Review Article

The Fate and Factors Determining Arsenic Mobility of Arsenic in Soil-A Review

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Arsenic which is found in several different chemical forms and oxidation states and causes acute and chronic adverse health effects is a toxic trace element widely distributed in soils and aquifers from both geologic and anthropogenic sources. Arsenic which has a mysterious ability to change color, behavior, reactivity, and toxicity has diverse chemical behavior in the natural environment. Arsenic which has stronger ability to readily change oxidation state than nitrogen and phosphorus due to a consequence of the electronic configuration of its valence orbitals with partially filled states capable of both electron donation and acceptance although the electronegativity of arsenic is greater than that of nitrogen and similar to that of phosphorus. Arsenate (V) is the thermodynamically stable form of As under aerobic condition and interacts strongly with solid matrix. However, it has been known that adsorption and oxidation reactions of arsenite (III) which is more soluble and mobile than As(V) in soils are two important factors affecting the fate and transport of arsenic in the environment. That is, the movement of As in soils and aquifers is highly dependent on the adsorption-desorption reactions in the solid phase. This article, however, focuses primarily on understanding the fate and speciation of As in soils and what fate arsenic will have after it is incorporated into soils.

Key words: Arsenic, As chemical form, As mobility, As solubility, Adsorption and desorption
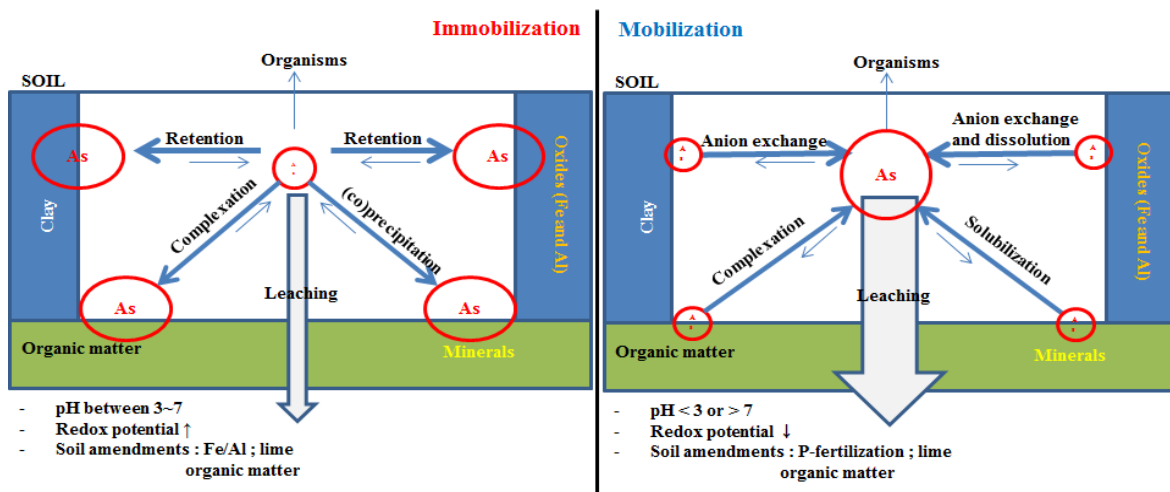
Soil-As interactions and strategies to manage As availability and mobility in soils. Asterisk denotes liming and organic matter application, which may cause either As fixation or release depending on the case (Jiménez, 2012).

Introduction

Arsenic (As) is an element belonging to the group V-A as a metalloid. Because arsenic more easily forms anions, its nonmetal properties dominate. When arsenic is in an oxidation state of +5, it acts similar to phosphorus, a fact that has many implications for the way in which it reacts in soil, as well as its potential toxicity. The most common oxidation states of As are -3, 0, +3, and +5. Arsines and metal arsines are those in which As has an oxidation state of -3, and these forms are very unstable under oxidizing conditions. Under aerobic conditions, the oxidation state of As tends to be +5, and when this occurs at a pH between 2 and 3, arsenic acid (H_3AsO_4) is formed. When the pH rises to values between 3 and 11, this compound disassociates to $H_2AsO_4^-$ and $HAsO_4^{2-}$ (Smedley and Kinninburgh, 2002). Under anaerobic conditions, the predominant As species is H_3AsO_3. Arsenic also biomethlyates easily (Barán, 1995).

