Mechanisms of Arsenic Adsorption in Calcareous Soils

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ABSTRACT

Arsenic (As) contamination in soil and water is a serious environmental issue. Release of As in soil solution as bioavaiolable form is controlled by its retention mechanisms. The factors controlling As adsorption need to be reviewed in the light of recent advancements in understanding the processes operative in calcareous soil and sediments. The dominant As ionic species in the soil environment are As(III) ($H_2AsO_3^-$) or As(V) ($HAsO_4^{2-}$) depending upon soil pH. Arsenic is retained in soil by adsorption on surface of iron and aluminum oxides and hydroxides and by ligand exchange. Silicate clays (kaolinite, illite and montmorilonite) also adsorb As by coprecipitation with silicates. Soil calcite adsorbed As by forming precipitation. Organic matter, PO_4, SO_4 and MoO_4 affects As adsorption as humate and **phosphate ion behave like arsenate and compete for adsorption on adsorption sites. Dominant mechanismof As retention may be due to well crystallized goethite. This paper represents dominant mechanisms of As retention in calcareous soils and sediments.**

INTRODUCTION

Arsenic (As) is a ubiquitous trace element with mean lithosphere concentration of 5 mg kg^{-1}. In soils As is generally in the order of 5-10 mg kg^{-1} and concentration above 20 mg kg^{-1} soil is considered high (Smedley and Kinniburgh, 2000). Due to potential risk to human and environment health, As contamination in soils and water is a concern worldwide. Arsenic sources are weathering of minerals (Bhumbla and Keefer, 1994; Yan-Chu, 1994; Mandal and Suzuki, 2002; Foley and Ayuso, 2008; Mailloux *et al.*, 2009) and anthropogenic activities including various industrial wastes, mining activities, application of sewage sludge and wastewater, and agricultural in puts (Chilvers and Peterson, 1987). Historic use of pesticides and herbicides has also resulted in substantial accumulation in soils (Hiltbold *et al.*, 1974). The lithogenic As is of serious concern in Bangladesh, India, and Vietnam. High concentration of As in soil and water has also been noted in developed countries, e.g., US (Peryea and Creger, 1994; U.S. Geological Survey. http://oregon.usgs.gov/pubs_dir/Online/Html/WRIR98-4205/) and South Australia and Tasmania (Merry *et al.*, 1983). Site specific geo-chemical processes which control bioavailability of As need to re-evaluated in the light recent development in the study area.

Arsenic oxidation state governs its toxicity, chemical form and solubility in natural and disturbed environments. Two inorganic As forms dominate in soils: arsenate (As(V)) and arsenite (As^{III}), the later being more mobile and toxic. Arsenate and phosphate (PO_3^{-4}) are chemically similar and so tend to compete for potentially As-bearing phases of soil. Thermodynamically, the As(V) species ($HAsO_4^{2-} > H_2AsO_4^-$) are more abundant in soil solutions that are oxidized more at pH > 9. The As^{III} forms ($H_3AsO_3^0$, $HAsO_2^0$, $H_2AsO_3^-$, AsO_2^-, are relatively anoxic soil solutions with pH < 7 (Khaodhiar *et al.*, 1999). Iron oxides/hydroxides in soil are thought as major constituents which control As adsorption in acidic as well as in alkaline environment (Taggart et al., 2004). The surfaces of Al oxides/hydroxides and silicate clays such as kaolinite, montmorilonite may play a role in As adsorption in acidic soils. The carbonate minerals are expected to adsorb As in calcareous soils. The role of Mn oxides and biogenic particles in the As adsorption in soils appears to be limited to acidic soils. Chemisorption of arsenate and arsenite on soil colloid surfaces, especially those of Fe oxide/hydroxides and carbonates, is thought to be a common mechanism for As solid phase formation (Sadiq, 1995; Yang and Donahoe, 2007). Silicate clays retain As by inner sphere surface complexation and strong specific ion adsorption (Keon *et al.*, 2001). At extremely low As concentration, a ligand exchange reaction of $H_2AsO_4^{2-}$ with surface OH groups form the monodentate complex and at high concentration the sorption of arsenate was dominated by the formation of bidentate surface complexes (Gao *et al.*, 2006). $CaCO_3$ form precipitation in soil with As and form inner-sphere complex at the calcite surface, whereby AsO_4 units link via corner- sharing to Ca octahedral.

