

2 Sorption and Desorption of Arsenic by Soil Minerals and Soils in the Presence of Nutrients and Organics

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1 Introduction

Arsenic is an element ubiquitous in the Earth's crust and is extremely toxic for humans, animals and plants. Its occurrence in natural environments may be due to natural processes (weathering reactions, biological activities and volcanic emissions) as well as anthropogenic activities (Matera and Le Hécho 2001; Frankenberger 2002; Mandal and Suzuki 2002; Smedley and Kinniburgh 2002). The mean content of arsenic in soils is of the order of 5–10 mg kg⁻¹. Arsenopyrite (FeAsS) is the most abundant arsenic-containing mineral and other minerals include realgar (AsS), orpiment (As₂S₃), olivenite (Cu₂OHAsO₄). Arsenic-bearing herbicides and pesticides have been widely used in agricultural practice until the mid-1900. In particular, lead arsenates and especially schultenite (PbHAsO₄), were used extensively as insecticides in orchard soils (Cancés et al. 2005). As a result

of application of arsenical pesticides to fruit crops in orchard soils concentrations of arsenic in the range 366–732 mg kg⁻¹ have been quoted (Ure and Berrow 1982).

Natural contamination of ground waters by arsenic has become a crucial water quality problem in many parts of the world (Berg et al. 2001; Chakrabarti et al. 2002; Smedley and Kinniburgh 2002, and references there in). Arsenic in drinking water is much more bioavailable than arsenic in soil, because water-soluble arsenic is rapidly sorbed by humans (Yang et al. 2003). Recently, the European Union and the USA with National Priorities List (NPL) have fixed a limit of 10 µg As L⁻¹ in drinking water. In Bangladesh, over 75% of water used for irrigation came from groundwater. A huge amount of arsenic is thus transferred from the contaminated aquifer to the surface soil-plant system (Smedley and Kinniburgh 2002; Martin et al. 2007a).

In soils, surface and ground waters arsenic is found in -3, 0, +3 and +5 oxidation states, but its prevalent forms are the inorganic species, arsenate [As(V)] and arsenite [As(III)]. Relative to other oxyanion-forming elements, arsenic is among the most problematic in the environment because of its relative mobility over a wide range of redox conditions. Arsenic is relatively mobile under reduced conditions (Smedley and Kinniburgh 2002). It may occur as methylated forms in environmental systems, but these organic species are usually rare in soils and surface waters. The methylated monomeric arsenic species are: monomethylarsonic acid (H₂AsO₃(CH₃), MMAs^v), methylarsinous acid (H₂AsO₂-CH₃, MMAs^{III}), dimethylarsinic acid (HAsO₂-(CH₃)₂, DMAs^v), dimethylarsinous acid (HAsO-(CH₃)₂, DMAs^{III}), trimethylarsine oxide (AsO-(CH₃)₃, TMAsO^v), and trimethylarsine (As-(CH₃)₃, TMAs^{III}). Methylation can be carried out by a variety of organisms ranging from bacteria to fungi to mammals and is believed to be part of a detoxification mechanism in living organisms. The arsenic compounds present in natural environments have recently been comprehensively reviewed by Francesconi and Kuehnelt (2002).

The mobility of arsenic compounds in soils is affected by sorption/desorption on/from soil components or co-precipitation with metal ions. The importance of oxides (mainly Fe-oxides) in controlling the mobility and concentration of arsenic in natural environments has been studied for a long time (Livesey and Huang 1981; Frankenberger 2002 and references there in; Smedley and Kinniburgh 2002). Because the elements which correlate best with arsenic in soils and sediments are iron, aluminum and manganese, the use of Fe salts (as well as Al and Mn salts) is a common practice in water treatment for the removal of arsenic. The coprecipitation of arsenic with ferric or aluminum hydroxide has been a practical and effective technique to remove this toxic element from polluted waters

(Scott et al. 1995; Rancourt et al. 2001; Thirunavukkarasu et al. 2003). Iron-arsenic coprecipitates have been found in natural environments (Pichler et al. 1999; Frankenberger 2002).

Arsenite is 25–60 times more toxic than arsenate, which mainly arise from its state as H_3AsO_3 at $\text{pH} < 9.0$ as compared to the charged arsenate species which predominate in a wide pH range (H_2AsO_4^- between 2.5 and 7, HAsO_4^{2-} between pH 7 and 12) (Frankenberger 2002; Smedley and Kinniburgh 2002). Bioavailability of arsenic in soil may be affected by inorganic (mainly phosphate added as fertilizer) or naturally occurring organic molecules, which may affect the sorption/desorption processes of this metalloid onto/from soil components (Violante et al. 2005a,b). From the toxicological point of view ingestion of inorganic arsenic can result in both cancer (skin, lung and urinary bladder) and non cancer effects (skin lesions). Recent data suggests that some methyl arsenic species (MMAs^{III} and DMAs^{III}) can be as toxic or more toxic than inorganic species (arsenate and arsenite) (Francesconi and Kuehnelt 2002; Le 2002).

The aim of this Chapter is to provide the current state of knowledge on the factors (pH, surface coverage, residence time, presence of organic and inorganic ligands) which influence the sorption/desorption processes of arsenic by soil minerals and soils integrating the existing literature on this subject with our recent findings.

2 Sorption onto Soil Components

Arsenate and arsenite are sorbed primarily by chemisorption at reactive sites of variable charge minerals, such as metal oxides and short-range ordered aluminosilicates (allophane, imogolite) and at the edges of phyllosilicates (Manceau 1995; Raven et al. 1998; Frankenberger 2002; Violante and Pigna 2002; Ona-Nguema et al. 2005). The carbonates also play an important role in the arsenate sorption of calcareous soils in the pH range 9–12 (Goldberg and Glaubig 1988).

Usually, elements in anionic form are not easily sorbed on soil organic matter, but arsenate and arsenite were found to be bound to natural organic matter probably held to organic groups through a bridging hydrolytic species of Al and Fe (Thanabalasingan and Pickering 1986; McBride 2000). Binding mechanisms of arsenite and arsenate to dissolved humic acids have been proposed (Buschmann et al. 2006). At all pH values, arsenate was more strongly bound than arsenite maximum binding being around pH 7.0 (Buschmann et al. 2006; Ritter et al. 2006).

Sorption of arsenic onto minerals and soils varies with pH. Frost and Griffin (1977) reported that arsenate sorption by kaolinite and montmorillonite exhibited a maximum at pH 4.0–6.0, whereas arsenite was sorbed steadily from pH 4.0 to 9.0 on kaolinite and peaked at pH 7.0 on montmorillonite. Later, Manning and Goldberg (1996a) found that distinct arsenate adsorption maxima occurred at approximately pH 5.0 for kaolinite, 6.0 for montmorillonite and 6.5 for illite. Sorption of arsenite onto phyllosilicate clay minerals has also been studied (Manning and Goldberg 1997a).

Arsenate and arsenite have different trend in sorption on variable charge minerals (Inskeep et al. 2002). Many studies have demonstrated that arsenite is sorbed on Al-oxides, phyllosilicates and calcite in a lesser extent than arsenate, whereas the opposite is true for iron oxides (Frankenberger 2002; Martin et al. 2007a). The sorption of arsenate onto Fe- and Al-oxides usually increases by decreasing pH, but rapidly decreases above pH 7.0, probably because at pH > 7.0 the surfaces of these oxides are negatively charged, their point of zero charge (pzc) being approximately 6.5–7.5 (Hsu 1989; Cornell and Schwertmann 1996; Kampf et al. 2000). The sorption of arsenite onto Fe oxides is highly pH dependent with the envelope centered at about pH 9.0. Raven et al. (1998) showed that arsenite has a greater sorption capacity on ferrihydrite and goethite than arsenate except at very low solution concentrations. Furthermore, Martin et al. (2007b) ascertained that iron oxides can sorb more arsenite than arsenate, although the K of Langmuir isotherms which is a constant related to the binding energy is always lower for arsenite than for arsenate.