Inorganic arsenic is present in soil, water, air, and food such that humans are constantly exposed to this contaminant (Mandal and Suzuki, 2002). The range at which arsenic is present in soils varies normally between 0.2 and 40 mg kg^{-1}, while in urban areas the concentration in atmospheric air is approximately 0.02 mg m^{-3}. On a global level, drinking contaminated water is the major source of exposure to this contaminant (Smedley and Kinninburgh, 2002). It is estimated that some 137 million people are exposed to waters contaminated with arsenic, a quarter of them showing symptoms associated with long-term exposure in at least five South Asian countries: Bangladesh, India, Nepal, Tailandia, and Myanmar (Caussy, 2003). The World Health Organization (WHO) recommends a maximum level of arsenic in waters of 10 mg L^{-1} (Bissen and Frimmel, 2003) ; however, the concentration of arsenic in surface waters is greater than 2,000 mg L^{-1} in certain regions of Bangladesh and India (Tripathi et al., 2007). Soil and water are the main sources of human exposure to arsenic at any given location, either by consumption (Rodríguez et al., 2003), inhalation, or direct skin contact (DEFRA, 2002). Because arsenic accumulates in vegetables, fruits, and other plants that grow in contaminated soils, another important pathway of exposure is the transfer of arsenic within the food chain (Meharg and Hartley-Whitaker, 2002).

The chemistry of As in soils is the outcome of the equilibrium tendencies of several simultaneously or discretely interacting factors. Important factors effecting these interactions are soil solution chemistry, solid phase formation, adsorption and desorption, effect of redox conditions, biological transformations, volatilization, and cycling of As in soils (Muhammad, 1995).

The physics of arsenic

Metal elements are classified according to two important
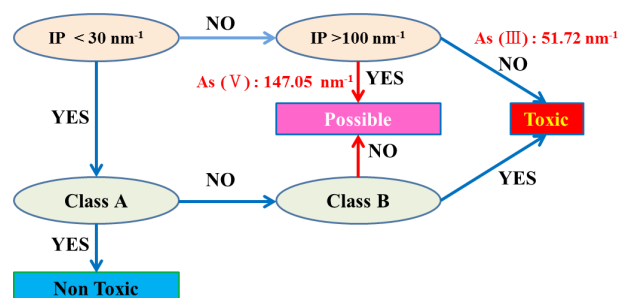
Fig. 1. Flow diagram for the toxicological classification of a metal cation at circumgenital pH using the criteria of ionic potential (IP) and Class A or B character.
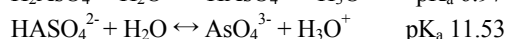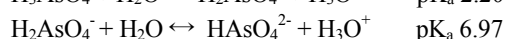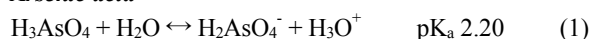
characteristics with respect to their biochemical behavior in soils and aquatic systems. The first of these is the ionic potential (IP), which is the valence of a metal cation divided by its ionic radius in nanometers. Metal cation with IP < 30 nm^{-1} tend to be found in circumneutral aqueous solutions as solvated chemical species (free cations); those with 30 < IP <100 nm^{-1} tend to hydrolyze readily in circumneutral waters; and those with IP > 100nm^{-1} tend to be found as oxyanions. Arsenic element has different valence states, it may fall into different classes: As^{3+} (IP = 51 nm^{-1}) hydrolyzes, whereas it has just been shown that As^{6+} (IP = 147 nm^{-1}) an oxyanion species in aqueous solution (Fig. 1). The second important characteristic of metal elements is their Class A or Class B behavior. A metal cation is Class A if (1) it has low polarizability (a measure of the ease with which the electrons in an ion can be drawn away from its nucleus) and (2) it tends to form stronger complexes with O- containing ligands than with N- or S- containing ligands. A metal is Class B if it has the opposite characteristics. If a metal is neither Class A nor Class B, it is termed borderline.

