

Arsenic Adsorption on Iron Oxides in the Presence of Soluble Organic Carbon and the Influence of Arsenic on Radish and Lettuce Plant Development

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Arsenic Adsorption on Iron Oxides in the Presence of Soluble Organic Carbon and the Influence of Arsenic on Radish and Lettuce Plant Development

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(Abstracts)

Chapter 2:

Germination and Growth of Radish (*Raphanus sativus*) and Lettuce (*Lactuca sativus*) Exposed to Arsenite and Arsenate in Hydroponic Growth Solution

Little information is available on the survival, uptake, and dry mass production of vegetable seedlings and maturing plants in arsenic enriched environments. Such information is however very important to many vegetable growers in areas of subsistent agricultural like Bangladesh or home-gardeners in closer proximity of As sources such as metal smelters.

Accordingly we conducted research investigating (i) the germination and radical formation of radish and lettuce seeds at varying As (V) and As (III) concentrations and (ii) radish and lettuce plants in solution culture. Seed germination studies demonstrated that 0.1mM and 0.025mM are toxic threshold levels of As (III and V) for radishes and lettuce, respectively, while As (V) is more toxic to radish seeds than As (III). Arsenic (III and V) impacted both germination and radical development in radish seeds. For lettuce we observed that As had no impact on germination but reduced radical length significantly ($p < 0.01$). At most equimolar concentrations, As (III) was more toxic than As (V) in lettuce seeds (0.025 – 0.10mM As), a result contrary to those obtained in radish seeds (0.05 – 0.5mM As). The hydroponic growth studies showed that losses and increases in dry weight are a function of absorbed As and are dependent on the source of As: As (V) or As (III). Moreover, the effect of absorbed As (V) or As (III) on dry weight reductions and increases differed between root and shoot portions of the plants and are crop dependent. Tissue-As (originally solution As (V)) was more toxic at the radish root level and tissue-As (originally solution As (III)) was more toxic at the radish shoot level. Conversely for lettuce, As (III) caused reductions in dry weight, while As (V) had a stimulating effect on biomass production. Lower As (V) concentrations in plant tissue throughout the lettuce study and at low As (V) concentrations (0.02mM) in the radish study may be explained by the molar ratio of P:As of approximately 5. From a food nutrition safety standpoint, studies need to concentrate on sub-lethal levels in order to ensure the proper formation of the harvestable portion of the plant.

Chapter 3:

Adsorption of Arsenate (V) and Arsenite (III) on Goethite in the Presence and Absence of Soluble Organic Carbon

The environmental fate of arsenic is of utmost importance as the U.S. EPA has recently proposed to tighten the arsenic drinking water standard from 50 ppb to 5 ppb. In

natural systems the presence of dissolved organic carbon (DOC) may compete with As for adsorption to mineral surfaces, hence increasing its potential bioavailability. Accordingly, the adsorption of arsenate As (V) and As (III) on goethite (α -FeOOH) was investigated in the presence of either a peat humic acid (Hap), a Suwannee River Fulvic Acid (FA) (IHSS) or citric acid (CA). Adsorption edges and kinetic experiments were used to examine the effects of equimolar concentrations of organic adsorbates on arsenic adsorption. Adsorption envelopes were conducted over a pH range of 11 to 3, while the kinetic studies were conducted at pH 6.5 for As (V) and pH 5.0 for As (III). Arsenate adsorption was inhibited in the order of Hap > FA > CA while arsenite adsorption was inhibited in the order of CA > FA > Hap. Humic acid reduces As V adsorption starting at pH 9, with a maximum reduction at pH 6.5. Fulvic acid slightly inhibited As (V) adsorption starting at pH 5, and this inhibition increased with a decrease in pH. No effect was observed in the presence of CA. Arsenite adsorption is inhibited by HA starting a pH 7 and increases with a decrease in pH, while FA and CA reduce As (III) adsorption beginning at pH 8, with a continuous reduction as the pH decreases. The differential extent of As V adsorption in the presence of the organic acids suggests that the distribution and the respective densities of the abundant functional groups (phenol/ catechol OH or COO⁻) are significant in the adsorption of As (V). Furthermore, larger organic acids may hydrophobically partition to surfaces via a more favorable entropy driven reaction mechanism which may influence As (V) diffusion and its subsequent adsorption to surfaces. The decrease in As (III) adsorption is caused by its reduced affinity for the surface at pH values lower than 9, and the simultaneous increase in surface activity by the organic substances' via their COO⁻ functional groups. The results of these experiments suggests that dissolved organic carbon substances are capable of increasing the bioavailability of As in soil and water systems in which the dominant solid phase is a crystalline iron oxide.

Chapter 4:

Adsorption of Arsenate and Arsenite on Ferrihydrite in the Presence and Absence of Dissolved Organic Carbon (DOC)

The adsorption of As (V) and As (III) on synthetic 2-line ferrihydrite in the presence and absence of a peat humic acid (Hap), Suwannee River Fulvic Acid (FA) or citric acid (CA) was investigated. Previous work with goethite has demonstrated the ability of DOC materials to reduce As (V) and As (III) adsorption. In this study, a batch technique was used to examine the adsorption of arsenic (III and V) and DOCs on ferrihydrite in the pH range from 3 to 11. The results obtained demonstrated that As (V) adsorption on ferrihydrite was reduced only in the presence of CA. Arsenate reduced the adsorption of all organic acids except Hap. Both FA and CA reduced As (III) adsorption on ferrihydrite, while Hap had no effect. Fulvic and citric acid adsorption on ferrihydrite was reduced in the presence of As (III), however, adsorption increases of FA and CA were observed at lower pH, which is consistent with a decrease in As(III) adsorption. The peat humic acid had no effect on As (III) adsorption, and we believe that the adsorption process of Hap and As (III and V) on ferrihydrite are independent of each other. The observed differences between this study and the study on goethite are believed to be an intricate function of ferrihydrite's surface characteristics, which affects the mechanisms

of surface adsorption and hence the affinity of organic acids such as Hap, FA, and CA for the ferrihydrite surface. As such, the adsorption of DOCs to ferrihydrite are assumed to be energetically less favorable and to occur with a fewer number of ligands, resulting in lower surface coverage of weaker bond strength. Additional factors for the observed differences are discussed. This work demonstrates the importance of the solid phase in adsorption processes and functional group composition, as noticeable differences are observed in comparison to a crystalline Fe-oxide solid phase.

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Chapter 1

Introduction

The twentieth century is characterized by humankind's enormous achievements in the scientific and technological arena. Within one hundred years, humankind has invented the automobile, has learned how to fly, has extracted natural resources in greater and more efficient ways, and has improved agricultural productivity and efficiency, among many other achievements. Over the course of one hundred years, humankind has also established a legacy for these achievements: the ecological and environmental deterioration of our biosphere. As a consequence, environmental science has been growing and gaining increased importance.

Environmental science quickly branched off into several sub-categories, which are inclusive of older and more established scientific fields like biology, chemistry, physics, and geology. One of the sub-categories is soil chemistry. Coupled with the fields of chemistry, physics, biology, and geology, soil chemistry explored initially issues of concern to agriculture. With the onset of environmental pollution caused by all economies (rural and urban), the focus has shifted to a broader scope, in which the thermodynamics and kinetics of soil systems and their integral components are being investigated. This approach to learning is manifested in the methodologies employed by the *Bauhaus*, and is accepted to be a teaching method designed and practiced by the late Walter Gropius. Gropius, a first world-war officer in the German army, believed like few others of his time (e.g.: Herman Lietz) that the learning experience and the progress of understanding were inherently connected to the researcher's ability and understanding of studying the individual components of any one system in a hands-on fashion. It is in this manner that soil chemistry is and needs to be approached, if present and future toxic materials in soil-plant systems are to be understood.

One such pollutant of great environmental concern is arsenic. Arsenic contamination of the environment has primarily been caused by the use of lead-arsenate pesticides and erosion and leaching of exposed mine sites. Arsenic's translocation into waterbodies is the primary cause for the infection of humans and animals, known as arsenicosis (www.who.org). Dr. Mohammad A.K. Azad from the Department of Nutrition and Chemistry of the National Institute of Preventive & Social Medicine in Dhaka Bangladesh, summarizes the health issues concerning as follows: As little as 125mg of As is lethal to human beings when ingested. Arsenic is four times as poisonous as mercury, and may cause acute, sub-acute, and chronic toxicity within human receptors depending on the amount and frequency of arsenic ingested. Almost all of the human body's organs are affected, while clinical symptoms may not show up until six months to two years after initial digestion. The organ systems most widely affected are the general skin area, the liver, nervous systems, cardiovascular system, hemopoietic system, respiratory system, and the endocrine system. The primary cause for contracting arsenicosis is the ingestion of water containing arsenic (www.who.org). Among many other countries (Argentina, Chile, India, Japan, USA, and more), Bangladesh is the most recent and possibly most vulnerable country affected by increased levels of arsenic in ground and drinking waters (www.who.org). The World Health Organization (WHO) estimates that there are approximately 70 million people at risk of contracting

arsenicoses. Sedimentation processes with arsenic laden soils began as early as 25 to 80 thousand years ago in the Quaternary era. These sedimentation processes created rocks and pockets high in arsenic content. Overutilization of ground water for agricultural and other purposes and an increased use of phosphate fertilizer are assumed to be the major reasons for the dissociation of arsenic from these rocks and pockets, subsequently causing the contamination of the groundwater. Bangladesh's geographic location places it below the river deltas of the Ganges, Brahmaputra, and Meghna rivers, totaling a catchment area for arsenic laden sediments of approximately 1.5 million square kilometers (www.who.org).

Arsenic (As) is a member of the Nitrogen Family with both metallic and non-metallic properties, and is a naturally occurring element in the earth's crust, air, and all living matter (Tamaki and Frankenberger, 1992). Man has introduced arsenic into the environment by different means and for different purposes. As a natural component of coal and ores, As is liberated in coal-burning power plants, and from mine tailings. Arsenic's chemical properties, i.e. its close chemical resemblance to phosphorus, and its biotoxicity, was made use of in various agriculturally applied pesticides and food additives for livestock. Redox potential and pH have marked effect on the arsenic species present in any one system, while the redox potential controls the oxidation states of arsenic, and pH affects the degree of protonation of the acidic forms of arsenic. Arsenic has variable oxidation states: As(-III), AsH₃(g), As (0), As(s), As(III), AsO₃³⁻, and As(V), AsO₄⁴⁻, (Tamaki and Frankenberger, 1992) (Wachaupe, 1983) (Massecheleyn *et al.*, 1991). The oxidation state of arsenic is largely influenced by its environment's redox potential and pH properties. Arsenate (As V) is found under oxidizing conditions with a pE range from +8 to -9 and a pH range from 1 to 14, however, arsenite (As III) is the prevalent form at pE values below and around zero (Wachaupe, 1983) (Tamaki and Frankenberger, 1992). Proton activity (H^+) in solution will determine the extent of protonation for As (V), As (III), and arsenite methylated species (MAA, cacodylic acid). High pH systems will favor deprotonated forms of arsenic, and low pH systems favor protonated forms of As (Tamaki and Frankenberger, 1992). Similar to phosphate, the solubility in solution of As (V) is controlled by iron (Fe) and aluminum (Al) levels at low pH and calcium (Ca) in alkaline conditions (Robins, 1980). For an excellent review of different As (V) – metal solubility, see Robin's work (1980).

