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Chemistry of inorganic arsenic in soils: kinetics of arsenic adsorption–desorption

E. Smith · R. Naidu

Abstract The influence of ionic strength, index cations and competing anions on arsenate (As^V) adsorption–desorption kinetics was studied in an Alfisol soil. A flow-through reactor system similar to that developed by Carski and Sparks (Soil Sci Soc Am J 49:1114–1116, 1985) was constructed for the experiments. Arsenate adsorption kinetics for all the treatments were initially fast with 58–91% of As^V adsorbed in the first 15 min. Beyond 15 min, As^V adsorption continued at a slower rate for the observation period of the experiments. Changes in the solution composition had differing effects on the cumulative amount of As^V adsorbed by the soil. Ionic strength and different index cations had little effect on the amount of As^V adsorbed, while the presence of phosphate decreased the amount of As^V adsorbed from 169 to 89 and 177 to 115 g As^V μg^{-1} in 0.03 M sodium nitrate and 0.01 M calcium nitrate, respectively. Considerably less As^V was desorbed than was adsorbed, with only between 2 to 17% of the adsorbed As^V desorbed. The presence of phosphate increased the amount of As^V desorbed by 17%, but other changes in the solution ionic strength or index cation had little effect on the amount of As^V desorbed.

Keywords Inorganic arsenic · Soils · Adsorption–desorption · Kinetics

Introduction

Arsenic (As) sorption on pure mineral and soil surfaces has been extensively studied to evaluate its mobility and fate in soils, surface and groundwater. Sorption reactions have been the focus of these studies, as in most cases, these processes control the concentration of As in soil solutions and therefore the bioavailability of As in the environment (Fendorf et al. 1997). Although the extent of adsorption and desorption of As by mineral surfaces (Anderson et al. 1976; Pierce and Moore 1980; Manning and Goldberg 1997a; Grafe and Sparks 2005) and soils (Manning and Goldberg 1997b; Smith et al. 1999) has been widely studied, limited information is available on the kinetics of the sorption reactions and the factors that influence such reactions. Knowledge of sorption reaction rates is useful for providing an insight into reaction mechanisms and the processes occurring on the adsorbing surface (Skopp 1986).

In most studies, information on the kinetics of As sorption has been obtained using batch methods (e.g., Anderson et al. 1976; Pierce and Moore 1980; Fuller

E. Smith (✉) · R. Naidu
Centre for Environmental Risk Assessment and
Remediation, University of South Australia, Mawson
Lakes, SA 5095, Australia
e-mail: Euan.Smith@unisa.edu.au

R. Naidu
CRC for Contamination Assessment and Remediation of
the Environment, Mawson Lakes, SA 5095, Australia

et al. 1993; Scott and Morgan 1995; Raven et al. 1998). Based on such studies, numerous researchers have reported that the adsorption of both arsenate (As^V) and arsenite (As^{III}) on pure minerals and soils is rapid (Anderson et al. 1976; Pierce and Moore 1980; Raven et al. 1998). For example, Elkhatib et al. (1984) reported that the initial reaction of As^{III} with five surface and subsurface soils that had a range of chemical and physical properties (coarse-loamy, mixed, mesic Typic Hapludults; fine-loamy, mixed, mesic Typic Hapludults; coarse-loamy, mixed, mesic Fluventic Dystrochrepts; fine, mixed, mesic Typic Hapludalfs) was rapid, with more than 50% (5–500 mg $As^{III} l^{-1}$) of the original As^{III} being adsorbed in the first 30 min. Raven et al. (1998) also observed that the adsorption of both As^V and As^{III} on ferrihydrite was rapid, with As^{III} adsorption being considerably faster (i.e., achieved equilibrium) than As^V at the concentrations studied. The higher rate of As^{III} adsorption may be related to the nature of the adsorption mechanism of the ions and the surface coverage of the As species on the ferrihydrite surface (Raven et al. 1998). After 2 h, they found that 99.7 and 98.3% of As^{III} and 79.6 and 83.4% of As^V were adsorbed at pH 4.6 and 9.2, respectively, and it was considered that complete adsorption occurred after 96 h. Although batch methods provide valuable insight into chemical reactions at equilibrium (Skopp 1986), there are several disadvantages with these techniques. A major drawback of batch techniques is that they are closed systems, and desorbed species are not removed from the system being studied (Sparks 1989; Harter 1991). The presence of the desorbed species in the batch reactor may inhibit desorption of ions from the solid phase (Sparks 1989; Amacher 1991). Data interpretation is therefore difficult, as reverse reactions must be taken into account, unless there is only one reaction and it is unidirectional (Amacher 1991). An alternative method to the batch technique that significantly decreases reverse reactions by continually removing solution from the reaction chamber and preventing the accumulation of desorbed species is the stirred-flow method. The stirred-flow technique has been used to study time-dependent sorption reactions (Carski and Sparks 1985; Seyfried et al. 1989; Toner et al. 1989; Bar-Tal et al. 1995; Yin et al. 1997). Furthermore, the stirred-flow technique exposes the adsorbing surfaces to a constant solution concentration of adsorbent that is continually being removed until the easily accessible sorption sites are saturated, allowing the apparent reaction rate to be measured.