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There are many factors which affects the As adsorption in soil. The concentration of phosphate (PO_4) is the main factor which affects the As adsorption negatively, and organic matter (OM) has also negative affect on the As adsorption because both OM and PO_4 has a competition for adsorption sites with arsenate. pH also increase or decrease As adsorption depending on type of adsorbent and form of As (Reilly *et al.,* 2001). Sorption kinetics is also important in understanding the adsorption/desorption processes, and transport of arsenate in soil and sediments. Understanding of the arsenate reaction kinetics involving in calcareous soils is poor (Yolcubal and Akyol, 2008). Therefore, As chemistry in calcareous soil needs to be reviewed in the light of recent research developments. Objective of this review is to determine dominant processes and factors affecting As retention in calcareous soils.

Arsenic Adsorption by Metal Oxides

Most important iron oxide in calcareous soil and sediments is goethite. Goethite (α-FeOOH) consist of double bands of FeO(OH) octahedra which share edges and corners to form 2×1 octahedra tunnel partially bonded by H-bonds (Schwertmann and Cornell, 2000). It exhibits needle-shaped crystals with grooves and edges and has surface area of 30-273 $m^2\ g^{-1}$ and particle size in the range of 2-75 nm. Goethite is the most common iron oxide in calcareous soils (Memon et al., 2009) and due to its high surface area may play important in As retention because arsenate adsorbs strongly to iron-oxide surfaces (Dzombak and Morel, 1990; Waychunas *et al.*, 1993). Iron oxides such as goethite sorbs arsenate through ligand exchange mechanism.

Most arsenate and arsenite oxyanions replaced two singly coordinated surface OH groups to form binuclear bridging complexes Fe-O-AsO(OH)-O-Fe and Fe-O-As(OH)-O-Fe (Sun and Doner, 1996). Arsenite mainly reacted with doubly coordinated surface OH groups, whereas arsenate reacted with triply coordinated surface OH groups. $HAsO_2^{2-}$ ion participate in ligand exchange reactions displacing singly coordinated surface hydroxyl groups to adsorb as a binuclear species (Lumsdon *et al.,* 1984). Bidentate binuclear complexation remains the major bonding mechanism for arsenate adsorption on goethite. The three types of arsenate - goethite surface complexes also depend on the surface cover oxides age level. At extremely low surface coverage, a ligand exchange reaction of $H_2AsO_4^{2-}$ with surface OH groups formed the monodentate complex (Gao *et al.,* 2006). At high surface loadings, the sorption of arsenate was dominated by the formation of bidentate surface complexes after a second ligand exchange reaction occurred; however, along with the surface coverage, the pH of the samples was also different (the two lowest loading levels in their study had higher pH values). Arsenate forms inner-sphere bidentate complexes on both goethite and ferrihydrite. But, at very low surface coverage, monodentate complexes may form on crystalline goethite under the conditions. It has been found that the fraction of monodentate bonds decreased as the arsenate coverage increased for the amorphous iron oxide samples and seen that the primary sorptive complex was a bidentate binuclear bridging complex (Gao *et al.,* 2006).

However, desorption of arsenate from iron-oxide surfaces becomes favored as pH values become alkaline (Fuller and Davis, 1989; Dzombak and Morel, 1990; Dixit and Hering, 2003; Mamindy-Pajany et al., 2009). Where pH values are above about 8, the negative net surface charge of iron oxide can repel negatively charged ions such as arsenate.

Langmuir equation best fit the adsorption isotherm (Lakshmipathiraj *et al.,* 2006). The diffusion and adsorption coefficients of arsenate ion were $3.84\times10^{11}\ cm^2\ s^{-1}$ and 194l mol^{-1}, respectively. The activation energy of adsorption reaction was of the order of 20 kJ mol^{-1} to 43 kJ mol^{-1} and maximum adsorption capacity was 4.7 mg g^{-1} goethite. The adsorption of arsenate by goethite increase as pH decreases and maximum adsorption was observed around pH 5 (Giménez *et al.,* 2007; Dimirkou *et al.,* 2009).