Adsorption of As in soil environments is dependent on a number of factors. Oxidation state, local pH environment, the dominant solid phase, and other ions in the system limit the extent of As adsorption (Massecheleyn *et al.*, 1991). Arsenate as well as arsenite undergoes specific adsorption on variably charged surfaces in the form of ligand exchange (Fendorf, 1997; Grossl *et al.*, 1997). Oxyanions, behaving as acids in soil solution, undergo ligand exchange reactions on variably charged surfaces of Al -, Fe -, and Mn-oxides. Adsorption is maximized at or around the pK_{a1} of the exchanging acid. Hence the oxidation state of the arsenic species becomes important, because As (V) is a strong acid, while As (III) is weak acid (Jacobs *et al.*, 1970). Likewise the pH of the environment is important as it relates to the degree of protonation of the arsenic species as well as the surface functional groups, and may furthermore influence the oxidation state of arsenic at high pH and trace amounts of MnO₂ (Manning and Goldberg, 1997a). The specificity with which As (V) and As (III) bind to surface functional groups relates to the importance of specific surface area (SSA) and functional group density along such

surfaces. The point of zero charge (PZC) for a particular surface influences the adsorption of arsenic as well, as electrostatic repulsive forces can overcome some of the van der Waal's attractive forces and the specificity of the adsorption reaction. Arsenate and As (III) adsorption therefore at pH above the PZC will be lower than at pH below the PZC (Manning and Goldberg, 1996a; Manning and Goldberg, 1997a; Manning and Goldberg, 1997b; Xu *et al.*, 1988). Wachope, 1975, recorded an order of adsorptivity for various arsenic species and phosphate on Mississippi flood planes: phosphate < cacodylate < arsenate ~ methylarsonate [Wachope, 1975 #39]. Manning *et al.*, 1997, demonstrated arsenic affinity for different surfaces and reported increasing adsorption in the order of: montmorillonite > kaolonite > illite > amorphous alumina (Manning and Goldberg, 1996a).

Adsorption sites are however not reserved per se for arsenic species alone. Inorganic as well as organic ligands other than As (V) or As (III) undergo ligand exchange reactions as well, and will in many cases compete with arsenic for the same adsorption sites. This gives rise to the notion of competitive adsorption. The relevance to this competition is that ligands other than arsenic have the potential to increase the bioavailability of arsenic in soil systems. Among the inorganic ligands competing with As (V) or As (III) for adsorption sites are phosphate (PO_4^{3-}), molybdate (MoO_4^{2-}), selenate (Se (IV)), selenite (Se (III)), and to some extent sulfate (SO_4^{2-}) as well (Manning and Goldberg, 1996b; Melamed *et al.*, 1995; Xu *et al.*, 1988).

Organic substances such as the humic and fulvic acid fractions in soils as well as some of the more simple aliphatic acids (citric and oxalic acid) are known to interact with inorganic soil particles via a number of different mechanisms (electrostatic attraction, covalent bonding, ligand exchange, others) (Gu *et al.*, 1994; Kaiser *et al.*, 1996; Moore *et al.*, 1992; Parfitt *et al.*, 1977; Schulthess and Huang, 1991; Stevenson, 1994; Varadachari *et al.*, 1997). The large size of humic and fulvic acids (compared to the distinctively smaller oxyanions) and their large number of reactive surface functional groups allows them to physically block and occupy surface functional groups on variable charged surfaces. Hereby, carboxylic acid functional groups were identified to be the key structures for ligand exchange on oxide surfaces and minor role was attributed to acidic phenol groups. In addition, humic and fulvic acids are able to affect the aggregation of soil particles resulting in a decreased surface area and subsequently a decreased number of available surface sites for adsorption (Fontes *et al.*, 1992). Previous work has concentrated on the effects of soil organic matter, and its acids (humic, fulvic, aliphatic acids) on the sorption of PO_4^{3-} , and to a lesser extent on the adsorption of selenate and selenite, and other cationic species (Geelhoed *et al.*, 1998; Gerke, 1993; Sibanda and Young, 1986; Zuyi *et al.*, 2000). Sibanda and Young (1986) showed that phosphate adsorption was reduced by both fulvic and humic acids at pH 4 and 7, and more so at pH 4 (Sibanda and Young, 1986). Gerke (1993) investigated phosphate adsorption on poorly crystalline Fe-oxides over time, and noted reduced phosphate adsorption in the presence of humic substances, however to a greater extent at pH 7 (Gerke, 1993). Higher phosphate adsorption at pH 4 was explained by an inhibition of crystallization and organic complexing of Fe, which exhibits higher affinity for phosphate retention than Fe as Fe-oxides (Gerke, 1993). Geelhoed *et al.* (1998) investigated the effect of citrate on phosphate adsorption and noticed a strong reduction in citrate adsorption to goethite, while the adsorption of phosphate to goethite in the presence of citrate was only

undermined at pH less than 7 and mostly at pH around 5. The reduction of phosphate adsorption to goethite was explained by a reduced number of available binding sites on the surface occupied by the complexed citrate (Geelhoed *et al.*, 1998).

Almost no work has been conducted on the effects of organic ligands on the adsorption of arsenic species to variably charged surfaces. Xu *et al.*, 1988 are the only known researchers to have investigated the effect of organic ligands (fulvic acid) on the adsorption of As (V). These researchers noted a reduction of As (V) adsorption onto alumina in the pH range between 3 and 7.5.

A discussion of soil arsenic becomes relevant in the light of its effects upon plant life, as plants are the only known autotrophs, and constitute the major entrance into the animal and human food cycle. Arsenic research in the plant sector may be ordered into two broad categories: Research pertaining to tolerance towards arsenic, and research pertaining to the effects of arsenic on plant functioning.

The effect of arsenic on plants is dependent on a series of factors, mainly those which govern arsenic solubility in soils (thus the amount of arsenic not adsorbed or held by soil constituents), as well as the arsenic species (Wachaupe, 1983). Arsenite is considered to be more toxic than arsenate, which is more toxic than methylated species of arsenic (cacodylate and monosodium methanearsonate (MSMA)) (Carbonell-Barrachina *et al.*, 1997a; Jiang and B.R., 1993; Wachaupe, 1983). The toxic effects of arsenic are also plant specific. Different plants have different tolerance to arsenic. This has been established by many researchers (Carbonell-Barrachina *et al.*, 1994; Carbonell-Barrachina *et al.*, 1997b; Cox *et al.*, 1996; Fargasova, 1994; Jain and Gadre, 1995; Sheppard, 1992; Wachaupe, 1983), and many others. For various sensitivities of plants towards arsenic see Sheppard (1992) and Wachaupe (1983). Meharg *et al.* (1994) identified a arsenate tolerant phenotypes of velvetgrass (*Holcus lanatus* L.) whose arsenate tolerance was very much related to the nutritional status with respect to phosphate and its inherent ability to prefer phosphate at all times and conditions over arsenate (Meharg *et al.*, 1994). This information reveals that the uptake process of the arsenic species is critical in understanding and predicting plant responses to soil environments where arsenic is present.

Plant uptake of arsenic from arsenic contaminated soils is a four-step process with the ultimate step being the one of a toxic reaction in the plant (Wachaupe, 1983).

1) Arsenic is adsorbed to the root surface; 2) arsenic moves from the exterior to the interior of roots; 3) arsenic is translocated to some site of action; and 4) a toxic biochemical reaction occurs in the plant.

After arsenic has entered the plant, it is translocated throughout the plant freely; this is especially the case for arsenate. Translocation within the plant occurs both symplastically and appoplastically, with a common pathway being root → xylem → leaves → phloem (Wachaupe, 1983).

The differential toxicity and toxic effects of arsenate to plants determines the fate of arsenic in the plant. Arsenate, which is analogous to phosphate, is considered less phytotoxic than arsenite, which upon membrane contact has immediate destructive effects. This effect of arsenite is ascribed to its binding to sulfhydryl groups on root and other membranes, which effectively inhibits proper (root) membrane functioning. Hence, arsenite translocation in the plant is usually not observed as much. Arsenate, however, is

transported freely, and may substitute for phosphate in the plant's oxidative phosphorylation, where ATP is produced. The substitution of arsenate for phosphate results in the lack of ATP production, and the plant is effectively deprived of its source of energy. Arsenite is considered to be also an uncoupler of the oxidative phosphorylation responsible for the production of ATP (Carbonell-Barrachina *et al.*, 1997b). Arsenic distribution in plants follows the order of: roots > shoots > leaves > fruit, when the source of arsenic is in soils.

The extent and degree of a phytotoxic reaction in an arsenic environment are plant and arsenic species specific, while the concentration of arsenic in the growth medium has obvious effects upon the degree and extent of the phytotoxic reaction (Carbonell-Barrachina *et al.*, 1994; Carbonell-Barrachina *et al.*, 1997b; Cox *et al.*, 1996; Fargasova, 1994; Jain and Gadre, 1995; Sheppard, 1992; Wachaupe, 1983). Emphasis in research has been put on the effects of arsenate and arsenite on macro- and micronutrient uptake (Carbonell-Barrachina *et al.*, 1994; Carbonell-Barrachina *et al.*, 1997b) and especially on the role of phosphate towards arsenate toxicity (Cox *et al.*, 1996; Meharg *et al.*, 1994; Rumburg *et al.*, 1960). In the case of phosphate, these authors noted detoxification effects of phosphate when plants were subjected to As (V). The effect of As (III) on plant nutrient uptake is remarkable to the effect that As (III) will destroy proper root functioning and hence unrestricted nutrient uptake. In the case of micronutrients, Carbonell-Barrachina *et al.* (1994) showed that the effects of arsenite contamination of tomatoes caused a reduction in the absorption and accumulation of boron (B), copper (Cu), manganese (Mn), and zinc (Zn), while absorption of iron (Fe) increased (Carbonell-Barrachina *et al.*, 1994). Decreased absorption as well as translocation to aerial parts was ascribed to the structural damage caused by the modus operandi of As (III). The same authors investigated the effects of As (III) on the absorption and accumulation of certain macronutrients again in tomato plants: calcium (Ca), potassium (K), magnesium (Mg), nitrogen (N), and phosphorous (P) (Carbonell-Barrachina *et al.*, 1998). As (III) levels lowered vegetative growth and fruit yield and diminished dry and fresh weights of tomato plants. A reduction of root P, Ca, and Na was observed, while root N and K increased. Foliar concentrations of Ca, K, and P were reduced below deficiency thresholds, but were deemed not important enough to explain the effects of As (III) as a simple nutritional disorder (Carbonell-Barrachina *et al.*, 1998).