In previous published papers (Smith et al. 1999, 2002), research was focused on the interactions of As in the soil–solution environment and identified several parameters, such as pH, ionic strength (I), index cation and competing anions, that influence As adsorption. In this study we investigated the effects of I, index cations and other anions on the kinetics of As^V sorption. Such information is lacking in the literature as most kinetic studies to date have focussed on the adsorption from soils in constant background electrolyte solutions. Few studies have investigated the effects of ionic strength (I), index cation, and competing ions and such information and would assist in evaluating the mobility and therefore the bioavailability of As^V at contaminated sites. The objectives of this study were to examine the kinetics of As^V adsorption and desorption in the presence of different ions that have been reported to influence As^V adsorption.

Materials and methods

Soil

The Ah horizon (0–100 mm) of an uncontaminated soil was collected from an uncultivated site in northern New South Wales, Australia. This soil represents one of the major soil groups in this region, and the area has a well-documented history of As contamination through the application of As-based pesticides for the control of cattle ticks. Many of the soils surrounding the former cattle dip sites contain elevated As concentrations ranging between <100 to >14,000 mg kg^{-1} (Smith et al. 2003). The soil sample collected from the field was air-dried and crushed to pass through a 2-mm stainless-steel sieve. Following crushing, the soil was stored in an airtight polythene container for analyses. Pertinent properties of the soils are shown in Table 1, and analyses of these properties are as described previously by Smith et al. (1999).

Kinetic experiments

Apparatus

The stir-flow reaction chamber used was a modification of the stir-flow chamber developed by Carski and

Table 1 Pertinent soil properties

Soil group	pH	CEC (mmol kg^{-1})	TC (%)	Particle size (%)				Extractable Fe and Al (mmol kg^{-1})				Total As (mg kg^{-1})
				Clay	Silt	Fine sand	Coarse sand	Oxalate		Citrate-dithionite		
								Fe	Al	Fe	Al	
Alfisol	6.01	32	1.6	7	4	28	59	12	0.06	86	52	0.67

Sparks (1985). It was constructed from stainless steel and consisted of three parts (Fig. 1): (1) a reaction chamber 22.5 mm in diameter with a maximum depth of 40 mm, (2) an adjustable plunger with an inlet port through the centre of the plunger and (3) a cover with a teflon seal and an outlet port. Over the outlet port, a 25-mm diameter 0.45-μm nylon filter was fitted to retain soil in the reaction chamber. The position of the inlet port in the stirred-flow chamber differed from that developed by Carski and Sparks (1985) as it was observed in preliminary studies that the mixing of the soil by the magnetic stirrer led to a significant transfer of soil from the mixing chamber to the inlet port. Modification of the stirred-flow cell reaction chamber included the fitting and repositioning of a filter to the inlet port.

A magnetic stirrer was used to ensure adequate mixing in the reaction chamber. The stirring speed was maintained at a rate that ensured good mixing of soil particles, but with minimum soil particle abrasion. The speed of the magnetic stirrer was standardised for all experiments. A flow rate of 1.5 ml min^{-1} was kept constant throughout the

Fig. 1 Design of stirred-flow reactor modified from Carski and Sparks (1985)

experiment, with both the inlet and outlet solutions being pumped using a peristaltic pump.

Experimental

Adsorption kinetics A soil sample (0.5 g) and the teflon-coated magnetic stirrer were placed in the reaction chamber. To this, 5 ml of 27 μM As^V solution in a background electrolyte was quickly added to the reaction chamber, and the chamber was immediately sealed. The same solution that was added to the reaction chamber was then pumped into the reaction chamber at a rate of 1.5 ml min^{-1}. This flow rate was periodically checked throughout the studies. Effluent solution was collected with a fraction collector at various sample periods, ranging between 0.25 to 10 min. All experiments were conducted at a temperature of 20 ± 2°C.

Initially, blank background curves for As^V sorption without soil in the chamber were determined with the same As^V solution that was used in later experiments. The kinetic experiments were conducted in duplicate for both the blank (background) and As^V sorption curves. Time zero was defined as the moment of entry of the first drop of effluent solution into the first tube of the fraction collector. The As concentration in the effluent solution was analysed using flame atomic absorption spectrometry with hydride generation, and the amount of As^V adsorbed was calculated from the difference between the amount added and amount remaining in solution. Solution pH and other ions also present in the effluent solution were also analysed where sufficient solution was collected by inductively coupled plasma atomic emission spectroscopy.