The chemistry of arsenic in soils

Inorganic As chemistry form in oxidized soil solutions Among the As species found in the soil environment, compounds of As(V) and As(Ⅲ) are the most important inorganic As species in the soil, because their compounds are highly soluble in water (Vaughan, 1993) and may change valency states depending on the pH (Masscheleyn *et al.*, 1991) and redox conditions (Marin *et al.*, 1993). The equilibria for arsenic acid (As V) and arsenous acid (AsⅢ) in aqueous solutions are given in Eq. 1 (O'Neill 1990, Smith 1998).

Arsenic acid

$$H_3AsO_4 + H_2O \leftrightarrow H_2AsO_4^- + H_3O^+ \qquad pK_a\ 2.20 \qquad (1)$$
$$H_2AsO_4^- + H_2O \leftrightarrow HAsO_4^{2-} + H_3O^+ \qquad pK_a\ 6.97$$
$$HASO_4^{2-} + H_2O \leftrightarrow AsO_4^{3-} + H_3O^+ \qquad pK_a\ 11.53$$

Arsenous acid

$$H_3AsO_3 + H_2O \leftrightarrow H_2AsO_3^- + H_3O^+ \qquad pK_a\ 9.22$$

$$H_2AsO_3^- + H_2O \leftrightarrow HAsO_3^{2-} + H_3O^+ \qquad pK_a\ 12.13$$
$$HAsO_3^{2-} + H_2O \leftrightarrow AsO_3^{3-} + H_3O^+ \qquad pK_a\ 13.4$$
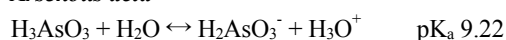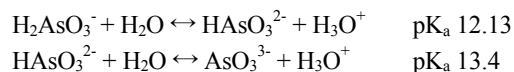
Geochemical systems are commonly interpreted in terms of their response to redox potential (Eh) and pH. The most thermodynamically stable species over the normal soil pH range 4-8 are H_3AsO_3, $HAsO_4^-$ and $HAsO_4^{2-}$(Smith 1998).
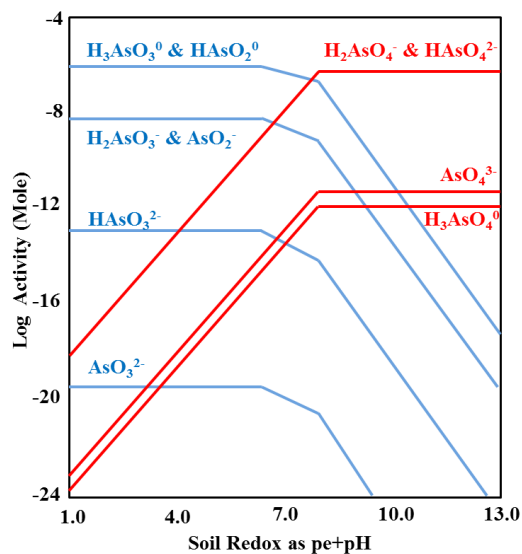
Organic complex of As in soil solution Organic matter is a chemically reactive component of all soils. Organic molecules generally carry a net negative charge in soil solutions. As chemistry form in a oxic as well as in an anoxic soil solutions are negatively charged oxyanions. Because of similarity in the nature of charges on both organic molecules and As chemical forms, As has demonstrated a limited affinity for organic complexation in soil. Comparing the chemical behavior of arsenate with that of phosphate in soils, Johnson and Hiltbold (1969) commented that one of the striking differences appears to be the inability of As to form organic complexes. It is probable that, within a soil organism, As may bind to organic molecules and be released to soil solution when its tissues are biodegraded. Arsenic has also been applied to several soils as organ arsenical biocides (Muhammad 1995).