While differences amongst plant species have been noted in reference to the extent and type of arsenic applications, growth media, as well as the effects of arsenic on the nutritional status of certain plants, there remains little understanding on the effects of basic physiological differences amongst plants, and how these could influence the uptake of arsenic species. For root applied arsenic, the total root area, but also the total root mass may have decisive influence on the absorption and accumulation of arsenic in above and below ground parts of the plants and may give further insights into tolerance levels and mechanisms.

In light of current and past research findings pertaining to the subject of arsenic in the environment, we believe that research is necessary which provides insight into: (i) the role of dissolved organic carbon substances on the adsorption of arsenate as well as arsenite on crystalline and non-crystalline inorganic phases, (ii) and the accumulation and

tolerance mechanisms/ levels for two physiologically different plant species, when subjected to varying concentrations of the respective arsenic species.

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Chapter 2

Germination and Growth of Radish (*Raphanus sativus*) and Lettuce (*Lactuca sativus*) Exposed to Arsenite and Arsenate in Hydroponic Growth Solution

Abstract. Little information is available on the survival, uptake, and dry mass production of vegetable seedlings and maturing plants in arsenic enriched environments. Such information is however very important to many vegetable growers in areas of subsistent agricultural like Bangladesh or home-gardeners in closer proximity of As sources such as metal smelters.

Accordingly we conducted research investigating (i) the germination and radical formation of radish and lettuce seeds at varying As (V) and As (III) concentrations and (ii) radish and lettuce plants in solution culture. Seed germination studies demonstrated that 0.1mM and 0.025mM are toxic threshold levels of As (III and V) for radishes and lettuce, respectively, while As (V) is more toxic to radish seeds than As (III). Arsenic (III and V) impacted both germination and radical development in radish seeds. For lettuce we observed that As had no impact on germination but reduced radical length significantly ($p < 0.01$). At most equimolar concentrations, As (III) was more toxic than As (V) in lettuce seeds (0.025 – 0.10mM As), a result contrary to those obtained in radish seeds (0.05 – 0.5mM As). The hydroponic growth studies showed that losses and increases in dry weight are a function of absorbed As and are dependent on the source of As: As (V) or As (III). Moreover, the effect of absorbed As (V) or As (III) on dry weight reductions and increases differed between root and shoot portions of the plants and are crop dependent. Tissue-As (originally solution As (V)) was more toxic at the radish root level and tissue-As (originally solution As (III)) was more toxic at the radish shoot level. Conversely for lettuce, As (III) caused reductions in dry weight, while As (V) had a stimulating effect on biomass production. Lower As (V) concentrations in plant tissue throughout the lettuce study and at low As (V) concentrations (0.02mM) in the radish study may be explained by the molar ratio of P:As of approximately 5. From a food nutrition safety standpoint, studies need to concentrate on sub-lethal levels in order to ensure the proper formation of the harvestable portion of the plant.

Introduction

High levels of arsenic (As) have been reported in areas where arsenicals have been used as pesticides, herbicides, and fungicides (such as in orchards and vineyards) and in areas of mining (Bowell, 1994; Carbonell-Barrachina *et al.*, 1997a; Tamaki and Frankenberger, 1992). Until 1968, As was praised for its efficacy as a pesticide, however, its toxicity and appearance in the human food chain have stirred political and public concern (Walsh and Keeney, 1975). In soil environments, As exists in the +3 or +5 valance state as the oxyanions, arsenite (AsO_3^{3-}) and arsenate (AsO_4^{3-}), respectively. Their occurrence relative to one another is a function of pH and electrochemical potential (Eh) (Massecheleyn *et al.*, 1991). Typically, As (V) is present under aerobic conditions, while As (III) is the predominant form under waterlogged (anaerobic) conditions. The bioavailability of either form of As in natural waters is regulated by their sorption onto soil colloidal surfaces. Both As (V) and As (III) bind via ligand exchange mechanisms to variably charged surfaces of aluminum and iron oxides, which is dependent on pH. For

example, sorption of AsO_4^{3-} on the iron oxide goethite tends to decrease with increasing pH. Adsorption to these surfaces is mostly favored at or around the pK_{a1} of the oxy-acid, and may be reduced by competing ligands such as phosphate (Fendorf, 1997; Grossl *et al.*, 1997; Jacobs *et al.*, 1970). Generally, arsenate binds more strongly to soil constituent surfaces than arsenite and consequently arsenate is considered to be less mobile than arsenite. Additionally, high levels of iron (Fe), Al (Al), calcium (Ca) as well as other metals may influence the solubility of As (Robins, 1980). Thus, the availability of As to plants is influenced by the chemical conditions immediately surrounding roots (rhizosphere).

Plant uptake of As from contaminated soil involves the following four-steps, that ultimately results in phytotoxicity: 1) As is adsorbed to root surfaces; 2) As moves from the exterior to the interior of roots; 3) As is translocated to some site of action, and 4) a toxic biochemical reaction occurs in the plant (Wachope, 1983). Arsenic phytotoxicity is caused by the disruption of several metabolic processes, including photosynthesis, respiration, growth regulation, and reproduction. In roots, anions are strongly adsorbed to root surfaces (arsenate > arsenite), after which a metabolically driven and selective transfer to the symplasm and transport vessels occurs (Wachope, 1983). After As (especially arsenate) has entered the plant, it is freely translocated throughout the plant. Translocation within the plant occurs both symplastically and appoplastically, with a common pathway being from root to xylem, xylem to leaves, and leaves to phloem (Wachaupe, 1983). When arsenite is taken up by tomato and bean plants, As concentrations in plant tissues are significantly correlated to increasing As (III) treatment levels and most As accumulates in the root, followed by lesser amounts in stems, leaves, and finally fruit (Carbonell-Barrachina *et al.*, 1997).

Arsenate, which is analogous to phosphate, is considered less phytotoxic than arsenite. Arsenite, by binding to sulfhydryl groups, destroys radicular root membranes upon contact, hence, arsenite translocation in the plant is limited. However, arsenite's destructive effects on root membranes have significant impact on macro- and micronutrient uptake, and water uptake (Carbonell-Barrachina *et al.*, 1997a; Carbonell-Barrachina *et al.*, 1998; Carbonell-Barrachina *et al.*, 1994). Conversely, arsenate is transported freely throughout plants and may substitute for phosphate during oxidative phosphorylation. Substitution of arsenate for phosphate restricts ATP production and the plant is effectively deprived of its source of energy. Additionally, As (V) inhibits the enzyme activity and production of chlorophyllase and other photosynthesis related enzymes (Jain and Gadre, 1995; Jiang and B.R., 1993). Arsenite is also considered to be an uncoupler of the oxidative phosphorylation responsible for the production of ATP (Carbonell-Barrachina *et al.*, 1997b).

Overall, plants growing on As laden soils distribute As in the following order: roots > shoots > leaves > fruit. Adequate P fertilization of velvetgrass (*Holcus lanatus* L.) has been shown to significantly inhibit the influx of As in both As tolerant and non-tolerant strains of velvetgrass (Meharg *et al.*, 1994). This suggests that As is taken up similar to phosphate and root surface area must be considered since phosphate uptake has been closely related to root length, total root surface area and the associated number of uptake sites for phosphate. Furthermore it is important to establish how arsenic influences seed germination and radical development. Sensitivity of plants to arsenic has been summarized by Wachaupe (1983), but there is little information on the sensitivity of

edible crops such as radish and lettuce, which also represent two crops with noticeably different root systems (Wachope, 1983). For experimental purposes, radish and lettuce are well-suited edible crops for evaluating As germination, uptake and phytotoxicity, since their maturation period is approximately 30 days. The objectives of this research were twofold. One was to determine As toxicity, added as either arsenate or arsenite, to seed germination of lettuce and radishes, and two, to determine the uptake and partitioning of either arsenate or arsenite in radish and lettuce plants when exposed to varying levels of As. The information gleaned from these experiments will help determine what levels of As restrict germination of these edible crops and provide information on As phytotoxicity as well as determine how much As might ultimately be available to consumers.

Materials and Methods

Seed Germination Studies

This study examined radish (*Raphanus sativus*), *Cherry Belle*, and lettuce (*Lactuca sativus*) (vigor pak: Waldman's Green Lettuce) seed germination when exposed to increasing levels of arsenate and arsenite. Experiments were conducted in Petri Dishes (*Falcon*TM) lined with WhatmanTM 42 filter paper that were cut to size. Prior to seed addition, 5ml of either double deionized water (control) or arsenite or arsenate treatment solutions were added to the petri dishes. Arsenite and arsenate treatment solutions consisted of 0, 1.0, 0.5, 0.1, 0.05, and 0.025mM As. Each treatment was replicated three times in a completely randomized experimental design. Lettuce experiments were modified relative to radish experiments, where only 3ml of treatment solutions were added to each dish and the As treatment concentrations were reduced to only 0.1, 0.05, and 0.025mM As, since results from an earlier radish study revealed that the upper As concentrations were too high. Stock solutions for arsenate and arsenite were prepared in double deionized water from Na₂HAsO₃ and Na₂HAsO₄ and the pH of both stock solutions was brought to pH 5.5 using 0.1 M HNO₃. For both radish and lettuce experiments, 10 seeds were randomly placed into each petri dish, which was subsequently sealed with parafilm and placed in the dark for a minimum of 72 hours, but no more than 80 hours.

The germination test for lettuce seeds was repeated in light with concentrations of 0.1, 0.05, 0.025, 0.0125, and 0.01 mM As. This was necessary because germination was below 60% for lettuce in the control and virtually absent in all treatment levels. Treatments were evaluated for percent germination and average radical length. Statistical analysis of variance and trends for treatment effects on percent germination and radical length was performed using Statistical Analysis Software (v.6.12) (SAS Institute, 1997/1998). Mean radical lengths were compared using Waller-Duncan's multiple range test ($p < 0.05$).

Hydroponic Growth Studies

Radish (*Raphanus sativus*), *Cherry Belle* and lettuce (*Lactuca sativus*) (vigor pak: Waldman's Green Lettuce) seeds were germinated in a moist paper towel with a sheet of linen placed between seeds and paper towel to avoid root damage during transplanting. The paper towel and seed assembly was folded and rolled, and placed into a 1000 mL Pyrex glass beaker that contained 100mL of half strength nutrient starter solution. The

beaker was covered with aluminum foil perforated with two to three holes that allowed for proper gas exchange. Seedlings were transplanted after four to five days, depending on radical length and cotyledon development.

Each seedling was placed in a 2 L brown Nalgene™ bottle with roots suspended from the mouth of the bottle by a Styrofoam disc. The bottles were filled to the bottom of the disc with a starter nutrient solution (Table 1). An aeration tube was inserted into each bottle and the bottles were placed in a controlled environment growth chamber at 21 C receiving 12 h of light per day at a PPF of 400 $\mu\text{mol m}^{-2} \text{s}^{-1}$. All plants were allowed to acclimate in nutrient solutions for 5 d prior to initiation of As treatments. The As treatments consisted of 0, 0.02, 0.1, and 0.5 mM of either As (III) or As (V). The pH, EC, E_h and dissolved oxygen content were monitored daily using hand held portable meters. Every two days pH was adjusted to 5.5 with 0.1 M HNO_3 and nutrient refill solutions were applied and the amounts recorded.