Chemical behavior of arsenate is similar to that of phosphate and may form different surface complexes (inner-sphere complexes) on inorganic soil components: monodentate, bidentate-binuclear and bidentate-mononuclear complex in different proportions depending on pH and surface coverage (Hsia et al. 1994; Sun and Doner 1996; Fendorf et al. 1997; O'Reilly et al. 2001). Arsenite and arsenate seem to form similar surface complexes with metal oxides with arsenate more strongly held on these soil components. Surface complexes of arsenate and arsenite on iron oxides have been studied using infrared (Sun and Doner 1996) and extended x-ray absorption fine structure (EXAFS) spectroscopy (Manceau 1995; Waychunas et al. 1996; Fendorf et al. 1997; Farquhar et al. 2002; Ona-Nguema et al. 2005). The general consensus is that both arsenate and arsenite form mainly bidentate binuclear complexes with two adjacent iron octahedral corner sites with a slight longer d(As-Fe) for arsenite. However, arsenite seems to form both inner- and outer-sphere complexes onto Fe-oxides and outer-sphere complexes on Al oxides (Goldberg and Johnston 2001; Arai et al. 2001). Recently EXAFS study (Ona-Nguema et al. 2005) indicates that at high surface coverage arsenite forms bidentate mononuclear edge-sharing and

bidentate binuclear corner-sharing onto ferrihydrite and hematite, but dominantly bidentate binuclear corner-sharing sorption complexes onto goethite and lepidocrocite (with minor amount of monodentate mononuclear edge). Unfortunately, no information is available on the possible complexes of methylated forms of arsenic onto soil components.

Goldberg (2002) found that arsenate and arsenite sorption on amorphous Fe-oxide and Al-oxide as a function of solution pH showed negligible ionic strength dependence in the range 0.02 to 0.1 mol L⁻¹. However, arsenite showed decreasing sorption with increasing ionic strength in the range 0.1 to 1.0 mol L⁻¹, indicative of outer-sphere sorption mechanism. Arsenate and arsenite sorption lowers the pzc of Fe-oxides, but some authors showed that the pzc of Al-oxides shifts to lower pH values with increasing arsenate concentration, but does not shift to lower pH in the presence of arsenite (Jain et al. 1999; Goldberg and Johnston 2001; Martin et al. 2007b).

Sorption of arsenite on the surfaces of Mn-oxide facilitate the oxidation of arsenite to arsenate (Oscarson et al. 1981). In some environments contaminated with arsenite, the presence of Mn oxides decreases the potential toxicity of arsenite by converting arsenite to the less toxic arsenate and the subsequent sorption of this species (Smith et al. 1998). More recently, Tournassat et al. (2002) studied the oxidation of arsenate in 0.011 mol L⁻¹ arsenite suspension of well crystallized hexagonal birnessite and found that the surficial reaction sites are likely located on the edges of H-birnessite layers rather than on the basal planes. A protonated manganese precipitate (probably krautite) formed after 74 hrs of reaction whose long fibers were aggregated at the surfaces of birnessite. This study demonstrated that the oxidation reaction As(III)-MnO₂ transforms the toxic arsenite to a less toxic aqueous arsenate species, which subsequently precipitates with Mn²⁺ as a mixed As-Mn solid characterized by a low solubility product. Partial oxidation of arsenite on the surfaces of goethite has been demonstrated by Sun and Doner (1998) who found that after 20 days, more than 20% of arsenite, sorbed on the surfaces of goethite, was oxidized to arsenate. Manning and Goldberg (1997a) demonstrated that oxidation of arsenite to arsenate was enhanced in the presence of phyllosilicates by heterogeneous reactions with components on the surfaces of clay minerals. The relationship between soil properties and sorption of arsenite and arsenate has also been studied (Manning and Goldberg 1997b).

Sorption of methyl arsenic onto metal oxides has received scant attention. Lafferty and Loeppert (2005) found that MMAs(III) and DMAs(III) were not appreciably sorbed onto goethite or ferrihydrite within the pH range of 3 to 11, while arsenite was strongly sorbed to both the oxides. In contrast, MMAs(V) and arsenate were sorbed from pH 3 to 10 in great

amounts on the iron oxides, whereas DMAs(V) was sorbed only at pH below 7 on goethite and below 8 on ferrihydrite. These authors demonstrated that DMAs(V) is specifically sorbed by iron oxides only at pH values lower than the pzc, with no sorption at pH values above pzc. The retention behaviour of arsenate and MMAs(V) were similar, but with a weaker bond between MMAs(V) and iron-oxide surfaces than between arsenate and iron oxides (especially at high pH values). According to these authors the difference in apparent bonding strength of MMAs(V) and arsenate might be due to the electron donating characteristics of the methyl group of MMAs(V).

3 Influence of Competing Anion

The presence of inorganic and organic ligands affects the sorption of arsenic onto soil minerals and soils by competing for available binding sites and/or reducing the surface charge of the sorbents (Barrow 1992; Manning and Goldberg 1996a,b; Frankenberger 2002; Violante and Pigna 2002; Violante et al. 2005a,b; 2008, and references there in). The competition in sorption is affected by the affinity of the competing anions for the surfaces of the sorbents, the nature and surface properties of the minerals and soils, the surface coverage and the reaction time.

Goldberg (2002) found no evidence of any competition in sorption of arsenate and arsenite on Al or Fe-oxides and montmorillonite, but only a small and apparent competitive effect of equimolar arsenate on arsenite sorption on kaolinite and illite. The minor competitive effect in this study was due to the small concentrations of arsenic which is very low for saturation site. Competition for sorption sites is evident by increasing the surface coverage of the sorbents. Arsenate prevents arsenite sorption on metal oxides when the surfaces of the sorbents are saturated by the anions (Jain and Loeppert 2000; Violante and Pigna 2002).

The effect of phosphate on the sorption/desorption of arsenic in soil environments has received great attention, since application of phosphate fertilizers is a management practice that can have a direct effect on the concentration of arsenic in soil solution and may enhance arsenic's mobility (Manning and Goldberg 1996b; Smith et al. 1998; Jain and Loeppert 2000; Hongshao and Stanforth 2001; Frankenberger 2002 and references there in; Violante and Pigna 2002). Violante and Pigna (2002) studied the competition in sorption between phosphate and arsenate on selected phyllosilicates, metal oxides, and soil samples. They found that Mn, Fe and Ti oxides and phyllosilicates particularly rich in Fe (nontronite, ferruginous

smectites) were more effective in sorbing arsenate than phosphate after 24 hrs of reaction, but more phosphate than arsenate was sorbed on noncrystalline Al precipitation products, gibbsite, boehmite, allophane, and kaolinite. These authors found that competitiveness between the anions also changed at different pH values. In particular phosphate inhibited arsenate sorption more in neutral and alkaline systems than in acidic systems.

Smith et al. (2002) studied the effect of phosphate on the sorption of arsenate and arsenite by an Oxisol, a Vertisol and two Alfisols. The presence of phosphate (0.16 mmol L^{-1}) greatly decreased arsenate sorption by soil containing low amounts of Fe oxides ($< 100 \text{ mmol kg}^{-1}$: Alfisols. Fig. 1A), indicating competitive sorption between phosphate and arsenate for sorption sites. In contrast, the presence of a similar amount of phosphate had relatively little effect on the amount of arsenate sorbed by soils (Oxisol) with high iron content ($> 800 \text{ mmol kg}^{-1}$: Fig. 1B). A similar effect of phosphate on arsenite sorption was observed in low sorbing Alfisols (Fig. 2A) and high affinity Oxisol (Fig. 2B). However, the amount of arsenite sorbed by the Oxisol was much greater than the Alfisol.

Because the final surface coverage of competitive ligands onto the surfaces of the sorbents seems to have a great effect on their sorption, it appeared interesting to carry out experiments on the competitive sorption of phosphate and arsenate at pH 5.0 onto ferrihydrite or a noncrystalline Al-oxide $[\text{Al}(\text{OH})_x]$ at a surface coverage of each ligand of 50 or 100% and after 5–720 hrs of reaction (Del Gaudio, 2005). The surface area of ferrihydrite and $\text{Al}(\text{OH})_x$, determined by the method of Quirk (1955), was respectively of 230 and $135 \text{ m}^2 \text{ g}^{-1}$. The initial arsenate added/phosphate added molar ratio (ri) was 1, but some experiments were carried out at ri of 0.5. The anions were added to the sorbents as a mixture ($\text{AsO}_4 + \text{PO}_4$ [ri = 1] and $\text{AsO}_4 + 2\text{PO}_4$ [ri = 0.5]) or by adding arsenate 24 hrs before phosphate (*AsO₄ before PO₄*) or adding phosphate 24 hrs before arsenate (*PO₄ before AsO₄*).