Factors Determining Arsenic mobility in Soils

The effect of pH and Eh In contrast to what happens with other trace elements, a rise in pH often results in mobilization of arsenic in the soil. In general, a rise in soil pH causes a release of anions from within their exchange positions, such that arsenate and arsenite are released (Smith et al. 1999; Fitz and Wenzel 2002; Beesley et al. 2010b; Moreno-Jiménez et al. 2010a). However, several experiments (mainly with mine soils) have shown that high pH values, in the presence of sulfates and carbonates, can produce either a co-precipitation of arsenic in the subsequently formed oxyhydroxides and sulfates (García et al. 2009), or a precipitate such as calcium arsenate (which is slightly less insoluble than calcium phosphate) (Burriel et al. 1999). For this reason, some soils probably demonstrate their maximum As (V) retention at a pH near 10.5 (Goldberg and Glaubig 1988). In well-aerated alkaline soils, the solubility of As is limited by its precipitation as Ca or Fe arsenates (Xie and Naidu 2006). In soils with a high pH, carbonates can play an important role in the retention of arsenate (Zhang and Selim 2008). When the pH drops below 2.5, As (V) becomes completely protonated (Zhang and Selim 2008), rendering it less likely to be retained by soil particles.

As stated above, the distribution of As chemical forms in a solution is pH dependent, therefore, the soil solution pH was assumed to be 7 for this section (other pH values can also be

Fig. 2. Important inorganic chemical forms of As in soil solution.

assumed). The results of the thermodynamic calculations are plotted in Fig. 2. In an anoxic soil solution, i.e., pe+pH <6, the most abundant species of As are As (III), whereas, in an oxic soil solution (pe+pH > 10), As is mainly present as As (V) species. In suboxic soil solutions, i.e., pe+pH from 6 to 8, both As (III) and As (V) can be found in appreciable concentrations. Irrespective of redox conditions, arsenate species are distributed, in descending order (at pH 7), as; $HAsO_4^{2-} > H_2AsO_4^- > AsO_4^{3-} > H_3AsO_4^0$. The arsenite species, in descending order at pH 7, are distributed $HAsO_2^0 = H_3AsO_3^0 > AsO_2^- = H_2AsO_3^- > HAsO_4^{2-} > AsO_3^{3-}$.

The published literature differentiates total As concentrations into the two major groups As (III) and As (V) but not into individual chemical forms. To compare the results of the thermodynamic calculations and the experimental results, all As (III) and As (V) species were added together. These calculations partially supported the experimental results of Masscheleyn *et al.,* (1991) who investigated the influence of redox potential on As speciation in a contaminated soil. They showed that, at higher soil redox levels (pe+pH> 10), the major part of total As (65-98%) was present as As (V). With a decrease in the redox conditions, concentrations of As (III) species increased rapidly. Under the moderately reduced and reduced soil conditions (pe+pH<8), As (III) species were the most abundant form of As (Muhammad, 1997).

Under aerobic conditions, sulfides are easily oxidized, and as a consequence arsenic is released into the environment (Adriano 2001) ; when soil pH is between 3 and 13, the major species found are $H_2AsO_4^-$ and $HAsO_4^{2-}$ (Smedley and Kinninburgh 2002). In reducing environments, arsenic is found as arsenite, the predominant species of which is H_3AsO_3. Poor adsorption of As (III) results from its neutral character in soils (Lakshmipathiraj et al. 2006).