The effect of ionic strength (*I*) on the kinetics of As^V adsorption was studied in either (1) 0.03 M NaNO$_3$ or (2) 0.3 M of NaNO$_3$ in the presence of 27 μM As^V in each of the background electrolytes. The effect of different index cations was studied at
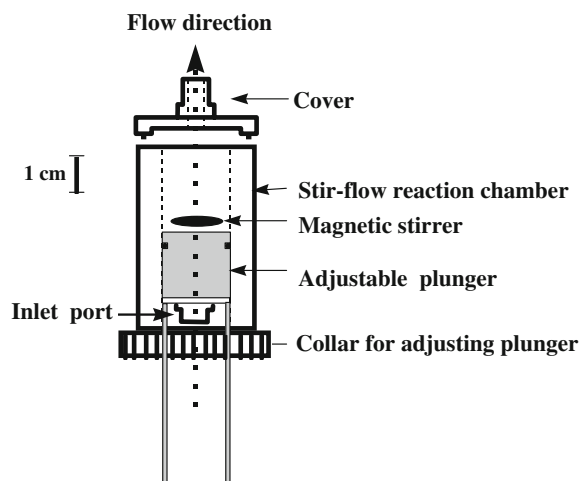
the same ionic strength using 0.03 M of NaNO$_3$ and 0.01 M of Ca(NO$_3$)$_2$. Anion competition was studied with the sorption studies conducted in the presence of phosphate (P). Phosphate (32 μM P) was added in solution with 27 μM As^V in a background electrolyte of either 0.03 M NaNO$_3$ or 0.01 M Ca(NO$_3$)$_2$. The concentrations of As^V and P utilised in this study were based on an analysis of extractable (soil:water 1:2) As^V and P concentrations in soil solution at 12 former cattle dip sites in northern New South Wales, Australia.

Desorption kinetics Initially soil (0.5 g) was equilibrated with As^V (27 μM As^V) in a background solution of 0.03 M NaNO$_3$ as described above for 2 h. Adsorption studies had shown that AsV adsorption was rapid and essentially completed within 2 h with a maximum amount of 200 μg g^{-1} As^V sorbed. Desorption was then initiated by passing through the chamber solutions containing (1) 0.03 M NaNO$_3$, (2) 0.3 M NaNO$_3$ or (3) 0.03 M NaNO$_3$ and 32 μM P.

Blank curves for As^V desorption without soil in the chamber were determined using solutions with the same composition. Analyses of As^V in effluent solutions were conducted as described above. Duplicate experiments were conducted for all desorption curves.

Data analysis

The cumulative amount of As^V adsorbed by the soil can be calculated from flow rates and concentrations of As^V in the effluent solutions (Schnabel and Fitting 1988). Arsenate adsorbed with time was evaluated using Eq. 1 (Yin et al. 1997), where q_a (t_i) is the cumulative sorption at time t_i (μg g^{-1}), C_i is the effluent concentration for the ith sampling period (μg l^{-1}), J is the flow rate (l min^{-1}), Δt_i is the sampling time interval (min), $c(t_i)$ is the concentration in the chamber at t_i (μg l^{-1}), V is the volume of the reaction chamber (l), W is the soil concentration in the chamber (g l^{-1}), and subscripts s and b refer to the chamber with and without soil present, respectively.

$$q_a(t_i) = \frac{[(C_{bi} - C_{si})J\Delta t_i/V] + [c_b(t_i) - c_s(t_i)]}{W} \quad (1)$$

The first term on the right-hand side of the Eq. 1 contains experimental data, while the second term is

calculated for specific times (Eick et al. 1990). The calculation can be done exactly if the kinetic model is known (Schnabel and Fitting 1988) or it can be approximated by averaging the effluent concentration for that time period and the succeeding one (Yin et al. 1997). The second method was used in this study. Estimated values are close to the real values when short time intervals are used (Schnabel and Richie 1987).

The cumulative amount of As^V desorbed is given by Eq. 2;

$$q_d(t_i) = \frac{[(C_{si} - C_{bi})J\Delta t_i/V] + [c_s(t_i) - c_b(t_i)]}{W} \quad (2)$$

where q_d (t_i) is the cumulative As^V desorbed at time t_i (μg g^{-1}).

The use of Eqs. 1 and 2 to calculate the cumulative amount of As^V adsorbed and desorbed by soil accounts for both the effect of dilution and the amount of As^V adsorbed by the stirred-flow reaction chamber (Yin et al. 1997). Several assumptions are made when studying sorption processes by the stirred-flow method. These have been highlighted by Yin et al. (1997) and are reiterated here. It is assumed that the sorption kinetics of As^V by the stirred-flow chamber is not affected by the presence of soil in the chamber. Although this is improbable, the presence of soil is likely to decrease the sorption rates of As^V by the chamber. Furthermore, the presence of soil will affect the rate of As^V adsorbed by the stirred-flow chamber for only a very short period of time as the stirred-flow reaction chamber adsorbs only a small amount of As^V compared with the amount of As^V adsorbed by the soil.