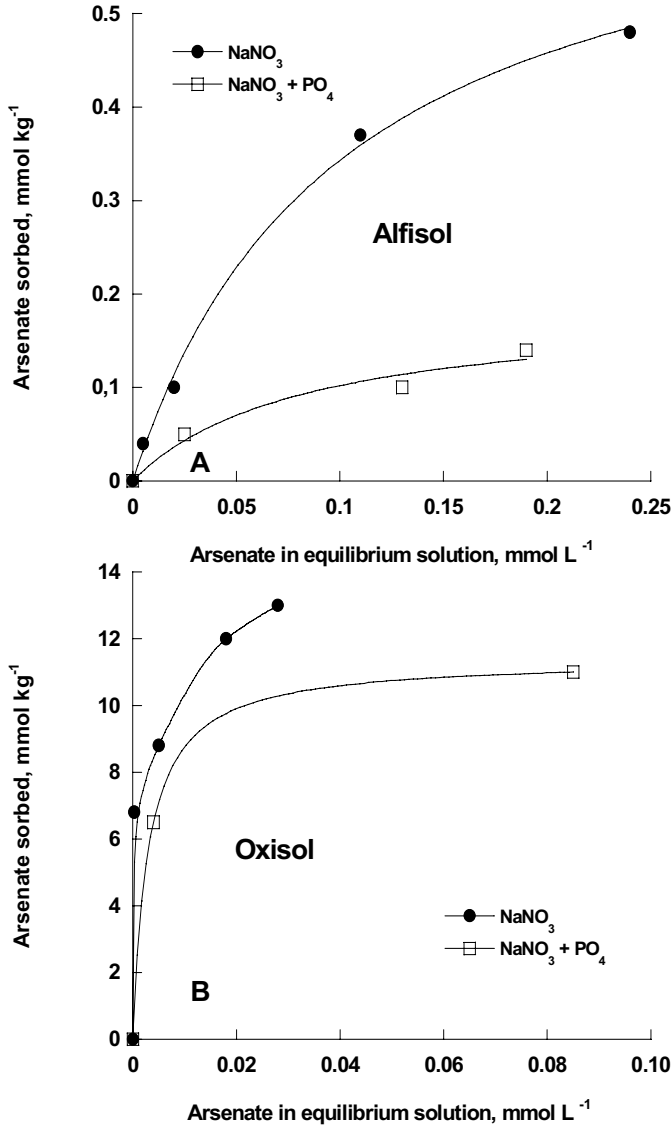


Fig. 1. Arsenate sorption (mmol kg⁻¹) on Alfisol (**A**) and on Oxisol (**B**) in the presence of sodium nitrate or sodium nitrate + phosphate (PO₄). Redrawn from Smith et al. (2002).

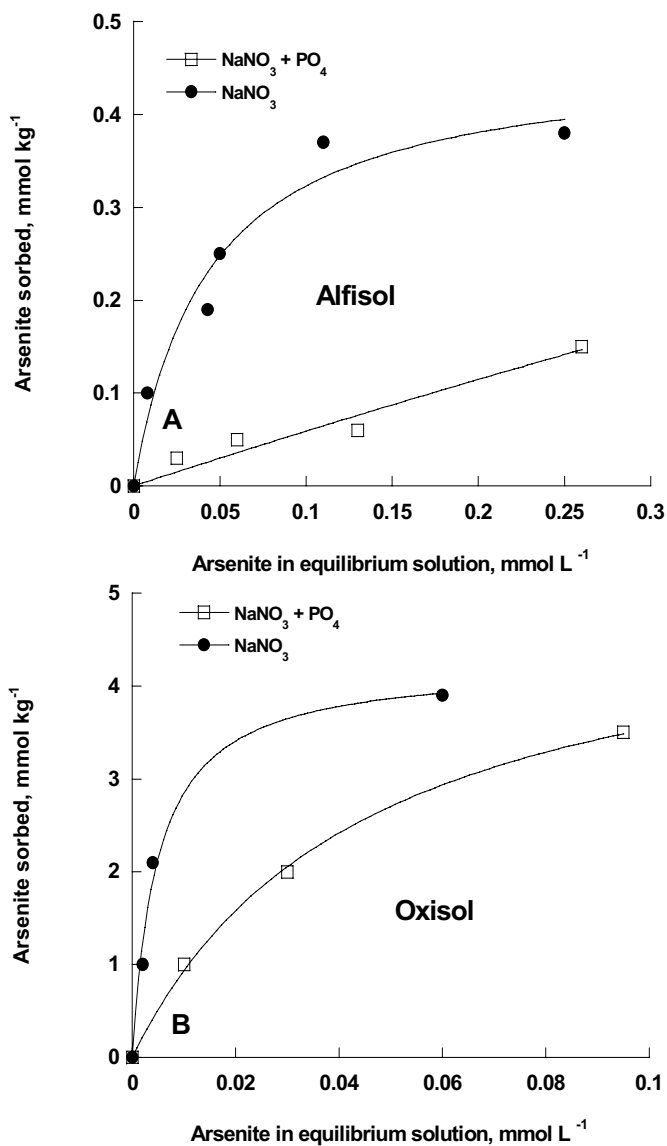


Fig. 2. Arsenite sorption (mmol kg⁻¹) on Alfisol (A) and on Oxisol (B) in the presence of sodium nitrate or sodium nitrate + phosphate (PO₄). Redrawn from Smith et al. (2002).

Figures 3 and 4 show the amounts of arsenate sorbed onto ferrihydrite and $\text{Al}(\text{OH})_x$ after 24 hrs of reaction with a surface coverage of arsenate and phosphate respectively of 50 or 100%. The numbers in parenthesis indicate the efficiency (in percentage) of phosphate in preventing sorption of arsenate calculated according to the expression of Deb and Datta (1967).

Efficiency of P (%) = $\{1 - [\text{As sorbed in the presence of P} / \text{As sorbed when applied alone}]\} \times 100$.

It appears evident that phosphate prevented arsenate sorption more onto $\text{Al}(\text{OH})_x$ than ferrihydrite and more when the surface coverage of both the ligands onto the sorbents was near 100% in comparison to that at 50%. In fact, in the $\text{AsO}_4 + \text{PO}_4$ systems the efficiency of phosphate in inhibiting arsenate sorption onto $\text{Al}(\text{OH})_x$ was of 49% and 79% respectively at 50% and 100% of surface coverage, whereas on ferrihydrite it was much lower viz., 8% and 41%, respectively. The sequence of anion addition strongly influenced arsenate sorption. Lower amounts of arsenate were sorbed in PO_4 before AsO_4 system and greater quantities of arsenate were sorbed in AsO_4 before PO_4 system as referred to $\text{AsO}_4 + \text{PO}_4$ system (Figs. 3 and 4).

The effect of other inorganic anions (sulfate, molybdate, silicate), low molecular mass organic ligands (LMMOLs, such as oxalate, malate, citrate, tartrate and succinate), and fulvic or humic acid on the sorption of arsenate and arsenite onto variable charge minerals and soils has been studied (Roy et al. 1986; Grafe et al. 2001; Liu et al. 2001; Violante et al. 2005a,b).

Sulfate poorly prevents arsenate sorption onto metal oxides and soils (Wu et al. 2001; Inskeep et al. 2002; Violante et al. 2005b). Violante et al. (2005b) found that high concentrations of sulfate (sulfate/arsenate molar ratio (rf) 4–10) retarded but not prevented arsenate sorption onto ferrihydrite (see their Fig. 15.10) or other metal oxides. Roy et al. (1986) showed that the sorption of arsenate by two soils (an Ultisol and a Typic Apludults) was reduced in the presence of molybdate.