The Role of Fe, Al and Mn Oxides, and Oxyhydroxides
Soils frequently retain important quantities of Fe, Al and Mn oxides, and oxyhydroxides. The distribution of these solids in the soil depends on both the pH and Eh of the soils involved. Under reducing conditions, the structure of Fe and Mn hydroxides is broken, and arsenic that was fixed to the interior or to the surface of these compounds is released. The activity of arsenic in the soil solution is controlled by reactions of retention and release along the surfaces of Fe, Mn, and Al oxides and hydroxides (Livesey and Huang 1981; Fitz and Wenzel 2002; De Brouwere et al. 2004), and soils with a large quantity of iron had a greater retention capacity of both arsenate and arsenite (Manning and Goldberg 1997), arsenite being retained in lower quantities than arsenate (Fitz and Wenzel 2002). As (V) has a high affinity for the surfaces of iron oxides, where it forms inner-sphere complexes; however, As (V) can also be retained in external-sphere complexes (Waychunas et al. 1993; Cheng et al. 2008). The results of several studies have shown that As(III) can be adsorbed and oxidized along the surfaces of some Fe-oxyhydroxides, such as goethite and ferrihydrite, or those of Mn (such as birmesite; Lin and Puls 2000). In other studies, it was demonstrated that the adsorption of As (V) on goethite, magnetite, and hematite is reduced when the pH is raised (Manning and Goldberg 1997; Giménez et al. 2007). Giménez et al. (2007) found that hematite had the largest sorption capacity, followed by goethite and then magnetite. Arsenate has a high affinity for the surfaces of iron oxides, as phosphate; however, arsenate has a lower affinity for aluminum oxides than phosphate (Adriano 2001). Under reducing conditions, when a large portion of the Fe and Mn oxides have been reduced, gibbsite (which is more thermo-dynamically stable in anaerobic conditions) is able to absorb some of the As released by other oxides (Mello et al. 2006). The adsorption of arsenic onto oxides depends on the duration of the interaction between As and the oxide, the release of arsenic being more difficult as the interaction time increases (Gräfe and Sparks 2006).

The addition of Fe to the soil in several forms immobilizes As. For example, additions of Fe oxides, iron-rich soils (those reddish in color), inorganic Fe salts or industrial byproducts, rich in Fe, together with $CaCO_3$, have all been used to raise the quantity of soil oxides, which, in turn, immobilizes As (Hartley et al. 2004; Hartley and Lepp 2008; Vithanage et al. 2007).

The Effect of Clay Minerals In general, the availability of arsenic is greater in sandy than in clay soils (Adriano 2001), although the retention of As in clays is less efficient than with oxides (Gräfe and Sparks 2006). Again, As (III) adsorbs to clay minerals less intensely than does As (V). There are many factors involved in the soil adsorption and desorption processes that affect As mobility. Among these

factors is the structure of primary and secondary minerals to which As comes into contact. Another factor is the duration of interaction that exists between the clays of a soil and arsenic; the adsorption of As (V) and As (III) by clay minerals increases with time (Lin and Puls 2000). Zhang and Selim (2008) suggest that isomorphic substitutions of Fe by Al in clays contribute to the adsorption of As. The anionic character of arsenic suggests that the mechanism of clay adsorption of this metalloid may be similar to that of P, through calciumbridging mechanisms (Fixen and Grove 1990). Frost and Griffin (1977) reported that montmorillonite can adsorb more As (V) and As (III) than does kaolinite, and the difference is derived from the increased surface charge of montmorillonite. Lin and Puls (2000) found that halosite and chlorite clays had a greater capacity to adsorb As(V) than did other clay minerals, and that kaolinite and illite/montmorillonite, adsorb As (V) to a moderate degree. Arsenic is initially adsorbed on the clay surface, but with time, it is incorporated into the structure of the mineral. It was demonstrated that Californian soils having a greater percent of clay and appreciable quantities of Fe oxides had a greater As retention capacity (Manning and Goldberg 1997).

Interactions with Organic Matter   Organic matter is of a heterogeneous chemical nature and constitutes a series of organic compounds of variable molecular weights that are differentially polymerized. This soil fraction is dominated elementally by carbon, oxygen, hydrogen, nitrogen, and phosphorus (in this order) and commonly has the following functional groups: carboxyls, carbonyls, alcohols, and amines (Stevenson 1982). The level of polymerization of humic compounds and their molecular weights influence their solubility: as these compounds diminish in size, they have a greater proportion of functional groups (organic, fulvic, and humic acids) and display higher solubility. If more highly polymerized, humic compounds have fewer functional groups, e.g., humins, and will display lower water solubility. The effect organic matter has on trace elements depends on the qualitative composition of the organic matter. An organic fraction that has a large molecular weight will more effectively retain trace elements, whereas a more soluble and lighter fraction tends to dissolve elements, either by chelating (metals) or by displacing (anions) them. Depending on what the predominant compound in the soil is, either of these effects will be observed in the soil (Eduardo Moreno-Jiménez 2012).