Treatments were arranged in a completely randomized factorial design with each treatment run in triplicate.

Table 1. Elemental distribution and concentrations of starter and refill nutrient solutions used for radishes and lettuce.

Salt	Starter Solution Concentration	Refill Solution Concentration
$\text{Ca}(\text{NO}_3)_2$	1mM	1mM
$\text{K}(\text{NO}_3)_2$	1mM	4mM
KH_2PO_4	0.5mM	0.5mM
MgSO_4	0.5mM	0.5mM
K_2SiO_3	0.1mM	0.1mM
FeCl_3	10 μM	2.5 μM
FeCl_3 & HEDTA	25 μM	5 μM
MnCl_2	3 μM	6 μM
ZnSO_4	4 μM	2 μM
H_3BO_3	2 μM	1 μM
CuCl_2	2 μM	2 μM
Na_2MoO_4	0.09 μM	0.03 μM

Analysis

After a 30 day growth period, radishes and lettuces were harvested. Radishes having received 0.1mM As (III) treatments were harvested 72hrs after As addition to avoid loss of biomass due to rot. Hence dry weights reported are a function of arsenic impact only, but not the additional effects decay. Plant roots were washed with copious amounts of doubly deionized water before being separated from stem and leaves. Plants were divided into two distinctive parts. One, above ground parts consisting of leaves, and green/ photosynthetic stems and two, below ground parts consisting of total roots including the radish bulb. Separated plant parts were oven dried at 60°C and dry matter production was recorded before digestion. E_h , pH, EC, and DO levels were recorded and 10 ml nutrient

solutions from each bottle were sampled and submitted for elemental analysis at the end of the growth period.

Dry plant parts were ground and placed into previously acid-washed 125 ml Erlenmeyer flasks, treated with 8 ml concentrated (15.8N) nitric acid, capped with plastic funnels, and allowed to stand overnight. The suspensions were heated for one hour at 120°C and allowed to cool. Appropriate amounts of 30% H₂O₂ were added to each digest, heated for 30 min at 120°C, and allowed to cool down and repeated two more times to insure complete digestion. After the final cooling period, 50 ml of doubly deionized water (DDI) were added to the contents of each flask and mixed well. A sub-aliquot was taken and diluted with DDI to 25 ml using previously acid-washed 25 ml volumetric flasks. The diluted digests were analyzed for total elemental content by Inductively Coupled Plasma spectrometry from Jarrel-Ash[®].

Statistical analysis of variance and trends for treatment effects on dry weight, and As content in above and below ground parts were performed using Statistical Analysis Software (v.6.12) (SAS Institute, 1997/1998). Means were compared using the Waller-Duncan multiple range test (kratio = 100, p < 0.05).

Results & Discussion

Seed Germination Studies

Radish

The effects of As (V) and As (III) on germination and radical length are graphically summarized in Figures 1A and 1B2. An inverse, linear relationship between As concentration and percent germination or radical length is observed. Arsenic concentrations of and exceeding 0.1mM significantly reduced percent germination and produced significantly shorter radicals. Below 0.10mM As, percent germination was not significantly different from the control, but radicals were significantly longer than the control, in which case As appears to have had a stimulating effect on radical growth. For equimolar concentrations of As at and above 0.1mM, As (V) inhibited germination more than As (III), and for equimolar concentrations of As at and above 0.05mM, As (V) produced shorter radicals than As (III), however, none of these observations were significantly different.

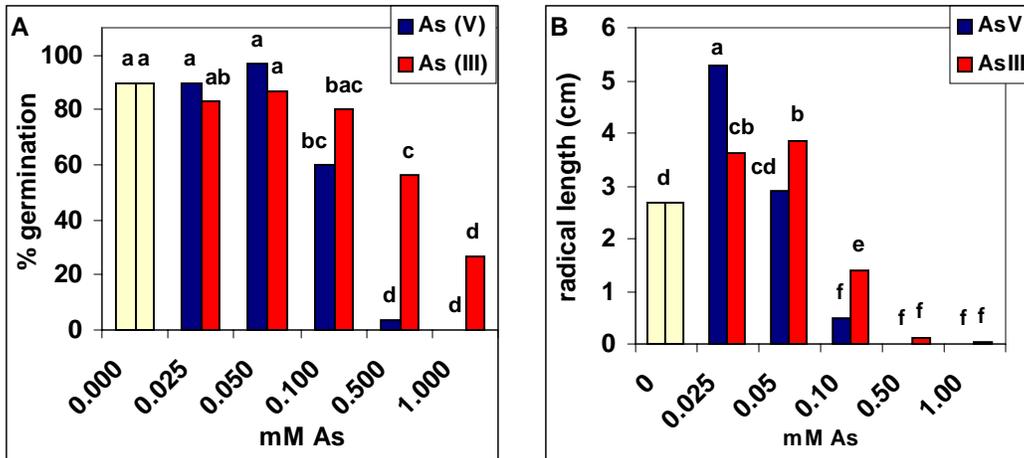


Figure 1: (A) Percent germination of radish seeds as a function of applied As concentration, and (B) Radical length of radish seeds in the presence and absence of As (V) and As (III). Numbers with the same letter denotation per graph are not significantly different for Waller-Duncan’s Multiple Range Test (kratio = 100, $p < 0.05$).

Hence, an As level of 0.1mM causes significant decreases in germination and radical development of radish seeds. Arsenate causes a more toxic response than As (III). This stands in contrast to accepted literature results, where As (III) has been recognized to be more toxic than As (V) (Wachope, 1983), (Sachs and Michael, 1973). The observed difference may be explained from the differential sites of action for As (III) and As (V). Arsenate is a successful uncoupler of the oxidative phosphorylation, while As (III) binds irreversibly to sulphhydryl groups and undermines proper root functioning. Germinating seeds require large amounts of energy (ATP) during germination and obtain energy by burning stored carbohydrates. We propose that ATP production was significantly undermined in the presence of 0.1 to 1.0 mM As (V), resulting in a tissue energy deficit expressed in a significant reduction in the number of germinating seeds as well as their radical development.

The effect of As (III) on germination was not as great as its effect on radical formation. Arsenite disrupts root functioning by destroying sites of protein synthesis and by binding irreversibly to protein sulphhydryl groups (Wachope, 1983). Hence, As (III)’s ability to reduce radical formation and growth becomes most apparent after rupture of the seed coat, i.e. imbibition and concentrations of and exceeding 0.1mM As (III).

At concentrations below 0.1mM As, we recognized that the germination rate was unaffected by the presence of As and radical length significantly exceeded that of the control by greater or equal than 1cm. Enhanced root growth of lemon trees grown in solution culture at 1ppm As has been reported (Walsh and Keeney, 1975). In our experiments, a response to As concentrations below 0.1mM, appeared to result in increased radical growth. An increase in root length is a common response when part or the entire root is subjected to a sub-lethal stress.

Lettuce

Arsenic affected both germination and radical formation and length of lettuce seedlings (Figure 2A and 2B). Arsenic (III and V) significantly reduced radical formation and length for concentrations greater or equal to 0.0125mM As. For equimolar concentrations, we observed shorter radicals in the presence of As (III) than As (V), which stands in contrast to radish seed results. At very low As concentrations (0.01mM), radical length was not significantly different from that of the control. Despite statistical significance, the practical implications of As (V) effects on lettuce germination at 0.01, 0.05 and 0.1 mM As (V) are less serious in comparison to As effects on radish germination. Arsenic (III and V), however, significantly decreased radical development in lettuce seedlings as observed earlier in radishes. We observed a significantly greater effect of As (III) than As (V) on radical length. Perhaps, As (III) affected sulfhydryl groups and protein synthesis sites of the root, while As (V) substituted at the cellular level for phosphate in the ATP synthesis process. A second difference that we observed was the relative sensitivity of lettuce seeds to As concentrations. Radish seeds showed a threshold concentration of 0.1mM As, while lettuce seeds were 0.025mM As. Hence, lettuce seeds are four times more vulnerable to As than radish seeds.

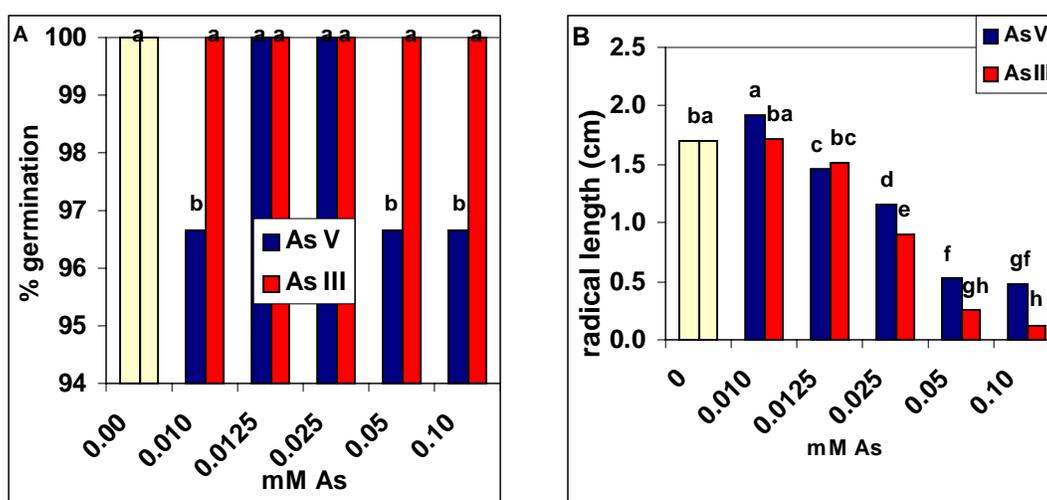


Figure 2: (A) % germination of lettuce seeds as a function of applied As concentration, and (B) Radical length of lettuce seeds as a function of applied As concentration. Numbers with the same letter denotation per graph are not significantly different for Waller-Duncan's Multiple Range Test (kratio = 100, $p < 0.05$).

At lower As (V) and As (III) concentrations, radical length of both radish (0.025 – 0.05mM) and lettuce (0.01mM) was greater than the control. Such a response may be attributed to a stimulant and/or stress effect at the radical (Walsh and Keeney, 1975). An alternative possibility may be removal of the seed coat in the presence of As. Removal of the seed coat in radishes has been shown to increase embryo exposure to oxygen and a subsequent increase in germination (Schopfer and Plachy, 1993; Stabell *et al.*, 1998).

From germination and radical length data, we surmise that radish seeds are more tolerant to higher As concentrations than lettuce seeds. One reason for this may be due to differences in seed size and thus the amount of stored energy available for imbibition and radical formation. A comparatively smaller lettuce seed is ultimately more dependent on the supply of energy and nutrients from its surrounding environment than larger more “energy rich” seeds.