Arsenic Adsorption by $CaCO_3$

Calcite has been implicated as playing a possible role in the retention and solubility of arsenic in calcareous soils and various other environments with abundance of carbonates. Yet, Arsenic sorption on calcite is less well understood and contradictions in literature occur on phenomenon. Average diameter of $CaCO_3$ is 2 to 8 µm and surface area of 5 to 10 m^2/g. Arsenate sorption on calcite increases from pH 6 to 10, peaks between pH 10 and 12, and decreases above pH 12 (Goldberg and Glaubig, 1988). In natural systems, arsenic may be incorporated into the lattice structure of calcite as arsenite under alkaline pH, thereby hindering the mobility of the metalloid when iron and/or manganese oxyhydroxides lose their adsorbing effectiveness (Di Benedetto *et al.*, 2006). Roman-Ross *et al.* (2006) showed that arsenite retention mechanisms on calcite changed from adsorption to coprecipitation with an increasing As(III) concentration. Arsenic adsorption and equivalent $CaCO_3$ correlate well in sediments amended with arsenic. Romero *et al.* (2004) suggested that arsenic retention in carbonate-rich aquifer material could be partly due to the adsorption onto calcite. Arsenate anions exhibit a great affinity for calcite surface sites at pH 8.3 and form inner-sphere complex at the calcite surface whereby AsO_4 tetrahedral units link via corner-sharing to Ca octahedral (Alexandratos *et al.*, 2007). Spectroscopic characterization of adsorption and incorporation mechanisms of arsenic in the calcite lattice under equilibrium conditions remained main focus of recent studies. It should be noted that none of these studies examined the retention of arsenate undergoing transport in natural calcareous soils where in other mineral phases (Fe, Al, and Mn oxyhydroxides) are limited (Yolcubal and Akyol, 2008).

Sequential extraction results showed that nonspecifically sorbed (easily exchangeable, outer sphere complexes) fraction of arsenate is dominant than the inner-sphere surface bound complexes of arsenate in the carbonate soil fraction, indicating high bioavailability and transport for arsenate in the carbonate-rich soils of which Fe and Al oxyhydroxide fractions are limited (Yolcubal and Akyol, 2008). Little or no arsenite sorbs on calcite within 24 h at an initial As concentration of 0.67 µM. In contrast, arsenate sorbs readily and quickly on calcite. Likewise, desorption of arsenate from calcite is fast and complete within hours, indicating that arsenate is not readily incorporated into the calcite crystal lattice. The degree of arsenate sorption depends on the solution chemistry. Sorption increases with decreasing alkalinity, indicating a competition for sorption sites between arsenate and (bi)carbonate. pH also affects the sorption behavior, likely in response to changes in arsenate speciation or protonation/deprotonation of the adsorbing arsenate ion. Finally, sorption is influenced by the ionic strength, possibly due to electrostatic effects (Sø et al., 2008).

Arsenic Adsorption by Silicate Clays

Adsorption affinity of clay mineral is less than that of oxide for As (Goldberg, 2002). Since pH influences distribution of arsenic species in solution and, also, activates the anion adsorption sites on clay minerals, thus it has the most profound role in adsorption. At low pH, hydroxyl groups exposed on the periphery of metal oxides, clay minerals and amorphous silicate minerals are protonated and acquire a positive charge. These protonated sites are then available for the interaction and adsorption of the arsenical anions present in solution (Sposito, 1989). Maximum adsorption of As(V) by kaolinite and montmorillonite occurs at pH 5.0 and maximum adsorption of $As^{(III)}$ at pH 8 to 9 (Griffin and Shimp, 1978; Goldberg, 2002). Manning and Goldberg (1996) reported distinct As(V) adsorption maxima at approximately pH 5.0 for kaolinite, 6.0 for montmorillonite and 6.5 for illite, and the maxima ranged from 0.15 to 0.22 mM As(V) kg^{-1}. The maximum adsorption capacity calculated by fitting adsorption isotherms to Langmuir equation were 0.86, 0.64, and 0.52 mg As^V g^{-1} kaolinite, montmorillonite and illite, respectively (Mohapatra *et al.*, 2007). AS(III) adsorbed on kaolinite and smectite on pH value 9, while As(V) adsorbed on kaolinite at pH 3 to 8 and on montmorilonite at pH 5 to 6 (Goldberg, 2002).