How soil organic matter affects arsenic is inconsistent: in some studies, the application of organic matter reduced the mobility of arsenic (Gadepalle et al. 2007), whereas, in others As is released after the application of compost (or there is a higher correlation between soluble carbon and soluble arsenic in soils; Mench et al. 2003; Clemente et al. 2008). Weng et al. (2009) have recently studied how fulvic and humic acids in

solution are able to reduce the capacity for arsenate retention in goethite through electrostatic competition. Therefore, dissolved organic matter can compete with arsenate and arsenite for soil retention positions (Bernal et al. 2009). Alternatively, some humic acids may form humic-clay complexes that have the capacity to retain As (Saada et al. 2003). Therefore, the relationship between soil arsenic and organic matter is complex and depends on multiple factors that include: the ratio of soluble organic carbon present, and the fractions of insoluble and stable humus, and the concentrations of Fe, Al, and Mn present in the organic matter (Gräfe and Sparks 2006). One important consideration, when adding organic amendments to a soil, is that the bioavailable fraction of As may be high (Beesley and Dickinson 2010), despite the fact that the total concentration of As is usually <30 mg kg^{-1} (Adriano 2001).

Other Factors Large differences in various soil parameters may exist during the year, and hence, the availability of trace elements in soil may also be variable (Vanderlinden et al. 2006). These variations result from changes in soil physical properties (humidity, aeration, porosity, temperature, etc.), chemical changes (pH, appearance of precipitates, Eh, etc.), and biological changes (microbial activity, vegetation cover,

etc.). Depending on the concentration of As present and the humidity regime in the soil, precipitates of insoluble salts (e.g., Fe and Ca arsenates, or co-precipitates with jarosite, gypsum or calcite) can form (de Brouwere et al. 2004 ; Zhang and Selim 2008; Cheng et al. 2008; Kreidie et al. 2011).

Adsorption and desorption processes

As with many other contaminants, the concentration of As in the soil solution concentration is controlled both by soil physical and soil chemical properties that influence adsorption-desorption processes. Compared to the large volume of literature on metal adsorption by pure silicate and oxidic mineral systems, little information is available on As adsorption and transport in soils. Studies on pure systems suggest that **As** has a high affinity for oxidic surfaces, although reactivity of oxides may vary considerably, depending on pH, charge density, and soil solution composition. Soil texture (Wauchope, 1975; Frost and Griffin, 1977), nature of constituent minerals (Walsh *er al.,* 1977; Pierce and Moore, 1980), pH, and the nature of competing ions have all been shown to influence adsorption processes (Smith, 1998).

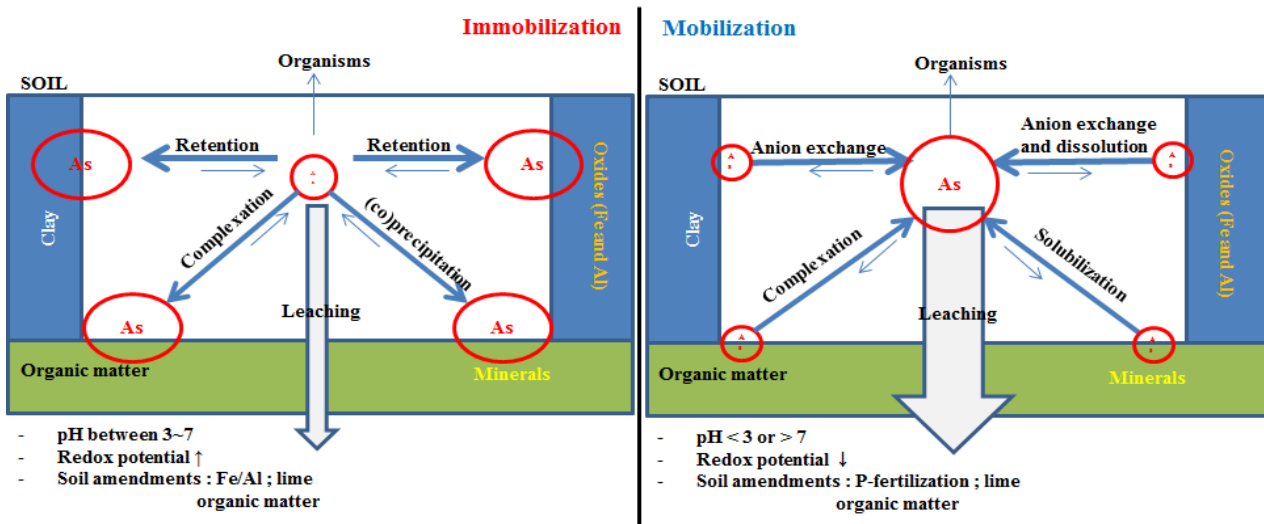Generally, clays particles are negatively charged silicates