Hydroponic Growth Studies

Radish

Arsenic treatment levels were chosen to be 0.50, 0.10, and 0.02mM As on the basis of results obtained from the previous seed germination study. Arsenate and As (III) linearly reduced root dry matter production by 54 to 86%, which was significantly different from dry weights of the control (Figure 3A). No significant differences were observed among treatments ($p < 0.05$). Radish bulbs were absent or severely deformed at all As concentrations exceeding 0.10mM. At 0.10mM As and above, radish roots were stunted and thin, with intermediate to strong discoloration (brownish – black). In the region of bulb formation, some filling could be noticed, however, in most cases, this region was rather elongated and also discolored.

Dry weight reductions and appearance of radish roots could be correlated to solution and tissue As levels, where arsenic uptake into radish roots increased with increasing As solution concentration (Figure 3B and 3C). Arsenite concentrations in radish roots were greater than As (V) concentrations at 0.02 and 0.10mM As, and approximately even at 0.50mM As. The maximum As uptake was 1560 ppm As at 0.50mM As (V) versus a minimum uptake of 92 ppm As at 0.02mM As (V). At 0.02mM As, significantly more tissue As (900 ppm As) was recorded for the As (III) than the As (V) treatment. Dry weights of radish roots could be correlated to concentrations of As in root tissue, and we observe an exponential dry weight reduction for plants, which absorbed As (V). Approximately 90 ppm As (V) caused a dry weight reduction of more than 50%, beyond which there was no significant reduction in dry weights. Conversely, As (III) concentration in root tissue was associated with a linear decrease in dry weight, and it required approximately 900 ppm As (III) to cause a similar dry weight loss of 50% (Figure 3C).

Dry weights of above ground radish tissue (shoot) decreased linearly with increasing As solution concentration (Figure 4A). Except for the 0.02mM As (V) level, all weight reductions were significantly different from the control and ranged from 46 to 62%. Radish leaves and stems showed signs of stunting, leaf curling, and necrosis, which increased in severity with increasing As concentrations. Radish leaves in the 0.50mM As (III) treatment were severely wilted after 24 hours and were harvested 72 hours after As (III) application in order to avoid any biomass loss due to decay.

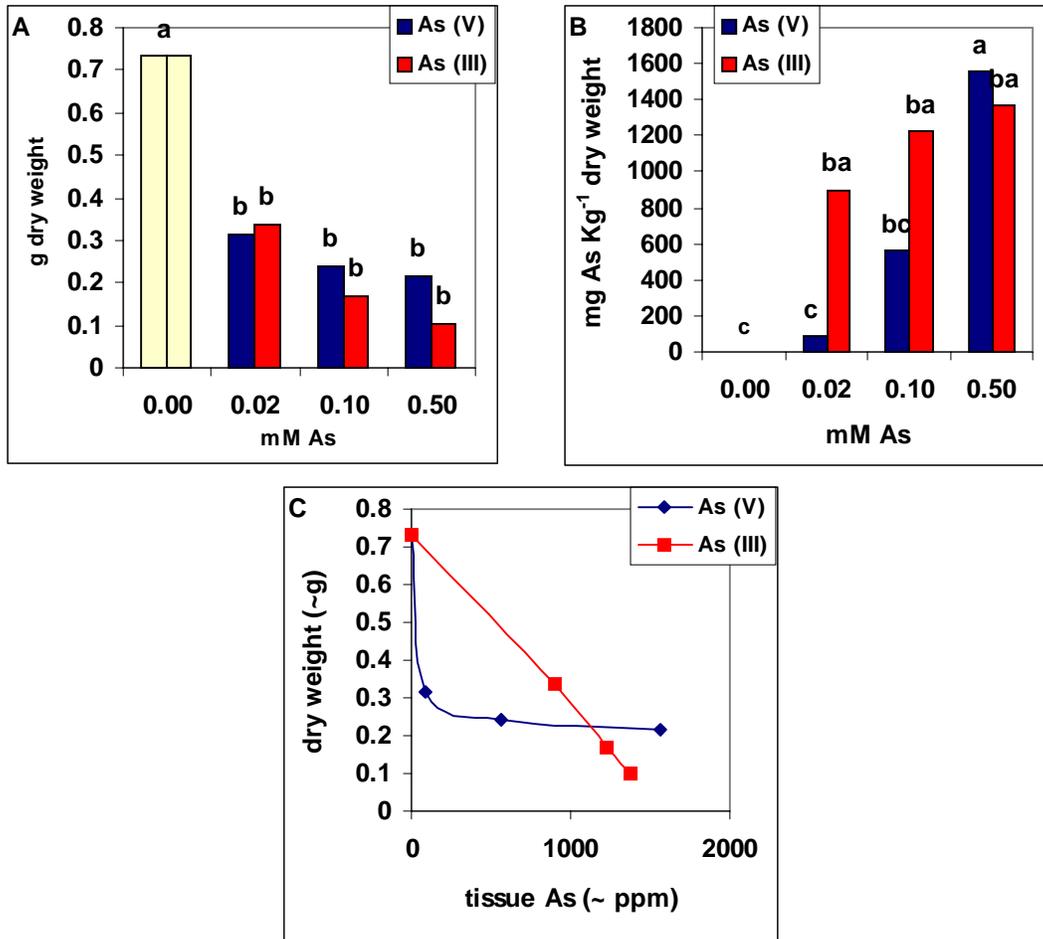


Figure 3: Below ground response of radish plants to As treatments; (A) dry weight (~g) as a function of solution As (~ mM), (B) As tissue concentration (mg As kg⁻¹ dry weight ~ ppm), and (C) dry weight (~ g) as a function of tissue As (~ ppm). Bars with the same letter denomination per graph, respectively, are not significantly different according to Waller-Duncan's Multiple Range Test (kratio =100, p < 0.05).

Dry weight reduction and appearance of radish shoots could be correlated to As uptake into shoot tissue of radishes, where tissue As concentrations increased with increasing As solution concentrations (Figure 4B and 4C). Arsenate uptake appeared linear with increasing As solution concentration, with significantly different tissue-As values occurring only between the highest and the lowest As (V) application. Arsenite uptake was exponential with increasing As concentrations in solution, and tissue-As values were significantly greater at the highest As (III) application than those levels recorded for lower As solution levels (Figure 4B). At the highest As application, there was significantly more As taken up from As (III) solutions than from As (V) solutions. The maximum amount of As taken up was 808 ppm As at 0.50mM As (III) versus 6 ppm As at 0.02mM As (V). Radish shoot dry weights could again be correlated to concentrations in shoots. Approximately 60 ppm As in the shoot caused a dry weight loss of more than 50%. Conversely, As (V) caused a similar drop in dry weight only after the

plant had adsorbed 400 ppm As (V). Tissue concentrations reported in this study are similar to those summary reported by Sheppard (1992) and Wachope (1983). However, canola was shown to respond differently to applied As (V) concentrations when grown in soil or solution culture (Cox *et al.*, 1996).

In our study with radish, a single addition of either As (V) or As (III) was made, which was based on results of a previously conducted seed germination study. At the end of the 30 day growing period, our results demonstrate that radish roots will absorb more As (III) than As (V) (Figure 5B). This stands in good agreement with the site of action for As (III) (Wachope, 1983). Arsenite binds irreversibly to sulfhydryl groups as well as tertiary and quaternary protein synthesis sites in roots. Therefore, As (III) accumulates at the root, rather than translocating throughout the plant as As (V) does (Carbonell-Barrachina *et al.*, 1995; Sachs and Michael, 1973). When substantial amounts As (III) appear in the shoots of plants, it is likely due to cellular death at the root level and an uncontrolled influx of water and As (III) into the plant. From our data, we believe that such a situation had occurred in the 0.50mM As (III) treatment and was occurring in the 0.10mM As (III) treatment as well. We observed strong root discoloration and a visually apparent loss of turgor (Figure 8). Figure 4B shows the substantial increase of shoot tissue As from 0.10 to 0.50mM solution As (III) concentration. The high uptake capability of radish roots for As (III) suggests that radish roots are capable of effectively sequestering As (III) in root tissue at low As (III) solution concentrations. At higher solution concentrations, cellular death at the root level appears largely responsible for the overall death of the entire plant.

Low As (V) absorption by radish roots may be the result of strong competition by phosphate at root uptake sites. Phosphate has been shown to reduce As (V) accumulation in velvetgrass (*Holcus lanatus* L.) by out-competing As (V) for high P/As (V) affinity uptake sites (Meharg *et al.*, 1994). Similarly, high phosphate concentrations were believed to remedy the effects of As (V) in canola grown in soil and hydroponic growth media (Cox *et al.*, 1996).

Our results also demonstrate that a loss in dry weight is a function of absorbed As and is dependent on the source of As: As (V) or As (III). Moreover, the effect of absorbed As (V) or As (III) on dry weight reduction differs between root and shoot (Figure 3C and 4C). At low solution concentrations (0.02mM As), radish root growth was 10 times more inhibited by As (V) than As (III) as is shown by 90 ppm of absorbed As (V) causing a similar 50% loss in dry weight as 900 ppm of absorbed As (III). Therefore it is important to speciate bio-available As in soil solution with respect to uptake by radishes.

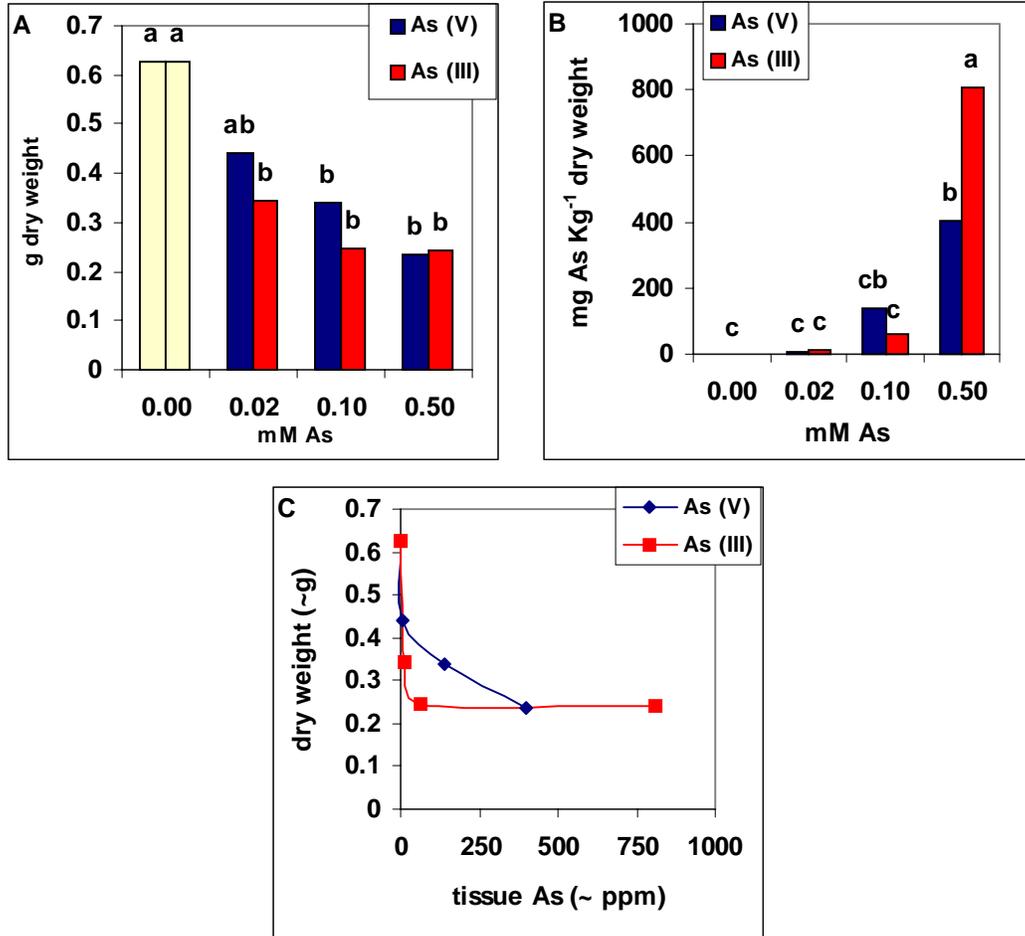


Figure 4: Above ground response of radish plants to As treatments: (A) dry weight (~ g) as a function of solution As (~ mM), (B) As tissue concentration (mg As kg⁻¹ dry weight ~ ppm), and (C) dry weight (~ g) as a function of As tissue concentration (~ ppm). Bars with the same letter denomination per graph, respectively, are not significantly different according to the Least Square Means Test by Tukey-Kramer for an uneven data set in (4B), and Waller-Duncan's Multiple Range Test (kratio =100, p < 0.05) in (4A).