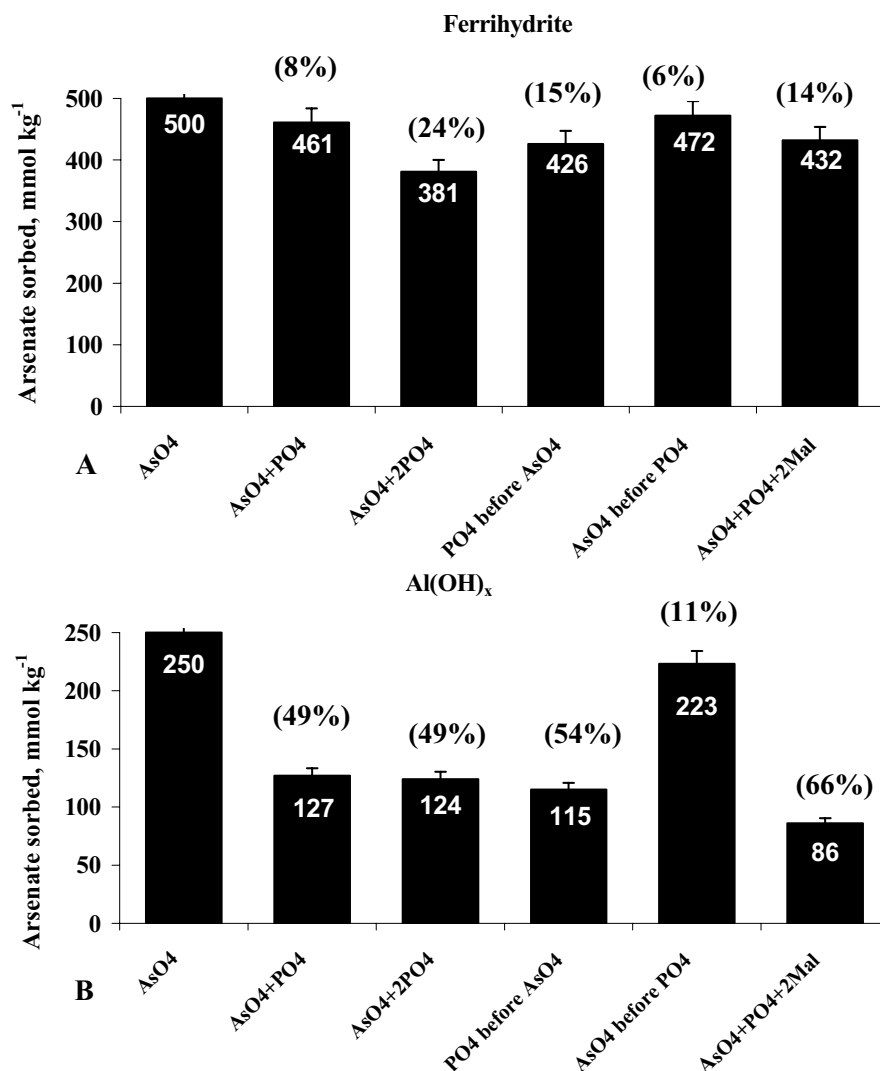


Fig. 3. Sorption of arsenate (AsO₄) onto ferrihydrite or Al(OH)_x in the presence of phosphate (PO₄) or phosphate and malate (Mal) at 50% surface coverage of arsenate and at initial AsO₄/PO₄ molar ratio of 1.0 or 0.5. Arsenate and phosphate were added as a mixture (AsO₄+PO₄; AsO₄+2PO₄) or phosphate was added 24 hrs before arsenate (PO₄ before AsO₄) or arsenate was added 24 hrs before phosphate (AsO₄ before PO₄). Arsenate, phosphate and malate were added as a mixture (AsO₄+ PO₄/Mal molar ratio of 1). The numbers in parenthesis indicate the effectiveness of phosphate in preventing arsenate sorption. From Del Gaudio (2005).

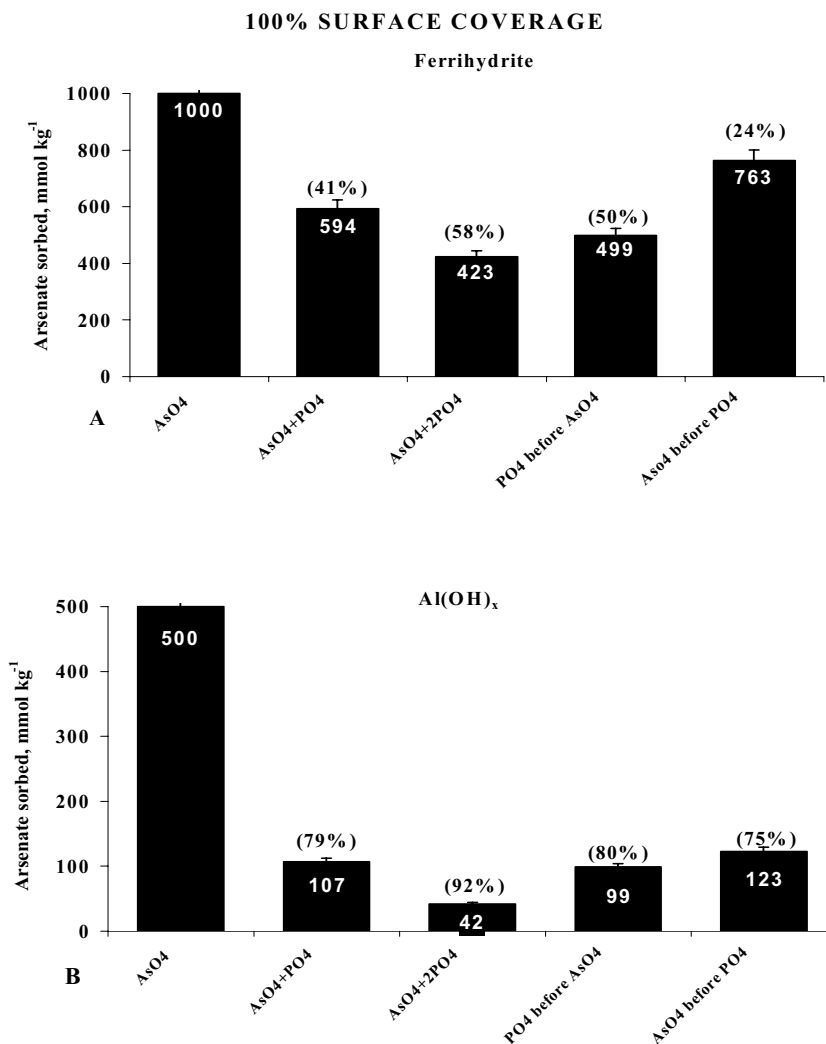


Fig. 4. Sorption of arsenate (AsO₄) onto ferrihydrite or Al(OH)_x in the presence of phosphate (PO₄) or phosphate and malate (Mal) at 100% surface coverage of arsenate and at initial AsO₄/PO₄ molar ratio of 1.0 or 0.5. Arsenate and phosphate were added as a mixture (*AsO₄+PO₄*; *AsO₄+2PO₄*) or phosphate was added 24 hrs before arsenate (*PO₄ before AsO₄*) or arsenate was added 24 hrs before phosphate (*AsO₄ before PO₄*). The numbers in parenthesis indicate the effectiveness of phosphate in preventing arsenate sorption. From Del Gaudio (2005).

The kinetics of sorption of arsenite and arsenate in the presence of sorbed silicic acid have been only recently examined (Waltham and Eick 2002). These authors demonstrated that the sorption of silicic acid (added 60 h before arsenic) decreased the rate and the total amount of arsenic sorbed. The amount of arsenite sorbed decreased as the surface concentration of silicic acid increased. Furthermore, the inhibition of arsenite sorbed ranged from about 4% at a pH of 6 and 0.1 mM silicic acid up to 40% at a pH of 8 and 1 mol L⁻¹ silicic acid. In contrast, silicic acid reduced the rate of arsenate sorption which decreased by increasing pH and silicic acid concentration, but the total quantity of arsenate sorbed remained nearly constant, indicating that arsenate was able to replace silicate.

Grafe et al. (2001) found that arsenate sorption onto goethite was reduced by humic and fulvic acid, but not by citric acid, whereas arsenite sorption was decreased by all three organic acids between pH 3.0 and 8.0 in the order of citric acid > fulvic acid > humic acid. Del Gaudio (2005) showed that the inhibition of malate (Mal) on arsenate sorption was negligible onto ferrihydrite (100% Arsenate surface coverage) even when malate was added before arsenate but not onto Al(OH)_x. At an initial Mal/As molar ratio of 1, the sorption of arsenate onto Al(OH)_x after 24 hrs of reaction was reduced by 40% (Fig. 5).

4 Sorption in Ternary Systems

Sorption of arsenate or arsenite in ternary systems has received scant attention. Some experiments on the sorption of arsenate onto ferrihydrite or Al(OH)_x in the presence of phosphate and malate (50% surface coverage of arsenate initial PO₄/AsO₄ molar ratio of 1 and Mal/PO₄+AsO₄ of 1; *AsO₄+PO₄+2Mal* systems) were carried out by Del Gaudio (2005). In *AsO₄+PO₄+2Mal* systems arsenate sorption was reduced much more on Al(OH)_x (66%) than on ferrihydrite (14%) (Fig. 3). Furthermore, it was found that the rf values were greater in *AsO₄+PO₄* system than in *AsO₄+PO₄+2Mal* system (0.5 vs 0.4), whereas, for ferrihydrite as the sorbent, the opposite was true (1.10 vs 1.05; data not shown). These findings demonstrate that malate competed with arsenate more for the surface sites of Al(OH)_x, than for those of ferrihydrite, whereas the opposite was true for phosphate. The sorption of three or more ligands onto soil components deserves attention.