Fig. 3. Soil-As interactions and strategies to manage As availability and mobility in soils. Asterisk denotes liming and organic matter application, which may cause either As fixation or release depending on the case (Jiménez, 2012).
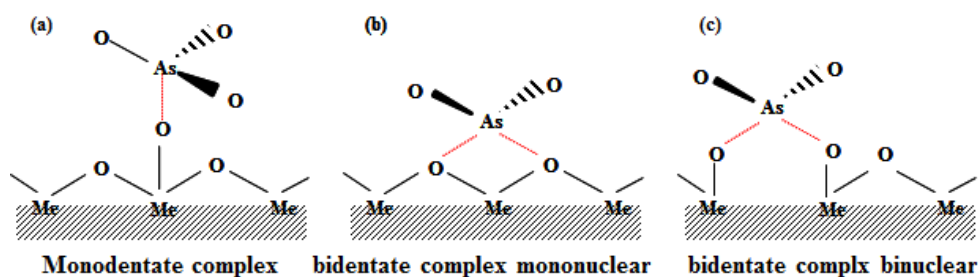

Fig. 4. Adsorption mechanisms of arsenate onto oxide minerals (Principle of soil chemistry, 2010).

minerals and, therefore, preferably adsorb positively charged ions, not As oxyanions, from soil solutions. However, it has been reported that sorption of As oxyanions from soil solution occurs by chemisorption or ligand exchange on clay surfaces, mainly by replacing or competing with phosphate (Frost and Griffin, 1977; Goldberg and Glaubig, 1988). Because of oxyanionic forms of As ions in soil solution and competition from phosphates, adsorption of As on clay surfaces is expected to be insignificant (Dickens and Hiltbold, 1967; Frost and Griffin, 1977; Huang, 1975; Pierce and Moore, 1980; Polemio *et al.,* 1982b). Contrary to the above, some investigators reported a significant correlation between clay content and As concentrations in the surface soil (Johnson and Hiltbold, 1969; Nightingale, 1987). pH dependent positive charge on clay surfaces may be responsible for the above association between As and clay. Several investigators (Greenland, 1975; Parks, 1967; Wada and Okamura, 1977) reported a wide pH range (4 to 8, with mean around 5.5) of isoelectric points for several clays. In acidic soils where positively charged clay particles exist, As adsorption could be observed (Muhammad, 1995).

Conclusions

Arsenic, a metalloid occurs naturally, being the 20th most abundant element in the earth's crust, and is a component of more than 245 minerals. These are mostly ores containing sulfide, along with copper, nickel, lead, cobalt, or other metals. Arsenic and its compounds are mobile in the environment. Weathering of rocks converts arsenic sulfides to arsenic trioxide, which enters the arsenic cycle as dust or by dissolution in rain, rivers, or groundwater.

Mobility on soil colloids is an important As scavenging mechanism. The adsorption capacity and behavior of these colloids (clay, oxides or hydroxides surfaces of Al, Fe and Mn, calcium carbonates, and organic matter) are dependent on ever-changing factors, such as hydration, soil pH, specific adsorption, changes in cation coordination, isomorphous replacement, crystallinity, etc. Because of the altering tendencies of soil colloids properties, adsorption of As has become a complex, empirical, ambiguous, and often a self-contradicting process in soils.

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