These results stand in contrast to other literature reports, for example 'Black Valentine' bean. A greater toxic effect by As (III) than As (V) on root growth inhibition was reported after 0.02mM As (V) or As (III) had been applied (Sachs and Michael, 1973). The researchers reported that after 3 and 7 days, more As (V) was associated with root tissue than As (III). Our study shows that at the same concentrations of 0.02mM As (V) or As (III) and a contact period of 14 days, 10 times more As (III) was associated with root tissue than As (V). The observed differences may be related to longer contact periods and a difference in tolerance and subsequent uptake capability for the prevalent As species in the aqueous environment. Radish plants are both more tolerant to As and accumulate more As compared to bean plants (Sheppard, 1992; Wachope, 1983). In contrast, absorbed As (III) at the shoot level was approximately 9 times more toxic than As (V) (Figure 6C). At equimolar solution concentrations (0.10mM As), a 45% decrease

in shoot dry weight was recorded for approximately 15 ppm As (III) versus 138 ppm As (V).

We therefore conclude that the development of a viable radish bulb is more dependent on the presence of As (V) than As (III). Arsenate reduced percent germination and radical development in radish seeds more than As (III), and decreased dry weights of radish roots at significantly lower tissue concentrations than As (III). At solution concentrations of ≥ 0.10 mM As (V and III), almost no radish bulbs formed. Small bulbs that were present were usually deformed and wilted. Hence from the point of view of nutrition-safety, (soil) solution concentrations below 0.10 mM As are more pertinent, because only adequate size and viable appearing bulbs are generally consumed. At solution concentrations of 0.02 mM As (III), 2 out of 3 radish bulbs formed, while for the same As (V) concentration, 3 out of 3 bulbs formed. On a dry weight basis, the intake of these fully mature radishes should generate concern, because the respective As intake is approximately 900 and 100 ppm for prevalent forms of arsenic as As (III) and As (V), respectively. For comparative reasons, the United States Environmental Protection Agency (U.S.E.P.A.) has set maximum As concentrations in drinking water at 50 ppb and is currently debating whether to reduce this concentration to 5 ppb, a decision is still pending. Additionally, an oral Reference Dose (RfD) set by the U.S.E.P.A. is based on the assumption that thresholds exist for certain toxic effects such as cellular necrosis. It is expressed in units of mg/kg-day and is an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during their lifetime. No clear consensus has yet been drawn within the U.S.E.P.A. for the As-RfD, but is generally set between 0.1 and 0.8 $\mu\text{g}/\text{kg} / \text{day}$ (URL: <http://www.epa.gov/iris/subst/0278.htm>, June 12, 2000). Using a body weight ranging from 35 to 75 kg for children to adults, we have estimated that the intake of one radish bulb from a 0.02 mM As (V) growth environment will result in an RfD of 0.35 to 0.76 $\mu\text{g}/\text{kg} / \text{day}$. In a 0.02 mM As (III) growth environment, the RfD will range from 3.27 to 7.01 $\mu\text{g}/\text{kg} / \text{day}$. These solution concentrations (0.02 mM) are not unusual in some parts of the world, for example Bangladesh, where high levels of As (0.05 to 3.5 mg As/L) have been found in well waters (Nickson *et al.*, 2000). Thus it is also likely that these populations would be receiving toxic levels of As from root crops.

Acute toxicity of arsenic compounds in humans is predominantly a function of their rate of removal from the body. Arsenite and As (V) are two of the more toxic forms of arsenic in general, and lethal doses for humans are approximately 1.5 mg As (III)/ kg of body weight. Acute As intoxication has mostly been associated with the consumption of strongly contaminated water, where As concentration ranged between 1.2 and 21.0 mg As L⁻¹ (World Health Organization, 1996). In humans, soluble arsenic compounds are rapidly absorbed from the gastrointestinal tract. Arsenate is rapidly and almost completely eliminated via the kidneys, while As (III) is eliminated from the body by the rapid urinary excretion of nonmethylated arsenic in both trivalent and pentavalent forms and by detoxification by sequential methylation of As (III) in the liver to monomethylarsonic acid (MMAA) and dimethylarsinic acid (DMAA). The ability to detoxify inorganic As becomes limited, when daily intake of As exceeds 0.5 mg (World Health Organization, 1996).

Our study emphasizes that solution As concentrations of 0.02mM will result in the significant absorption of As into radish tissue (90 to 900ppm), and should hence be regarded as an important additional source of integrated As next to contaminated water.

Lettuce

Arsenic treatment levels were chosen to be 0.06, 0.03, and 0.01mM As on the basis of the results obtained from the previous seed germination study. No significant difference was recorded for the dry weights of both above or below ground parts relative to their control nor to each other (Figure 5A and 5B). However, the trend was that As (V) treated plants produced 35 to 60% more dry matter than the control, while As (III) treated plants produced 50 to 65% less dry matter than the control.

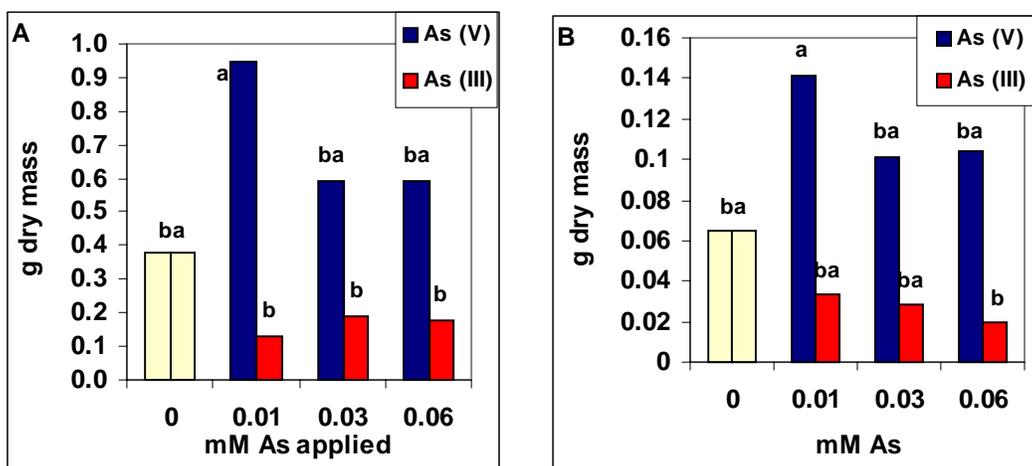


Figure 5: Dry weight production (~g) of lettuce plants as a function of As concentration (~ mM); (A) above ground, (B) below ground. Bars with the same letter denomination per graph, respectively, are not significantly different according to Waller-Duncan's Multiple Range Test (kratio =100, $p < 0.05$).

Dry matter production in As (V) treated plants dropped only from 0.01 to 0.03mM As, but remained constant at higher As (V) concentrations (0.06mM). These dry weight differences were reflected in the appearance of the lettuce heads and the roots. All As (V) treated lettuce showed larger and more developed lettuce heads than the control, while the root system was not visibly different from that of the control. Arsenite treated plants, however, became increasingly stunted above and below ground with increasing As (III) concentration. Also lettuce roots exhibited were very slender and thin and or rotting at the higher As (III) levels (Figure 9). Of all plants treated with As, only As (V) treated plants had viable (marketable) proportions, while As (III) treated plants were generally too small, e.g. 1 out of 3 lettuce heads was viable in the 0.01mM As (III) treatment.

Corresponding As uptake into lettuce roots increased with increasing solution As concentration (Figure 6), while dry weight reductions and increases could be correlated to

As concentrations in root tissue (Figure 7A and 7B). At equimolar concentrations, more As is taken up from As (III) solutions than from As (V) solutions (Figure 6). This also occurs at the lowest As (III) (0.01mM As) concentration compared to the highest As (V) concentration (0.06mM). This signifies that lettuce roots may prefer uptake of As (III) over As (V). At the 0.01mM As (V or III) level, this difference is significant, while at all other levels, As uptake from either As (V) or As (III) containing solutions remains statistically insignificant. The greater uptake of As (III) into lettuce roots may be similar to that of radishes, in which lettuce roots are capable of effectively sequestering As (III) in their roots. However, As (III) absorption in lettuce is less than in radishes and these values should be compared with great care as solution concentrations varied between the two studies, as did the root system of the two species.

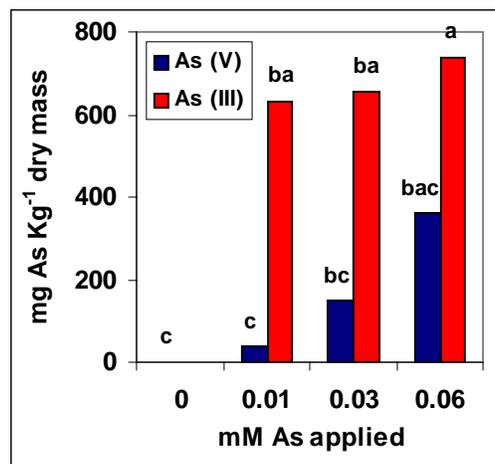


Figure 6: Arsenic Uptake (\sim mg As Kg⁻¹ dry weight) in lettuce roots as a function of solution As concentration (\sim ppm). Bars with the same letter denomination are not significantly different according to Waller-Duncan's Multiple Range Test (kratio =100, $p < 0.05$).