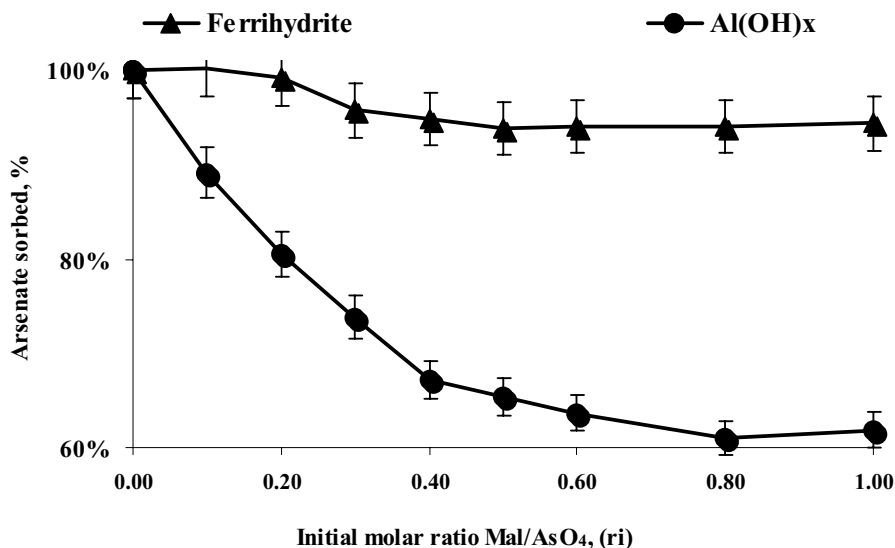


Fig. 5. Influence of increasing concentrations of malate (Mal) on the sorption of arsenate (AsO_4 ; 100% surface coverage) onto ferrihydrite or $Al(OH)_x$ at pH 5.0. Malate was added 24 hrs before arsenate (*Mal before AsO_4*). From Del Gaudio (2005).

5 Kinetics Sorption of Arsenate

The amounts of arsenate and arsenite sorbed onto soil components are affected by the time of reaction and presence of foreign ligands (Raven et al. 1998; Grafe et al. 2001; Frankenberger 2002; Violante and Pigna 2002; Pigna et al. 2006). We have carried out experiments on the kinetics of sorption of arsenate onto ferrihydrite and $Al(OH)_x$ in the absence or presence of phosphate and both phosphate and malate. Table 1 shows the amounts of arsenate and phosphate sorbed onto $Al(OH)_x$ at pH 5.0 after 0.03–168 hrs when these anions were added alone or as a mixture at 50% or 100% of surface coverage, whereas Fig. 6 shows the sorption of arsenate onto ferrihydrite and $Al(OH)_x$ (50% surface coverage) in the absence or presence of phosphate ($AsO_4 + PO_4$) or phosphate and malate ($AsO_4 + PO_4 + 2Mal$) during the first 24 hrs of reaction (Del Gaudio 2005; Violante and Pigna 2007 unpublished data). It appears evident that each ligand inhibited the sorption of the other; in fact, at 50% of surface coverage

(Table 1) arsenate and phosphate were completely sorbed onto Al(OH)_x within 3–5 hrs of reaction when added alone, but only after more than 168 hrs when added as a mixture. When the oxyanions were added together the arsenate sorbed/phosphate sorbed molar ratio (rf) continuously increased with time from 0.21 after 0.03 hrs to 0.94 after 168 hrs. The rf values were initially < 1 , since the sorption of phosphate was faster than that of arsenate. The rf reached the value of 1 only after 720 hrs (data not shown), indicating that all the ligands added were fixed on the surfaces of the oxide. On ferrihydrite at 50% surface coverage the rf values were initially greater than 1 and then decreased with time up to 1 (data not shown). Similar results were obtained by using hematites of different morphology and surface properties (Pigna et al. 2003). Clearly, an initial faster sorption of an anion onto the surface of a given sorbent affected the sorption of the other. A reduction in surface charge because of the initial sorption of phosphate or arsenate may also differently reduce the rate of anions sorption, which may be responsible for the observed residence time effect.

When the surface coverage of each ligand was 100%, the rf values increased more slowly from 0.19 to 0.41, as the time increased from 0.03 hrs to 168 hrs (Table 1). In fact, rf values increased 4.4 times from 0.03 to 48 hrs when the surface coverage was 50% and 2 times when the surface coverage was 100%. These findings indicate that when the surface coverage was high, being the sites not available for all the ligands added, there was a strong competition for sorption sites between arsenate and phosphate anions. Even after a reaction time of 700 to 1000 hrs the rf values were < 0.6 (data not shown). In the presence of both phosphate and malate ($\text{AsO}_4 + \text{PO}_4 + 2\text{Mal}$) arsenate sorption was strongly prevented; after 360 hrs of reaction 71% and 24% of arsenate was sorbed onto ferrihydrite and Al(OH)_x respectively (data not shown). From the results described before (Table 1; Fig. 6) it can be concluded that both competition for sorption sites and change in the surface charge of the sorbents occur simultaneously to explain the competition in adsorption between ions.

The kinetics sorption data of arsenate onto ferrihydrite and Al(OH)_x were tested by different models (first order, parabolic diffusion, and Elovich). The fit for the sorption data was obtained best using Elovich model (Fig. 7). Similar results were obtained by Pigna et al. (2006). At 50% surface coverage, the kinetics of sorption of arsenate on ferrihydrite could be explained best by assuming two processes, the first one (fast sorption) operating during the first 0.167 hrs of reaction when arsenate was added alone or during the first 24 hrs in the presence of phosphate ($\text{AsO}_4 + \text{PO}_4$ system) or phosphate and malate ($\text{AsO}_4 + \text{PO}_4 + 2\text{Mal}$ system) (Fig. 7A). A similar trend was not obtained using Al(OH)_x as sorbent

(Fig. 7B). This behaviour may be attributed to the higher affinity of arsenate for the iron than for aluminium oxides.

Table 1. Kinetics of reaction of arsenate (AsO_4) and phosphate (PO_4) onto $\text{Al}(\text{OH})_x$ when added alone or as a mixture (AsO_4^+ or PO_4^+) (initial AsO_4/PO_4 molar ratio of 1) at 50% or 100% surface coverage. rf indicates the AsO_4 sorbed/ PO_4 sorbed molar ratio (authors' unpublished data, 2007)

Time (hrs)	AsO_4 sorbed (mmol Kg^{-1})	PO_4 sorbed (mmol Kg^{-1})	AsO_4^+ sorbed (mmol Kg^{-1})	PO_4^+ sorbed (mmol Kg^{-1})	rf AsO_4/PO_4
50% Surface coverage*					
0.03	143	162	32	154	0.21
0.5	166	196	60	157	0.38
1	186	219	81	198	0.41
3	234	236	111	225	0.49
24	250	245	198	244	0.81
48	250	249	224	241	0.92
168	250	233	232	247	0.94
100% Surface coverage**					
0.03	155	193	27	139	0.19
0.5	167	263	21	176	0.12
1	216	299	49	193	0.25
3	260	345	57	252	0.22
24	407	491	95	382	0.25
48	486	495	189	466	0.40
168	498	496	197	476	0.41

*Two hundred fifty mmol AsO_4 added per kg of sorbent.