The kinetic data were fitted to a number of mathematical equations, including first order, second order, simple Elovich, and parabolic diffusion equations. The applicability of such empirical equations has been explained extensively by Sparks (1989). However, for the purpose of these studies, it should not be implied from the fitting of data to one particular kinetic equation that this is the only equation that could be used to describe the apparent sorption coefficients. Apparent sorption coefficients were determined so those trends in different treatments could be assessed. Data were also fitted to a one-site second-order model (Eq. 3) to determine the apparent rate coefficients (Yin et al. 1997);

$$q_{a(t+\Delta t)} = k_a(q_\infty - q_{a(t)})C_t\Delta t - k_{-a}q_{a(t)} \qquad (3)$$

where q_a is the concentration of As^V adsorbed by soil at time t (μg g^{-1}), k_a is the forward rate coefficient (l μg^{-1} min^{-1}), q_∞ is the concentration of As^V adsorbed at equilibrium (μg g^{-1}), C_t is the As^V solution concentration in the reaction chamber at time t (μg l^{-1}), k_{-a} is the reverse rate coefficient (min^{-1}), and subscripts t and Δt indicate quantities of time (min).

The desorption reaction of As^V from the soil can be expressed as:

$$q_{d(t+\Delta t)} = k_d + q_{d(t)}(q_o - q_{d(t)})\Delta t - k_{-d}q_{d(t)}C_t\Delta t \quad (4)$$

where q_o is the desorbable As^V concentration on the soil at the beginning, q_d is the concentration of As^V desorbed from the soil at time t (μg g^{-1}), k_d is the desorption rate coefficient (min^{-1}), and k_{-d} is the reverse rate coefficient (l μg^{-1} min^{-1}).

The model used by Yin et al. (1997) assumed that there is only one type of site involved in the sorption reaction. Although this represents a simplistic view of the heterogenous nature of the soil, it allows some insight into the reaction mechanisms between adsorbent and adsorbate. Yin et al. (1997) showed that for Hg^{II} the reverse reactions were insignificant, and the Eqs. 3 and 4 simplified to Eqs. 5 and 6.

$$q_{a(t+\Delta t)} = k_a(q_\infty - q_{a(t)})C_t\Delta t + q_a(t) \qquad (5)$$

$$q_{d(t+\Delta t)} = q_{d(t)} + k_d(q_o - q_{d(t)})\Delta t \qquad (6)$$

Therefore, Eqs. 5 and 6 were used to describe the experimental data from these studies.

Statistical analysis

All statistical analyses were conducted using GEN-STAT 5 (1997). The parameters for Eqs. 5 and 6 (k_a, k_d, q_∞ and q_o) were determined for the soil treatments by fitting a non-linear regression model that optimised the function in Eqs. 5 and 6. The graphical fit of the model, together with the residual diagnostics and standard errors of the parameter estimates, was investigated for assessing the model fit to the experimental data.

Initial statistical analyses suggested that the residuals from the non-linear regression modelling showed evidence of lagged correlation with time (i.e., values for a particular time are dependent on previous time point values). As a consequence, attention is not

focussed on R^2 values, but rather it is placed on the graphical fit of the model.

The parameter estimates for the unknown functions in Eqs. 5 and 6 (k_a, k_d, q_∞ and q_o) were computed via two sets of analyses. Firstly, where more than one experimental run was undertaken for each treatment, the values were averaged and then the models fitted. The other analysis obtained parameter estimates for each run of the treatments, and these estimates were used to determine whether there were treatment differences between the parameters. In addition to this, data were modelled for varying lengths of experimental runs.

Results and discussion

Sorption kinetics

Preliminary studies were conducted before studying the adsorption–desorption kinetics of As^V to ascertain whether As^V-soil reactions were instantaneous or kinetically controlled (Bar-Tal et al. 1990). If non-equilibrium conditions exist in the reaction chamber then stopping the flow through the chamber for a sufficient period of time before equilibrium conditions are established will result in a noticeable drop in the concentration of effluent solution once the flow is restarted. However, if the reaction is instantaneous then a plot of the effluent concentration versus time should be continuous. In the preliminary study, stopping the flow after 5 min for approximately 25 min reduced the effluent concentration of As^V by 24% (data not shown), indicating that non-equilibrium conditions exist within the reaction chamber and As^V sorption by the Alfisol is time dependent. Therefore, kinetic studies utilising the stirred-flow reactor are applicable for the sorption of As^V.