In contrast to the radish study, no As was accumulated in the above ground parts of lettuce except at the highest As (III) treatment level, where 48 ppm As were accumulated. This difference between radishes and lettuce suggests that lettuce plants have additional protective mechanisms beyond root sequestration, which will keep As confined at the root level. We suggest that a large root surface area in lettuce helps to diffuse stress over a greater root surface area, such that stress effects of As (III) and As (V) remain sub-lethal. Similar to radishes, As (V) uptake was low and is likely affected by high phosphate concentrations in solution. It has been shown by Hurd-Karrer (1939) that a molar ratio of P/As exceeding 5 will protect against As (V) toxicity in wheat (Hurd-Karrer, 1939). Oats have been shown to reduce the amount of As (V) uptake when increased phosphate was applied to nutrient solution (Rumburg *et al.*, 1960). Recent studies by Mackowiak and Grossl (1999) using the same hydroponic nutrient cultures, found that amorphous iron oxide plaques form on roots and these plaques provide a sink for phosphate. Similarly, As may sorb to these surface plaques, especially As (V), which

may prevent potentially lethal quantities of As from entering the plant.(Mackowiak and Grossl, 1999).

Dry weight losses and increases in lettuce shoot and root could be established as a function of As concentration in root tissue (Figure 7A and 7B). Arsenate tissue concentrations produced noticeable dry weight increases, especially at less than 50ppm tissue As, while increasing tissue As (III) concentrations decreased dry weights.

A stimulant effect of sub lethal As (V) doses has been noticed in the past for other crops as well, for example lemon plants (Walsh and Keeney, 1975) or corn (Woolson *et al.*, 1971). In the case of lettuce, root tissue As (V) concentrations of less than 40 ppm produced a 150% increase in dry matter in lettuce heads, however dry matter production sharply decreased above 40 ppm of root tissue As (V). However, the resultant dry weights for lettuce heads remain well above the dry weight of the control. In contrast, As (III) in the root tissue decreases dry weights of lettuce roots and shoots, which we ascribe to the destructive effect of As (III) on the uptake of water, and macro- and micronutrients (Carbonell-Barrachina *et al.*, 1994; Carbonell-Barrachina *et al.*, 1997b).

From the point of view of nutritional safety, there appears to be no danger from the consumption of lettuce exposed to low, sub-lethal concentrations of As, because no As is translocated into the shoot of lettuce. However, we assume that at higher concentrations of As (III) (0.06mM), some translocation of As from root to shoot will occur, resulting in stunted and wilted lettuce leaves. Non of the lettuce treated with 0.06mM As (III) were harvestable. In comparison to the previous seed germination study, applied As levels were less toxic to the maturing plants than to the seed. Seed establishment however precedes in the development of plants, and hence As toxicity levels must be differentiated between seeds and maturing plants.

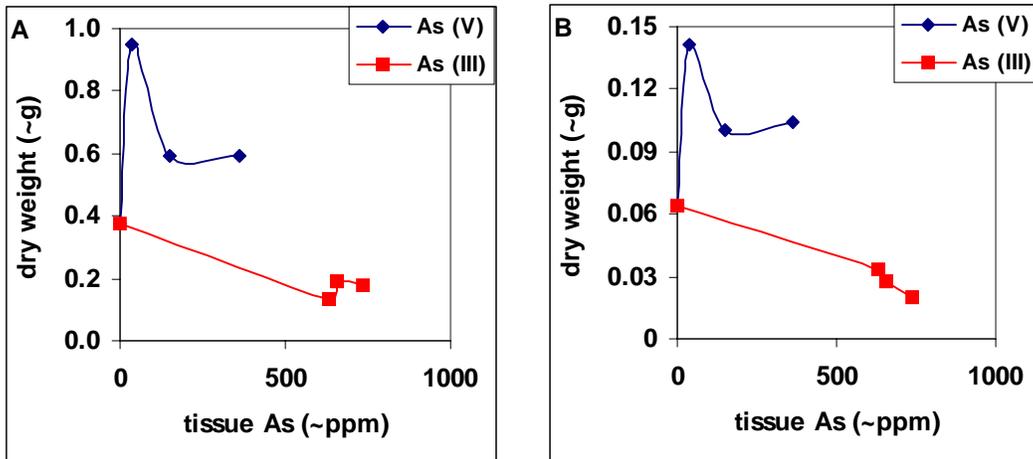


Figure 7. Dry weight (~ g) as a function of root tissue As concentration (~ppm). (A) Above Ground, (B) Below Ground.



Figure 8. Radish roots at harvest after 0.02mM As (III) treatments.

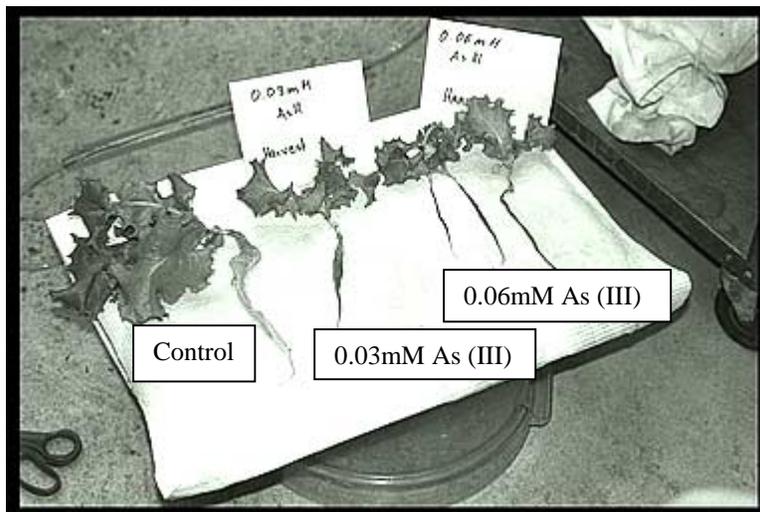


Figure 9. Lettuce roots and heads at harvest after 0.03, and 0.06mM As (III) treatments in comparison to the control.

Conclusion

Seed germination studies demonstrated that 0.1mM and 0.025mM As are toxic threshold levels for radishes and lettuce, respectively, while As (V) is more toxic to radish seeds than As (III). Arsenic impacted both germination and radical development in radish seeds. For lettuce we observed that As had no impact on germination but reduced radical length significantly ($p < 0.01$). At equimolar concentrations, As (III) was more toxic than As (V) in lettuce seeds, contrary to results obtained for radish seeds. The comparison of As doses for seeds and maturing plants suggests that toxic levels in seeds are not necessarily toxic to maturing plants. However, seed establishment is necessary for overall

plant growth. A possible mechanism responsible for the increased tolerance to As by maturing plants may be the capacity to produce As detoxifying phytochelators, such as glutathione. The capacity of a vegetable crop such as radish or lettuce to produce glutathione has significant implications on the amount of As uptake and tolerance. It has been shown that Indian Mustard grass will increase As uptake five times if additional dithiol arsenic chelators are added to hydroponic growth media (Pickering *et al.*, 2000; Schmoeger *et al.*, 2000; Sneller *et al.*, 2000).

The hydroponic growth studies showed that reductions and gains in biomass are a function of absorbed As and are dependent on the source of As: As (V) or As (III). Moreover, the effect of absorbed As (V) or As (III) on dry weight reductions and gains differ between root and shoot portions of the plants and are crop dependent. Tissue-As (originally solution As(V)) was more destructive to radish roots, while tissue-As (originally solution As(III)) was more destructive at the shoot level. Conversely for lettuce, As (III) caused reductions in dry weight, while As (V) had a stimulating effect on biomass production. Lower As (V) concentrations in plant tissue throughout the lettuce study and at low As (V) concentrations (0.02mM) in the radish study may be explained by molar ratios of P to As of approximately 5.

Because the harvestable portion of radishes and lettuce does not form at higher As solution concentrations, toxicity studies with respect to consumer protection need to focus on sub-lethal dosages. At 0.02mM As, 90 and 900ppm of As were absorbed by radish bulbs for As (V) and As (III) sources, respectively. In contrast, lettuce leaves were virtually free of any As (except at 0.06mM As (III)), but had nevertheless no harvestable leaves, because of the disruptive effects of As (III) at the root.

The effect of apparent physiological differences expressed at the root level suggests that bulbous crops can use these additional root tissues as an effective mean of sequestering large solution concentrations of As. An extensive and intricate rooting system as in lettuce may be responsible for diluting toxic effects over a larger root area and hence limit the translocation of As (III) into above ground tissue. More research is necessary to explore the risk associated with growing root crops in As and other toxic metal contaminated environments.

Acknowledgement

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Chapter 3

Adsorption of Arsenate (V) and Arsenite (III) on Goethite in the Presence and Absence of Soluble Organic Carbon

Abstract. The environmental fate of arsenic is of utmost importance as the U.S. EPA has recently proposed to tighten the arsenic drinking water standard from 50 ppb to 5 ppb. In natural systems the presence of dissolved organic carbon (DOC) may compete with As for adsorption to mineral surfaces, hence increasing its potential bioavailability.

Accordingly, the adsorption of arsenate As (V) and As (III) on goethite (α -FeOOH) was investigated in the presence of either a peat humic acid (Hap), a Suwannee River Fulvic Acid (FA) (IHSS) or citric acid (CA). Adsorption edges and kinetic experiments were used to examine the effects of equimolar concentrations of organic adsorbates on arsenic adsorption. Adsorption envelopes were conducted over a pH range of 11 to 3, while the kinetic studies were conducted at pH 6.5 for As (V) and pH 5.0 for As (III). Arsenate adsorption was inhibited in the order of Hap > FA > CA while arsenite adsorption was inhibited in the order of CA > FA > Hap. Humic acid reduces As V adsorption starting at pH 9, with a maximum reduction at pH 6.5. Fulvic acid slightly inhibited As (V) adsorption starting at pH 5, and this inhibition increased with a decrease in pH. No effect was observed in the presence of CA. Arsenite adsorption is inhibited by HA starting a pH 7 and increases with a decrease in pH, while FA and CA reduce As (III) adsorption beginning at pH 8, with a continuous reduction as the pH decreases. The differential extent of As V adsorption in the presence of the organic acids suggests that the distribution and the respective densities of the abundant functional groups (phenol/ catechol OH or COO⁻) are significant in the adsorption of As (V). Furthermore, larger organic acids may hydrophobically partition to surfaces via a more favorable entropy driven reaction mechanism which may influence As (V) diffusion and its subsequent adsorption to surfaces. The decrease in As (III) adsorption is caused by its reduced affinity for the surface at pH values lower than 9, and the simultaneous increase in surface activity by the organic substances' via their COO⁻ functional groups. The results of these experiments suggests that dissolved organic carbon substances are capable of increasing the bioavailability of As in soil and water systems in which the dominant solid phase is a crystalline iron oxide.

Introduction

Arsenic (As) is a naturally occurring element that has both metallic and non-metal properties. Its high toxicity and increased appearance in the biosphere has triggered public and political concern. Arsenic has been introduced in increasing quantities into the biosphere through past usage of arsenical pesticides (lead arsenate) and the release of arsenic through mining activities (Grossl *et al.*, 1997; Tamaki and Frankenberger, 1992; Woolson *et al.*, 1971). Ingestion of arsenic through water is the primary cause of arsenic poisoning in humans.