**Five hundred mmol added AsO_4 per kg of sorbent.

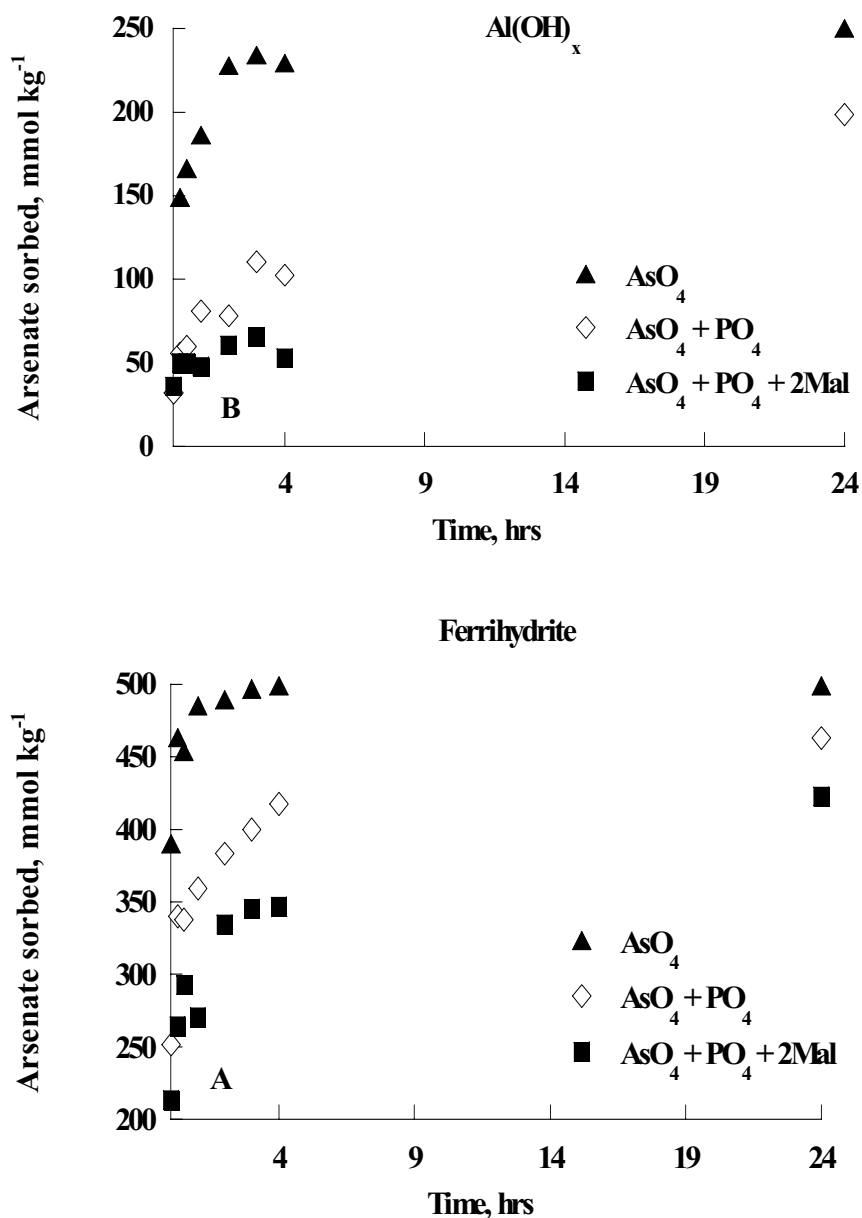


Fig. 6. Kinetics of arsenate (AsO_4) sorption onto ferrihydrite (A) or $Al(OH)_3$ (B) at pH 5.0 in the absence or presence of phosphate (PO_4) or phosphate and malate (Mal). Initial PO_4/AsO_4 molar ratio of 1 ($AsO_4 + PO_4$) and $AsO_4 + PO_4/Mal$ molar ratio of 1 ($AsO_4 + PO_4 + 2Mal$). Arsenate was added at 50% of surface coverage (authors' unpublished data, 2007).

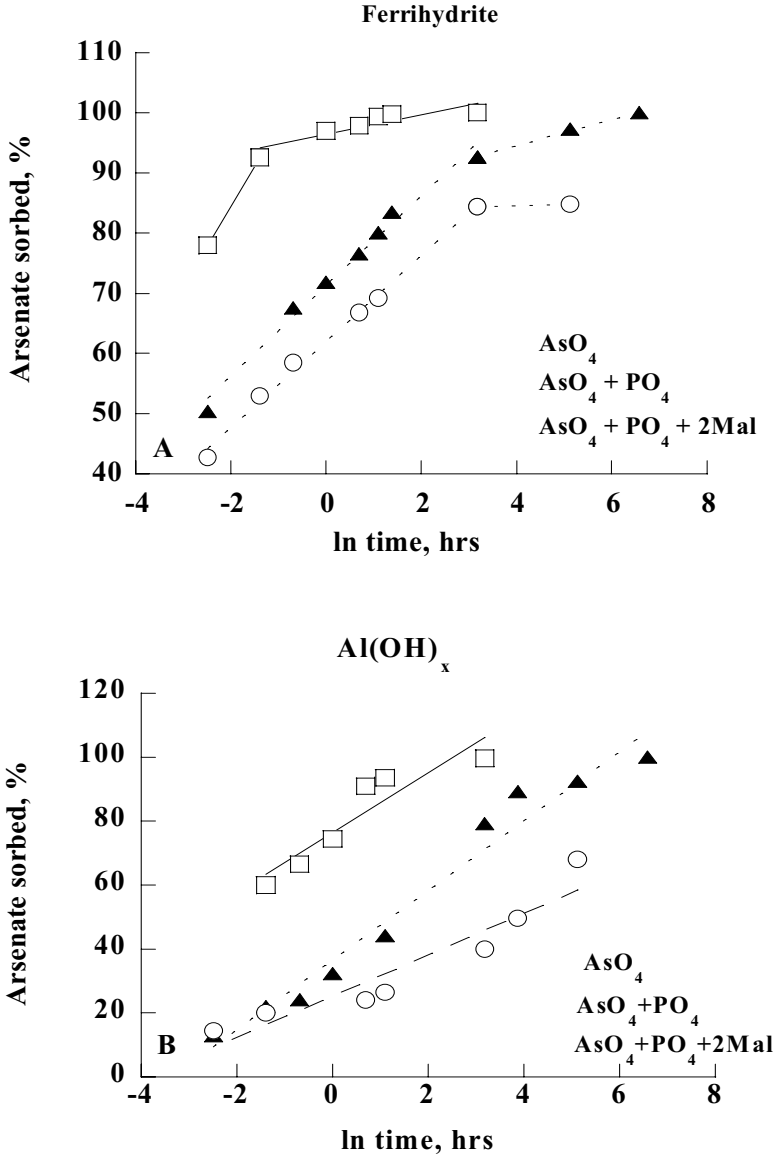


Fig. 7. Kinetics of arsenate (AsO_4) sorption onto ferrihydrite (A) or $Al(OH)_x$ (B) at pH 5.0 in the absence or presence of phosphate (PO_4) or phosphate and malate (Mal). Initial PO_4/AsO_4 molar ratio of 1 ($AsO_4 + PO_4$) and $AsO_4 + PO_4/Mal$ molar ratio of 1 ($AsO_4 + PO_4 + 2Mal$). Arsenate was added at 50% of surface coverage. The fit for the sorption data was obtained best using Elovich model (authors' unpublished data, 2007).

6 Desorption of Arsenate

Desorption of arsenic by foreign ligands (mainly phosphate) has received attention particularly in the last years. Goh and Lym (2005) evaluated the extractability of arsenate from the fine fraction of an acidic soil deliberately contaminated with arsenate and aged for more than 220 days by various salts such as Na_3PO_4 , Na_2CO_3 , Na_2SO_4 and NaCl . The results of arsenic extraction as a function of reaction time in the presence of phosphate, sulfate, carbonate and chloride (0.005 M) are reported in Fig. 8. Both chloride and sulfate solutions extracted less than 20% of arsenic from the soil. The percentages of arsenate extracted by carbonate were slightly higher than those mobilized by chloride or sulfate. Phosphate demonstrated the highest arsenic extraction efficiency among the anions used. The percentage of arsenic extracted by phosphate increased rather rapidly within short reaction times, and they continued to increase gradually toward equilibration (Fig. 8). Therefore, the effectiveness of the anions in mobilizing arsenic from the soil followed the order: $\text{PO}_4 \gg \text{CO}_3 > \text{SO}_4 \approx \text{Cl}$.

O'Reilly et al. (2001) studied the effect of sorption residence time on arsenate desorption by phosphate (phosphate/arsenate molar ratio of 3) from goethite at different pH values. Initially, desorption was very fast (35% arsenate desorbed at pH 6.0 within 24 hrs) and then slowed down. Total desorption increased with time reaching about 65% total desorption after 5 months. These authors found no measurable effect of aging on desorption of arsenate in the presence of phosphate. Furthermore, desorption results at pH 4.0 were similar to the desorption behaviour at pH 6.0. On the contrary, Arai and Sparks (2002) demonstrated that the longer the residence time (3 days–1 year), the greater was the decrease in arsenate desorption by phosphate from a bayerite.

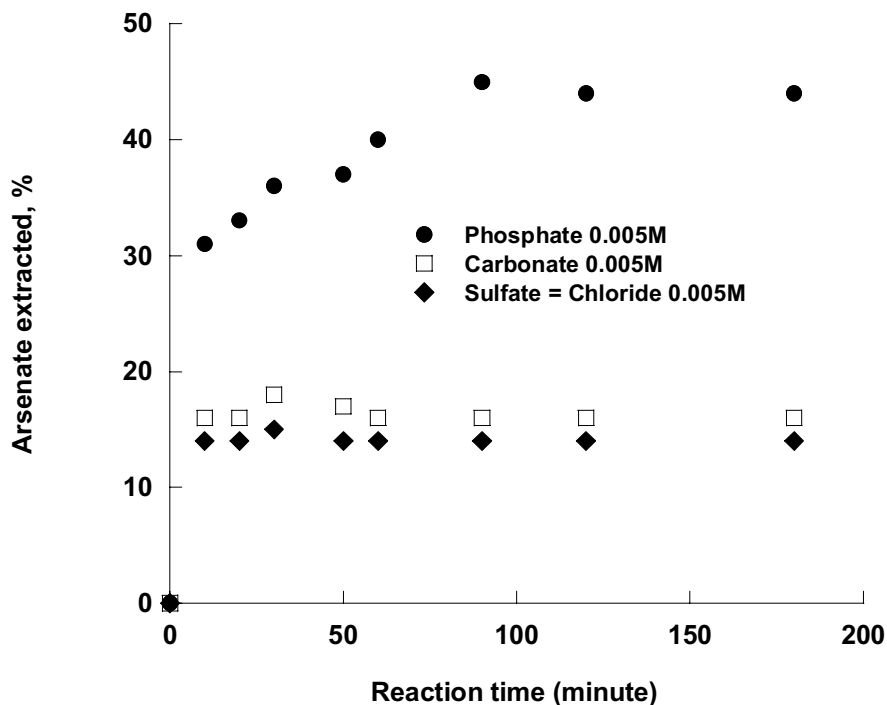


Fig. 8. Arsenic extraction from a reddish brown tropical soil deliberately contaminated with arsenate as a function of reaction time by 0.005M chloride, sulphate, carbonate and phosphate. Redrawn from Goh and Lym (2005).