The kinetics of As^V sorption by the Alfisol with different treatments are shown in Fig. 2. The sorption of As^V was initially fast (58–91% in the first 15 min), and this was followed by sorption at a slower rate that continued with all treatments for the duration of the study period. This biphasic sorption pattern is similar to Hg^{II} sorption by different soils observed by Yin et al. (1997) and has been reported in many other sorption studies in the literature. Fuller et al. (1993) and Raven et al. (1998) have reported similar As^V sorption kinetic behaviour on ferrihydrite surfaces,

Fig. 2 Effect of different treatments on the cumulative amount of As^V adsorbed by the Alfisol soil. Bars represent standard errors of means. Where no bar is seen, error is smaller than the symbol
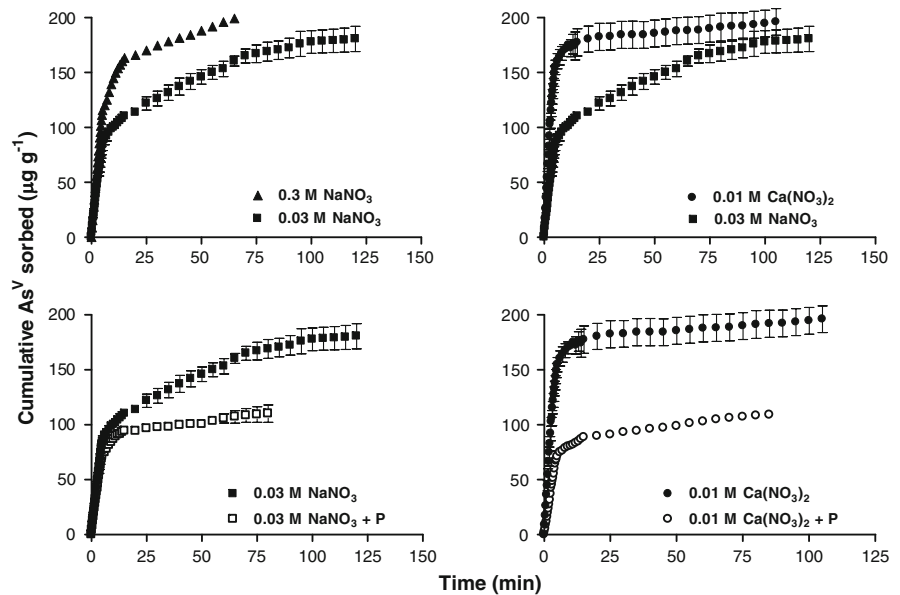
although Raven et al. (1998) reported that the rate of As^V sorption was dependent on solution pH and the As^V solution concentration. Similarly, Grafe and Sparks (2005) reported that the rate of As^V sorption by goethite was dependent on a range of factors including the number of sorption sites. Fendorf et al. (1997) have reported that at low As^V surface coverage of an Fe oxide surface, As^V is mainly retained through the formation of monodentate complexes and bidentate binuclear and bidentate mononuclear complexes at high As^V surface coverage. Raven et al. (1998) have postulated that the formation of bidentate complexes may be slower than the formation of monodentate complexes. Another possibility is that diffusion controlled reactions into soil particles may be responsible for the slow As^V sorption phase observed. Fuller et al. (1993) suggested that the slow sorption of As^V may be due to diffusion controlled reactions into the ferrihydrite crystal structure and modelled the kinetics using the parabolic diffusion equation, which has been used previously to model kinetic reactions in soils (Aharoni et al. 1991). In this study, the parabolic diffusion equation did not usually describe the data well (data not shown). However, this does not exclude the possibility that diffusion processes influence the slow reaction phase of As^V sorption. Aharoni et al. (1991) observed that several mathematical expressions may describe the sorption kinetics, and the sorption processes probably involve more than one sorption

mechanism. Therefore, one mathematical equation may not adequately describe the sorption of As^V observed in this study.

In some experiments, As^V sorption was not observed to apparent equilibrium. However, using GENSTAT 5 (1997) it was possible to predict the cumulative sorption capacity of the soil (q_∞) and optimise the other unknown functions in Eq. 5. It is therefore possible to compare the effect of the different treatments on the sorption capacity of As^V by the Alfisol soil. The sorption capacities of the soil without the presence of P in the influent solution were similar (Table 2) irrespective of the nature of the index cation and I of the soil solution. However, the presence of P decreases the estimated sorption capacity from 162 to 89 and 177 to 115 µg g^{-1} As^V in 0.03 M NaNO$_3$ and 0.01 M Ca(NO$_3$)$_2$, respectively. Studies examining the effect of anion or cation-

Table 2 Apparent equilibrium (q_∞) parameter for the sorption of As^V by the Alfisol soil

Treatments	q_∞ (µg g^{-1})	SE[a]
0.03 M NaNO$_3$	162	6.9
0.3 M NaNO$_3$	176	7.2
0.01 M Ca(NO$_3$)$_2$	177	5.8
0.03 M NaNO$_3$ + P	89	3.6
0.01 M Ca(NO$_3$)$_2$ + P	115	5.8