The mechanism of adsorption has been ascribed to inner sphere complexation (specific adsorption). Inner sphere surface complexation as the adsorption mechanism and strong specific ion adsorption have also been deduced from the electrophoretic mobility measurements (Mohapatra *et al.,* 2007). Thus clay minerals can effectively remove arsenic from solution. An increase in adsorption temperature results in decrease in the amount of As(V) adsorbed, which showed the interactions to be exothermic (Mohapatra *et al.,* 2007). The results of leaching study showed that kaolinite was very active clay constituent regarding both As^V adsorption and mobility. Evidence for direct competitive adsorption in the case of As(V) + P and possibly site-specific non-competitive adsorption for As(V) + MO have been reported (Manning and Goldberg, 1996).

Arsenic Adsorption by Organic Matter

Organic acids such as humic acid and fluvic acid may compete strongly with As(III) and As(V) for active adsorption sites on mineral surfaces influencing the mobility of As. The competition for active binding sites on mineral surfaces between organic acids and As species may result in lowering the levels of As retention, especially under acidic conditions (Wang and Muligan, 2006). Dissolved organic matter, whose concentrations range from 1–20 mg L^{-1} in most fresh waters and reach higher values in wetlands, may also influence arsenic mobility by several mechanisms. OM may greatly influence redox as well as complexation speciation of arsenic in freshwater environments and arsenite was consistently desorbed or prevented from sorbing to a greater extent than arsenate (Redman *et al.,* 2002). Fulvic or humic acids form stable complexes with mineral surfaces effectively blocking arsenic from adsorption on iron oxides, alumina, quartz or kaolinite. Organic anions have consequently been found to enhance arsenic leaching from soil material in which arsenic is mainly associated with the metal oxide fraction and also from fly ashes. The study also suggested a strong potential for DOM to mobilize As(V) from the studied materials. At pH 5.0, DOM concentrations of 2.5 and 5.0 mg C/L had negligible effect on As(V) leachability. With increasing DOM concentration from 10 to 30 mg C/L, increased the As(V) leachability into the solution. A small but substantial increase of arsenic mobility was also found in wetland soils in the presence of high DOC concentrations (Baur and Bladau, 2006).

Soil Factors Affecting As Adsorption

Competitive adsorption onto mineral surfaces between As(V) and other oxyanions such as PO_4, SO_4 and MoO_4 has been reported (Smith *et al.,* 2002). Waltham and Eick (2002) observed that silicic acid adsorption onto goethite could reduce the rate and total quantity of As(III) adsorbed by modifying the surface potential (e.g., reduce the isoelectric point) and blocking reactive functional groups. Phosphate addition enhanced As uptake by plant attributed to displacement of soil As by P from adsorption sites and release into the soil solution. The effect of compost on As uptake depended on soil properties (e.g. pH). In the soil with a neutral pH, compost treatments may have induced an anaerobic environment in the soil, which was favorable for the conversion of As(V) to the mobile As(III), thereby facilitating As uptake by the plant. In contrast, As adsorption onto organic matter applied in acidic soil may be responsible for the decrease of As uptake in the soil after treatment with compost. The plant As mainly from Fe–As and Ca–As fractions in soil. Both compost and phosphate amendments increased As leaching from soil in the absence of the plants, but decreased in the presence of the plants. For As contaminated soil, both treatments reduced As leaching regardless of the presence of the fern. The results indicate that growing plant with the application of phosphate rock is more effective for remediating As-contaminated soils (Cao *et al.,* 2003).

Changes in pH (both an increase and a decrease from the initial pH 6.4) can increase the amount of As(V) desorbed from kaolinite. Parameters obtained from modeling the kinetic data showed that the pH will mainly effect the slow desorption sites, and therefore a change in pH can have a long-term effect on As(V) desorption (Quaghebeur *et al.*, 2005).

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