The desorption of arsenate previously sorbed onto Fe- or Al-oxides or onto an Andisol containing 42% of allophanic materials (Vacca et al. 2002) by phosphate has been demonstrated to be affected by time of reaction, residence time of arsenate onto the surfaces and the pH of the system (Pigna et al. 2006; Pigna et al. 2007, unpublished data). Figure 9 shows the desorption of arsenate at pH 6.0 (phosphate/arsenate molar ratio of 4) when phosphate was added onto the soil (Andisol) sample 1, 5 or 15 days after arsenate (surface coverage of arsenate about 60%). After 60 days of reaction, 55% of arsenate was desorbed by phosphate when the residence time of arsenate onto the surfaces of the Andisol was 1 day, but 35 and 20% of arsenate was desorbed by phosphate with increase in the residence time up to 5 and 15 days. Further, it was also observed that by keeping the

surface coverage and residence time constant the desorption of arsenate by phosphate increased by increasing the pH of the system. The arsenate desorbed after 24 hrs of reaction ranged from 41% at pH 4.0 to 73% at pH 8.0 (data not shown). Pigna et al. (2006) have reported that the desorption of arsenate by phosphate from iron and aluminum oxides was affected by the crystallinity of the sorbents.

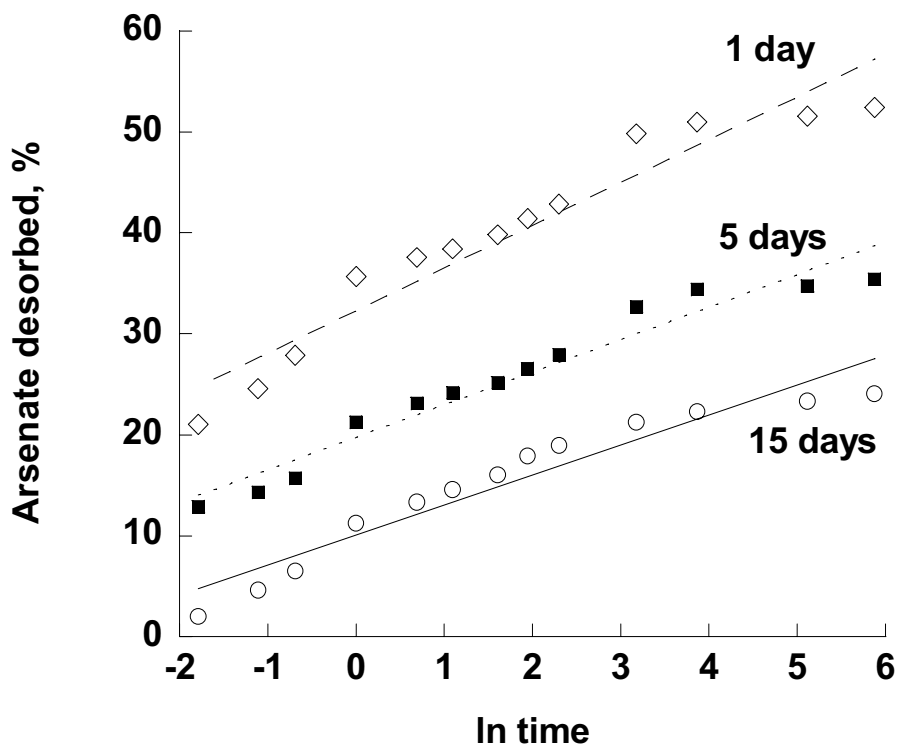


Fig. 9. Desorption of arsenate (AsO_4) from Andisol at pH 6.0 (phosphate/arsenate molar ratio of 4) when phosphate (PO_4) was added 1, 5 or 15 days after arsenate. Surface coverage of arsenate was about 60% (authors' unpublished data, 2007).

Desorption of arsenate, MMAs(V) and DMAs(V) from goethite and ferrihydrite by phosphate and sulfate was studied by Lafferty and Loeppert (2005). These arsenic compounds were desorbed more efficiently by phosphate than sulfate. In desorption envelopes, the amount of arsenate desorbed generally increased as the number of methyl groups increased

[arsenate < MMAs(V) < DMAs(V)]. Desorption of MMAs(V) by phosphate from ferrihydrite increased with increasing pH, as did desorption of arsenate, but MMAs(V) was desorbed in greater quantities than arsenate at any given pH. DMAs(V) was almost completely desorbed from ferrihydrite by phosphate. Desorption trends for arsenate, MMAs(V) and DMAs(V) from goethite were different from those observed for ferrihydrite, but no explanation were given for this phenomenon.

7 Effect of Phosphate on the Removal of Arsenic Coprecipitated with or Sorbed on Metal Oxides

Whereas studies have been carried out on the factors (surface coverage, residence time, pH) which influence the desorption of arsenate previously sorbed onto oxides, phyllosilicates and soils (O'Reilly et al. 2001; Liu et al. 2001; Arai and Sparks 2002; Violante and Pigna 2002; Pigna et al. 2006), scant information are available on the possible desorption of arsenate coprecipitated with iron or aluminum. In natural environments arsenic may form precipitates or coprecipitates with Al, Fe, Mn and Ca. Coprecipitation of arsenic with iron and aluminum are practical and effective treatment processes for removing arsenic from drinking waters and might be as important as sorption to preformed solids.

Recently, studies on the sorption of phosphate on and the removal of arsenate from aluminum-arsenate or iron-arsenate coprecipitates formed at arsenate/aluminum (or iron) molar ratio (R) of 0.1 and pH 4.0, 7.0 or 10.0 have been carried out (Violante et al. 2006, 2007). Figure 10 shows the sorption of phosphate on and the desorption of arsenate from two samples formed at pH 7.0 and R = 0.1, obtained by coprecipitating aluminum and arsenate (7R0.1) or by adding arsenate immediately after the precipitation of aluminum (7AR0.1). These samples, aged 30d at 50°C, showed similar surface area (about 135 m² g⁻¹), and mineralogy (presence of poorly crystalline boehmite) but different reactivity. In fact the sorption of phosphate onto 7AR0.1 was more than two times lower than on 7R0.1 (Fig. 10A), whereas greater amounts of arsenate were released from 7AR0.1 than 7R0.1 (Fig. 10B). Evidently, in the 7AR0.1 sample arsenate anions, added to a preformed aluminum precipitate, were sorbed on the external surfaces and occupied many sorption sites and, consequently, prevented the fixation of phosphate more efficiently than 7R0.1 where arsenate anions, being mainly enmeshed in the precipitate, were not easily accessible and not easily desorbed by phosphate. A similar behaviour was ascertained by using iron-arsenate coprecipitates (Violante et al. 2007).

