Therefore, in soil, As and P will compete with each other for soil sorption sites.

Arsenic and P belong to the same chemical group, and both have comparable dissociation constants for their acids and solubility products for their salts. Therefore, $H_2AsO_4^-$ and $H_2PO_4^-$ ions compete for the same sorption sites in soils, though some sites are preferentially available for the sorption of either $H_2PO_4^-$ or $H_2AsO_4^-$ ions. A number of studies have shown that among the competing anions, the $H_2PO_4^-$ suppresses As(V) sorption by soil more significantly than chloride (Cl^-), nitrate (NO_3^-), and sulfate (SO_4^{2-}) (Thanabalasingam and Pickering, 1986; O'Neill, 1995).

Conclusions

The results have shown that New Zealand soils differ widely in their capacity to adsorb As(III) and As(V). The amount of As(V) adsorbed was higher in all soils than As(III). The characteristics of soil were found to play a major role in the adsorption reactions. The soils (Egmont and Ramiha) with allophone, and high P retention capacity, higher organic matter and CEC adsorbed large amount of As(III) and As(V) than did soils with mica / illite and low in P retention and CEC. Phosphorus addition had decreased the adsorption of both As(V) and As(III) at lower levels, but, markedly increased the adsorption of As(III) and As(V) at higher levels.

Acknowledgement

The authors would like to thank the Massey University, New Zealand for the award of the MURF Post-Doctoral Fellowship and the Tamil Nadu Agricultural University, Coimbatore for granting permission and leave to undertake PDF programme.

Table 6. Effect of phosphate addition on the adsorption (mg kg^{-1}) of As(III) and As(V) by variable charge soils.

Soil		As (III) (mg L^{-1})						As (V) (mg L^{-1})					
		1	5	10	25	50	100	1	5	10	25	50	100
Egmont	-P	17	94	164	357	749	1589	19	94	186	459	868	1782
	+P	14	53	148	463	971	2000	20	44	98	446	989	1988
Manawatu	-P	8	58	150	420	862	1852	18	89	171	435	793	1828
	+P	12	77	174	471	986	1966	14	59	169	443	974	1938
Ramiha	-P	16	92	190	471	888	1885	19	94	180	454	850	1816
	+P	14	75	183	452	987	1996	19	99	198	495	932	2000
Tokomaru	-P	17	76	177	425	836	1789	19	86	144	426	834	1691
	+P	19	51	166	459	991	1898	16	40	130	350	711	1589
Blenheim	-P	15	90	179	435	897	1887	17	88	179	464	1030	1611
	+P	16	48	87	305	691	1601	15	42	129	373	1028	2000

References

Adriano, D.C. (2001) *Trace Elements in Terrestrial Environments: Biogeochemistry, Bioavailability and Risks of Metals*. Second Edition, Springer, New York.

Alam, M.B. and Sattar, M.A. (2000) Assessment of arsenic contamination in soils and waters in some areas of Bangladesh. *Water Sci. Technol*., **42**, 185-192.

Arai, Y., Lanzirotti, A., Sutton, S., Davis, J.A. and Sparks, D.L. (2003) Arsenic speciation and reactivity in poultry litter. *Environ. Sci. Technol.,* **37,** 4083-4090.

Bolan, N.S., Adriano, D.C. and Naidu, R. (2003) Role of phosphorus in (im)mobilization and bioavailability of heavy metals in the soil-plant system. *Rev. Environ. Contam Toxicol.,* **177**, 1 – 44.

Chiu, V.Q. and Hering, J.G. (2000) Arsenic adsorption and oxidation at manganite surfaces. 1. Method for simultaneous determination of adsorbed and dissolved arsenic species. *Environ. Sci. Technol.,* **34**, 2029-2034.

Mahimairaja, S., Bolan, N.S., Adriano, D. and Robinson, B. (2005) Arsenic contamination and its risk management in complex environmental settings. *Advances in Agronomy*, **86**, 1-82.

O' Neill, P. (1995) **In:** Heavy Metals in Soil. B.J. Alloway (Ed.) Arsenic. (Blackie Academic & Professional, Glasgow).

Oscarson, D.W., Huang, P.M., Defosse, C. and Herbillon. (1981) Oxidative power of Mn(IV) and Fe(III) oxides with respect to As(III) in terrestrial and aquatic environments. *Nature.,* **291**, 50-51.

Smith, E., Naidu, R. and Alston, A.M. (1999) Chemistry of arsenic in soils. I. Sorption of arsenate and arsenite by four Australian soils. *J. Environ. Qual*., 28, 1719-1726.

Steel, R.D. G. and Torrie, J.H. (1960) *Principle and Procedures of Statistics*. McGraw – Hill, New York, NY.

Thanabalasingam, P. and Pickering, W.F. (1986) Arsenic sorption by humic acids. *Environ. Poll*., **12,** 233-246.