[a] SE is the standard error of the estimated parameter

induced adsorption have reported several mechanisms may enhance the adsorption of the counter-ion at the surface. In the case of Ca or Cd adsorption in the presence of P, for example, the mechanisms may include: (1) precipitation of Cd^{2+} as $Cd_3(PO_4)_2$, (2) co-adsorption of HPO_4^{2-} and Cd^{2+} as an ion pair, (3) surface complex formation of Cd^{2+} onto the adsorbed HPO_4^{2-} and (4) HPO_4^{2-} induced Cd^{2+} adsorption (Bolan et al. 1999). Sadusky and Sparks (1991) observed that the amount of potassium (K) adsorbed by two soils (coarse-loamy, siliceous, thermic Typic Hapludult and loamy, siliceous, thermic Arenic Hapludult) at pH 5 and 6 was dependent on the accompanying anion. Sorption of K in the presence of anions, such as those of silicate (Si) and P, was greater than with chloride (Cl). This was attributed to the change in surface charge imparted when Si and P are specifically adsorbed onto variable-charge surfaces. Hundal and Pasricha (1998) studied the effect of temperature on the sorption of K by a soil (Udic Ustochrept) and reported that the cumulative amount of K adsorbed decreased with increasing temperature. They also observed that K sorption was greater in the presence of Cl compared with perchlorate (ClO_4). The authors attributed the increase in sorption of K in the presence of chloride to the formation of weak Ca–Cl complexes that decrease Ca competition with K for sorption sites on soil.

The presence of P has generally been reported to decrease As^V sorption when both anions are present in solution (Roy et al. 1986; Manning and Goldberg 1996; Darland and Innskeep 1997). Parfitt (1978) suggested that the sorption order of anions on soil surfaces was phosphate > arsenate > selenite = molybdate > sulphate = fluoride > chloride > nitrate. In this study, sorption sites are continually being exposed to a constant concentration of P and As^V due to the addition and removal of solution from the stirred-flow reaction chamber. With the continual replacement of solution in the stirred-flow reaction chamber, it is observed that P only decreases As^V adsorbed by between 35 to 48%. If the binding energy is the major factor controlling sorption of P or As^V, then at similar solution concentrations, P adsorbed will always be greater than As^V irrespective of the number of available sorption sites. The effect of P on As^V sorption may be indicative of the presence of sites that are specific for the sorption of either As^V or P. It was hypothesised that increasing the number of available sorption sites would increase the

amount of As^V adsorbed and may affect the rate of the sorption process. Increasing the number of sorption sites through the addition of 1% goethite with the Alfisol soil resulted in an increase in the amount of As^V adsorbed (data not shown). No kinetic data were obtainable after 15 min due to clogging of the stirred-flow reaction chamber. However, the kinetic data collected clearly illustrate that the number of available sorption sites strongly influences the cumulative amount and rate of As^V adsorbed by the soil.

Several kinetic equations were fitted to describe the apparent rate of As^V sorption on soil so that the effects of different treatments could be compared (Table 3). The various kinetic equations tested all had limitations in describing the apparent rate of As^V sorption by soil. This is evidenced by the fact that the first-order equation, which has often been used to describe reaction rates, described the sorption of As^V by soil well for the Na treatments, but not for the Ca treatments. This may be indicative of a different sorption mechanism influencing the sorption of As^V in the presence of Ca. As discussed by Smith et al. (2002), the presence of Ca in solution may increase As^V sorption in low adsorbing soils through an increase in the surface positive charge of the soil surface. However, the nature of these sorption sites is unknown, and the As^V mechanism may not be the same as in the presence of other index cations such as Na.

For all the treatments, the simple Elovich equation was found to describe As^V sorption reasonably well (data not shown). The Elovich equation assumes a heterogeneous distribution of sorption energies, and the energy of activation increases linearly with

Table 3 Goodness of fit of the model (Eq. 5) and estimated forward rate sorption coefficients (k_a) for the different treatments

Treatment	Fitted equation		Estimated
	SE^a	RMS^b	k_a (l μg^{-1} min^{-1})
0.03 M NaNO$_3$	0.0000232	1.95	0.0001425
0.3 M NaNO$_3$	0.0000183	1.55	0.0002713
0.01 M Ca(NO$_3$)$_2$	0.0000277	1.36	0.0002989
0.03 M NaNO$_3$ + P	0.0000247	2.49	0.0005583
0.01 M Ca(NO$_3$)$_2$ + P	0.0000306	0.86	0.0002820