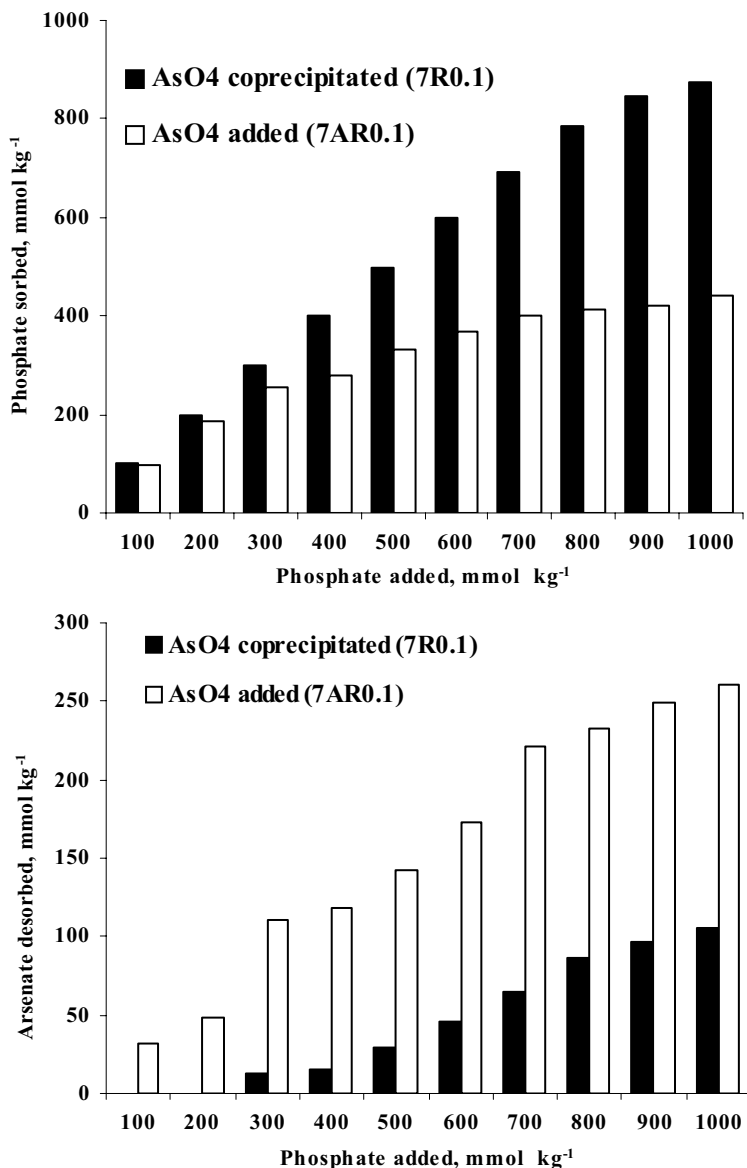


Fig. 10. Sorption of phosphate (PO_4) (A) and desorption of arsenate (AsO_4) (B) from two samples formed at pH 7.0 and $R = 0.1$, obtained coprecipitating aluminum and arsenate (7R0.1) or by adding arsenate (7AR0.1) immediately after the precipitation of aluminum. Reaction time was 24 hours. Redrawn from Violante et al. (2006).

8 Arsenic Sequential Extraction from Polluted Soils

Although sequential fractionation procedures generally do not allow assessing the precise association of elements with each soil mineralogical phase, they can provide operationally defined phase associations and may be a powerful tool for the identification of some of the main binding sites, allowing to assess the potential for remobilisation and bioavailability of arsenic in polluted soils (Wenzel et al. 2001; Martin et al. 2007a).

The fractionation of the arsenic may be carried out according to the method of Wenzel et al. (2001). Briefly, arsenic is sequentially extracted with: (1) 0.05M K_2SO_4 at 20°C for 4 h; (2) 0.05M KH_2PO_4 at 20°C for 16 h; (3) 0.2M NH_4^+ -oxalate buffer in the dark, at pH 3.25 and 20°C for 4 h; (4) 0.2M NH_4^+ -oxalate buffer + ascorbic acid at pH 3.25 and at 96°C for 0.5 h and finally (5) HNO_3/H_2O_2 or HCl/HNO_3 hot digestion. The obtained As fractions are defined by these authors as associated to: (1) non-specifically sorbed; (2) specifically-sorbed; (3) bound to amorphous and poorly-crystalline hydrous oxides of Fe and Al; (4) bound to well-crystallized hydrous oxides of Fe and Al; and (5) residual phases. These authors demonstrated that partitioning of arsenic among these fractions in 20 soils was (% , medians and ranges): (1) 0.24 (0.02–3.8); (2) 9.5 (2.6–25); (3) 42.3 (12–73); (4) 29.2 (13–39); and (5) 17.5 (1.1–38).

The arsenic extraction from two polluted Italian soils from Scarlino (Tuscany, Italy) containing high amounts of arsenic (104 mg kg^{-1} , Vetricella soil and 190 mg kg^{-1} , La Botte soil) was studied (Branco 2007). Arsenic was in the most part recovered in the crystalline oxides (about 60–63%; Figs. 11A and B). Another abundant fraction (19–20%) of arsenic was obtained by NH_4 -oxalate, which is effective for targeting amorphous Fe and Al oxides (Wenzel et al. 2001). The arsenic fraction extracted with KH_2PO_4 was about 7% for each soils. The fraction not specifically sorbed (easily exchangeable) that form outer-sphere complexes onto the mineral surfaces was very low (< 1%). The scarce residual arsenic fraction (11–13%) suggested a low presence of primary minerals rich in this metalloid (Fig. 11). About 90% of arsenic present in these soils was not available for plants.

Martin et al. (2007a) investigated the accumulation and potential release of arsenic in a paddy field in Bangladesh irrigated with arsenic contaminated groundwater. The oxalate-extractable fraction related to amorphous hydrous oxide-bound arsenic represented the dominant arsenic form in the surface layer (47%). A high percentage of arsenic was removed by phosphate (22%).

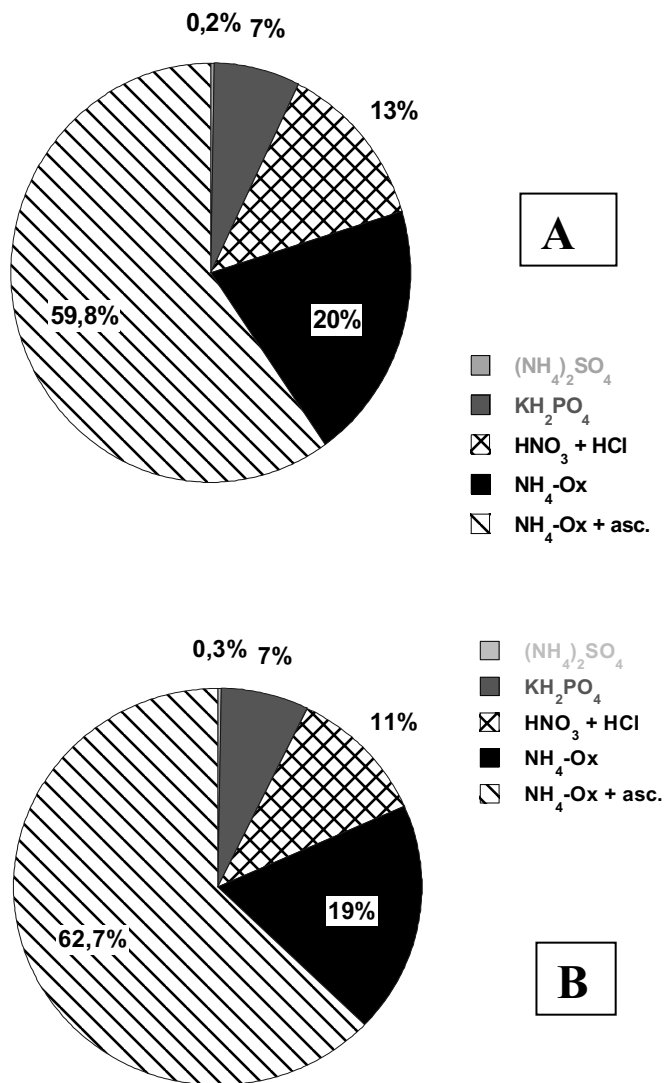


Fig. 11. Arsenate fractionation from two Italian polluted soils. (A) La Botte soil containing 190 mmol As kg⁻¹; (B) Vetricella soil containing 104 mmol As kg⁻¹. From Branco (2007).

9 Conclusion

Sorption and desorption of arsenic in terrestrial environment is affected by many factors as oxidation state of this element, pH, nature of sorbents, presence of organic and inorganic ligands, surface coverage, time of reaction and residence time of arsenic on the surfaces of the sorbents. Many studies have been carried out on competition in sorption between arsenic (mainly arsenate) in the presence of inorganic and organic anions onto soil components and soils in binary system, but scant experiments have been conducted on the sorption of arsenic in the presence of three or more ligands. Furthermore more information are available on the factors which affect the sorption of arsenic, than the desorption of arsenic. Unfortunately, the effect of organic ligands, both nutrients and LMMOL_s (root exudates or microbial metabolites) on the mobility of arsenite are tremendously poor. The mobility of arsenic present in coprecipitates with Al, Fe, Ca or Mn still needs to be observed. To predict the mobility and potential toxicity of arsenic in natural environments more studies are necessary on the concomitant effects the clay minerals, organic and inorganic ligands, time of reaction and surface coverage have on the sorption/desorption processes of arsenate and (mainly) arsenite.

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