[a] SE is the standard error of the fitted equation

[b] RMS is the root mean square, which is defined by [RSS/$(n - p)$]$^{0.5}$, where RSS is the residual sum of squares; n is the number of data points, and p is the number of parameters

surface coverage (Schnabel and Fitting 1988; Sparks 1989). Due to the nature of soil, there is a continuum of sorption sites that have a range of different sorption energies, and therefore, it would be expected that an empirical equation based on this mechanism may be applicable to soil. Although the Elovich equation has been widely used to describe kinetic data (Chien and Clayton 1980; Sparks and Jardine 1984), Ungarish and Aharoni (1981) have questioned the value of using the Elovich equation to describe the adsorption and desorption kinetics at very low and very high surface coverage due to the "poor fit" of data to the equation. This was also observed in this study (data not shown), with a "poor fit" of the collected data to the Elovich equation after short (low surface coverage) and long (high surface coverage) sampling times. It was therefore decided to use the one-site second-order equation (Eq. 5) rather than the Elovich equation to determine the apparent forward rate constants of the reactions.

The As^V sorption data fitted Eq. 5 well, and this is reflected in the low values of SE and RMS for the estimated parameters (Table 3). This implies that although the nature of the adsorbing surface differs, the assumption that there is one type of sorption site may be consistent at high surface coverage of As^V on the adsorbing surfaces. This is supported to some extent by Fendorf et al. (1997) who postulated that As^V formed three different types of surface structure on goethite depending on the surface coverage. Monodentate complexes were postulated to form at low surface coverage and bidentate complexes at high surface coverage, but a mixture of the two complexes may also occur at surface coverage in between. However, further studies need to be conducted to substantiate the kinetic model of sorption proposed by Yin et al. (1997).

The calculated average k_a values for all but the goethite treatments are shown in Table 3. The goethite treatment is not included because of the lack of experimental data. There were differences between the estimated k_a values for the different treatments, although an analysis of variance (GENSTAT 5 1997) showed that the differences were significant only at $p = 0.068$. Notably, the k_a values for the 0.03 M NaNO$_3$ and the 0.03 M NaNO$_3$ plus P treatments appear to be different k_a values compared to the other treatments. This may indicate that these treatments had different effects on the rate of As^V adsorbed. However,

a comparison of similar treatments [0.01 M Ca(NO$_3$)$_2$ compared with 0.03 M NaNO$_3$, 0.01 M Ca(NO$_3$)$_2$ + P compared with 0.03 M NaNO$_3$ + P] indicates the sorption capacity of the soil is similar in each treatment, although the rate of the sorption reaction is different. Investigations of the sorption kinetics of other ions have shown that k_a may or may not be affected by different soil treatments. Sadusky and Sparks (1991) reported that the nature of the anion and increasing soil pH from 5 to 6 had little effect on the apparent rate of K sorption by soils, although the amount of K adsorbed differed greatly with different anions and pH. In contrast, Toner et al. (1989) reported that increasing the pH of three soils (Typic Hapludult and Plinthic Paleudult) from pH 5 to 7 decreased the cumulative amount of nitrate (NO$_3^-$) sorbed, but increased the rate of NO$_3^-$ sorbed. Toner et al. (1989) attributed the observed increase in k_a to fewer sorption sites available for NO$_3^-$ sorption, due to the increasing pH of the soil surface, which increases the overall rate of sorption. Generally, there is little or no information available in the literature regarding the kinetics (rate and mechanisms) affecting As^V sorption. Although As^V sorption has been well studied, much of this research has been conducted after an equilibrium period has been attained. Using equilibrium methods is tenuous as the behaviour of contaminants in natural systems is almost always in disequilibrium. Further studies investigating these disequilibrium reactions are needed as the initial sorption reactions play a critical role in the subsequent sorption behaviour of As^V (Grafe and Sparks 2005).

Desorption kinetics

Considerably less As^V was desorbed than was adsorbed (Fig. 3). At the end of 100 min of desorption, only 2, 6 and 17% of the adsorbed As^V was desorbed from the Alfisol soil in the presence of 0.3 M NaNO$_3$, 0.03 M NaNO$_3$ and 0.03 M NaNO$_3$ + P, respectively. This suggests that once adsorbed, much of the adsorbed As^V cannot be readily desorbed into solution. The persistence of adsorbed metals in soils has often been reported (Bruemmer et al. 1988; Yin et al. 1997; McLaren et al. 1998) and has been attributed to diffusion into mineral lattices (Sparks et al. 1980) or through intraparticle pores (Sparks et al. 1980), but as noted earlier, the parabolic diffusion equation did not describe the data well.
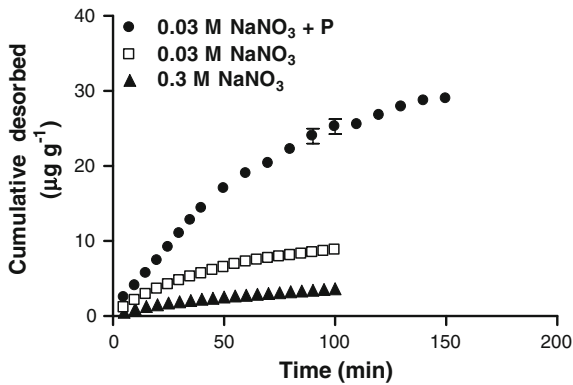
Fig. 3 Effect of different treatments on the cumulative amount of As^V desorbed from the Alfisol soil. Bars represent standard errors of means. Where no bar is seen, error is smaller than the symbol. Total amount of As adsorbed prior to desorption was 200 µg g^{-1}

The specific sorption of As^V to high affinity sites in soil may contribute to the observed slow reversibility of As^V. Extended edge X-ray absorption studies by Waychunas et al. (1993) and Fendorf et al. (1997) reported that As^V formed inner-sphere monodentate and bidentate bonds on the surface of Fe oxides, and the preferential bonding to high affinity sites may contribute to the slow reversibility. Although P was observed to increase the amount of As^V desorbed compared with the other treatments (Fig. 3), increasing the influent P concentration to 160 µM after 100 min of desorption in the presence of 32 µM P only resulted in a small increase in the amount of As^V desorbed (result not shown). This may indicate that some As^V remains irreversibly bound to the soil irrespective of the soil treatment. Darland and Innskeep (1997) have reported similar findings after studying the desorption of As^V from aquifer packed column material contaminated with As^V. They reported that even in the presence of P concentrations that exceeded the sorption capacity of the column by two orders of magnitude, approximately 40% of sorbed As^V remained bound to the aquifer materials.

Increasing I from 0.03 to 0.3 M NaNO$_3$ resulted in a smaller increase in the cumulative amount of As^V desorbed compared with the amount of As^V desorbed in the presence of P. Analysis of variance (GENSTAT 5 1997) showed that there was a significant difference ($p < 0.05$) in the amounts of As^V desorbed for the different treatments. The increase in the cumulative amount of As^V desorbed in the presence of P compared with I may be related to the nature of the mechanisms

by which P and I influence the As^V adsorbed by soil surfaces. Phosphate may compete with As^V for surface sorption sites when sites are limited (Manning and Goldberg 1996; Smith et al. 1999), and therefore direct competition between As^V and P may result in the increased desorption of As^V. Changing I, however, may influence As^V adsorbed only through its effects on the surface potential of the colloid (Smith et al. 1999). Therefore, once As^V is adsorbed, changes to the surface potential of the adsorbing colloid had little influence on the amount of As^V desorbed.

The small values of SE and RMS (Table 4) indicated that the one-site second order equation (Eq. 6) described the desorption data well. Although the three desorption treatments had different effects on the amount of As^V desorbed, an analysis of variance (GENSTAT 5 1997) found that there was little difference between k_d values (Table 4) with differences in the k_d values only observed at $p = 0.44$. It could be hypothesised that irrespective of the total amount of As^V desorbed by different treatments, the k_d of As^V desorption from the Alfisol does not alter. However, this hypothesis is drawn from fitting of the data to the one-site second order equation (Eq. 6) and is not drawn on any scientific observation. The equation does not describe how the different ions interact on the soil surface, and further studies are needed in this area.

Conclusions

The sorption of As^V on the Alfisol soil was characterised by an initially rapid phase, followed by a slower phase. The different treatments had little effect on the total amount of As^V adsorbed by the

Table 4 Goodness of fit of the model (Eq. 6), and estimated desorption rate coefficients (k_d) for the different treatments

Treatment	Fitted equation		Estimated
	SE[a]	RMS[b]	k_d (min^{-1})
0.03 M NaNO$_3$	0.000667	0.0322	0.01955
0.3 M NaNO$_3$	0.002060	0.0384	0.01930
0.03 M NaNO$_3$ + P	0.001180	0.2146	0.01420

[a] SE is the standard error of the fitted parameter

[b] RMS is the root mean square, which is defined by [RSS/ $(n - p)]^{0.5}$, where RSS is the residual sum of squares; n is the number of data points; and p is the number of parameters

Alfisol, as was observed in the presence of different cations or varying the ionic strength of the background solution, although the rate at which the maximum adsorption was achieved varied depending on the treatment. In contrast, the presence of P decreased the amount of As^V adsorbed by the Alfisol significantly. Although the apparent rate of As^V sorption varied with sorption treatments, an analysis of variance showed that the differences were significant only at $p = 0.068$. The amount of As^V desorbed from the Alfisol represented less than 17% of the As^V adsorbed. There were differences in the total amount desorbed for different treatments, with the presence of P greatly increasing the amount of As^V desorbed. These results suggest that As^V adsorption kinetics play an important role in controlling the transport and bioavailability of As^V in the soil environment.

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