The two most commonly occurring forms of As in the environment are As +5 and As +3 present as the oxyanions arsenate (AsO₄³⁻) and arsenite (AsO₃³⁻), respectively. Arsenite has been found to be the more mobile and toxic species in soil environments

(Sun and Doner, 1996). Arsenic bioavailability is a function of pH, redox potential, the presence and type of adsorbing surfaces, and microbial populations, which potentially could reduce arsenic to volatile methylated arsenic species (Massecheleyn *et al.*, 1991; McGeehan and Naylor, 1994; Onken and Hossner, 1996). The adsorption mechanisms of As (III) and As (V) have been well documented (Fendorf, 1997; Grossl *et al.*, 1997; Sun and Doner, 1996). Grossl *et al.* (1997) proposed that the adsorption of arsenate to goethite involved a two-step ligand exchange reaction by which an inner-sphere bidentate surface complex is formed. Sun and Doner (1996) established that As (V) and As (III) replace two singly coordinated surface OH groups on goethite to form binuclear bridging complexes.

The effects of pH and redox potential on the solubility and speciation of As was studied by Masscheleyn *et al.* (1991) for an As contaminated aeric ochraqualf. High soil redox potentials (200-500mV) decreased As solubility and most of the As was in the form of arsenate (65-98%). Under alkaline or reduced conditions (0-100mV), the solubility of As increased substantially due to the dissolution of iron oxyhydroxides and release of sorbed and co-precipitated As.

Competitive adsorption between As (V) and As (III) and other oxyanions on kaolinite, montmorillonite, and illite has been documented by Manning and Goldberg (1996). They found that phosphate adsorption was slightly greater at equal concentrations of P and As (V), while As (V) adsorption was greatly reduced when P was present at ten times the concentration of As (V). However, molybdate (MoO_4^{2-}) inhibited As (V) adsorption only at a pH less than four, illustrating the importance of pH and oxyanion speciation for specific adsorption.

The bioavailability of As in the environment may also be affected by naturally occurring organic molecules, which may compete with As for sorption to surface sites. While oxyanions such as PO_4^{3-} , SO_4^{2-} , MoO_4^{2-} have been shown to compete with As (V) and As (III) for mineral surface sites, there is relatively little information examining the role of dissolved organic carbon on the adsorption behavior of As species (Geelhoed *et al.*, 1998; Manning and Goldberg, 1996; Xu *et al.*, 1988). Research has demonstrated that adsorption of dissolved organic carbon occurs via multiple mechanisms including ligand exchange reactions of COO^- and phenol OH functional groups (Gu *et al.*, 1994). While there is very little information available on the effects of DOC on As adsorption, previous research has shown that phosphate adsorption onto soil constituent surfaces is decreased in the presence of humic and fulvic acids as well as simple aliphatic acids like citrate (Geelhoed *et al.*, 1998; Sibanda and Young, 1986). Sibanda and Young (1986) demonstrated that fulvic and humic acids strongly compete for adsorption sites with phosphate on goethite and gibbsite, and two tropical soils at pH 4 and pH 7 (Sibanda and Young, 1986). Fontes *et al.* (1992) studied oxisols from Brazil and determined that organic carbon compounds in the soil had COOH groups in their dissociated forms that would sorb to goethite surfaces. Furthermore, these researchers observed a reduction in phosphate adsorption on goethite in the presence of humic acid (Fontes *et al.*, 1992). In a similar study Geelhoed *et al.* (1998) showed that citric acid will lower phosphate adsorption on goethite at low pH values.

Accordingly, the objective of this research is to determine the effect of humic acid (peat), fulvic acid, and citric acid on the adsorption of As (V) and As (III) on goethite surfaces. The DOC compounds and Fe-oxide were chosen because they are commonly

found in natural soil and aquatic environments, and specific organic acids were chosen on the basis of their size and functional group content.

Materials and Methods

Adsorbent Preparation

The goethite used in all experiments was synthesized from reagent-grade $\text{Fe}(\text{NO}_3)_3$ using the method described in (Schwertmann and Cornell, 1991). We altered the goethite preparation procedure only in one aspect, namely by adding 4 M NaOH in a very slow, drop-wise fashion to achieve a higher specific surface area goethite. Excess salts were removed by electro dialysis until the conductivity of the wash solution was nearly equal to that of distilled, doubly deionized water. All solutions were prepared with double-deionized water and contact with glassware was avoided to prevent silica contamination. The clean goethite precipitate was subsequently washed for 1 hour with 0.40 M HNO_3 to remove any remaining amorphous phases, re-dialyzed and freeze-dried. X-ray diffraction (XRD) and thermo-gravimetric analysis (TGA) were used to verify the identity of the goethite. X-ray diffraction and TGA analyses were diagnostic for goethite and consistent with those present in Schwertmann and Cornell (1991). The specific surface area was $103 \text{ m}^2 \text{ g}^{-1}$, as determined by a five-point N_2 Brunauer-Emmett-Teller (B.E.T.) gas adsorption isotherm method.

Adsorption Edges

Adsorption edges were conducted to examine the influence of pH on As and DOC sorption on goethite. The adsorption of arsenate/arsenite and DOCs was examined as a function of pH (3-11) in a background electrolyte solution of 0.01M NaNO_3 at a constant adsorptive (1.0mM) and adsorbent concentrations ($2.5 \text{ g goethite L}^{-1}$). An appropriate quantity of N_2 purged goethite suspended in 0.01M NaNO_3 was added to a 500 ml Teflon lined flat-bottomed, water-jacketed reaction vessel (500 ml). The reaction vessel was covered with a removable glass lid containing entry ports for a mechanical stirrer, pH electrode, N_2 gas, burette tip, and pipette and allowed to fully hydrate overnight. The pH was adjusted to 11.00 using a Brinkmann Metrohm[®] 718 Stat Titrino and the dropwise addition of 0.10 M NaOH. Each adsorption edge was kept well stirred with the aid of a mechanical stirrer (CafraMo RZR-2000) spinning at $300 \text{ rev. min}^{-1}$. All experiments were conducted at $298^\circ \text{ K} \pm 0.1^\circ \text{ K}$ and 1 atm pressure under a N_2 environment to eliminate CO_2 influences.

After a minimum of 12 hours, appropriate volumes of adsorptives were added to the suspension. Adsorptives for the adsorption envelopes were obtained from stock solutions (0.10M As (V) and 0.10M As (III)) prepared from sodium salts. All DOC stock solutions were prepared using a background electrolyte of 0.01M NaNO_3 . A peat humic acid solution of 0.01M carbon was prepared by placing required amounts of freeze-dried humic acid in the background electrolyte at pH 8. The background electrolyte was previously purged with nitrogen for 20 minutes before the addition of the peat humic acid. While dissolving, the pH was maintained at 8.00, and the system was continuously

purged with nitrogen. The total acidity of the Hap is $9.95 \text{ mmol}_c \text{ g}^{-1}$ (Personal communication, P. Bloom, 2000). Suwannee River Fulvic Acid stock solution was prepared (0.01M carbon) in a similar manner at pH 7. A citric acid stock solution (0.01M carbon) was prepared by dissolving an appropriate quantity of sodium citrate salt in 0.01M NaNO_3 at pH 7. The total acidity of Suwannee River Fulvic Acid has been reported to be 13.9 and $14.2 \text{ mmol}_c \text{ g}^{-1}$ (Yates and von Wandruszka, 1999). Suwannee River Fulvic Acid and peat humic acid were obtained from the International Humic Substances Society (IHSS). The total acidity of CA can be calculated from its formula weight and the assumption that only COOH are active in the pH range of 3 to 11. The total acidity is then $15.62 \text{ mmol}_c \text{ g}^{-1}$.

Adsorption edges were conducted using three consecutive addition scenarios for the adsorptives. In the first scenario we added the DOC species before the arsenic species, the second scenario we added the arsenic species before the DOC species, and in the final scenario we simultaneously added both adsorptives. After the addition of each adsorptive, the pH was titrated to 11.00 and was allowed to equilibrate for a minimum of two hours.

The suspension pH was lowered either in half or full pH units from pH 11.00 to 3.00 using the pH-stat and 0.10 M HNO_3 . After a two-hour minimum equilibration time at each pH, a sample was removed from the reaction vessel. For arsenate, arsenite, and DOC edges, 12.00 ml aliquots were removed using a Rainin[®] automated digital pipet and filtered through a $0.10 \mu\text{m}$ Gelman metrical membrane into previously acid-washed polypropylene test tubes. The 12.00 ml aliquot was divided into equal 6 ml samples for the analysis of arsenic (As) and total organic carbon (TOC). For the competitive adsorption edges, aliquots of 18.00 ml were taken for each adsorptive. The 18.00 ml aliquots were divided again into equal volumes of 6ml for As analysis, As (V) speciation, and TOC analysis. Arsenic was measured using a Spectro[®] inductively coupled plasma atomic emission spectrometer (ICP-AES). Humic acid samples were analyzed using a Phoenix[®] 8000 Carbon Analyzer (Tekmar-Dohrman, Cleveland, OH). All adsorption edges were run in duplicate.

Arsenic Speciation

Arsenate species were measured using a colorimetric assay by Cummings et al. (1999). Samples were mixed with appropriate amounts of 25mM HCl and reagent mix to give a final volume of 3ml in a 4ml plastic cuvette. The reagent mix consists of four equal amounts of potassium antimony tartrate (0.544g/L), ammonium molybdate (24g/L), sulfuric acid (269.2ml conc. sulfuric acid/L), and ascorbic acid (43.2g/L). The reagent mix was prepared fresh within 2 hours prior to the assay. Arsenate standards of 0, 250, 500, 750, and $1000 \mu\text{M}$ were prepared from stock solutions of known concentrations. Standards and samples were placed into a water bath at $351 \pm 1^\circ\text{K}$ for exactly 10 min, immediately removed and placed in an ice bath for 5 min. Arsenate was speciated using a Beckmann Coulter DU-640[®] spectrophotometer using a wavelength (λ) of 640nm. Any observed difference between As content established by ICP-AES and the colorimetric technique was considered a reduction of As (V) to As (III). No such observation was made. To determine potential interference of the organic acids, we prepared samples of known As (V) concentration in a background of the respective organic acid, and followed

the procedure outlined above. No significant interference could be noted from the presence of Hap, FA, or CA.

Kinetic Studies

Kinetic studies were conducted to examine the influence of time on the competitive adsorption of As and DOC. These studies were conducted at a pH of 6.5 and 5.0 for As(V) and As(III), respectively. We chose pH 6.5 for the As (V) study, because at this pH we observed the greatest effects of Hap on As (V) adsorption, while a pH of 5.0 was chosen, because at this pH we observed strong effects by CA and lesser effects of Hap and FA on As (III) adsorption. We avoided pH values lower than 5.0 in order to prevent Hap precipitation from solution (Schulthess and Huang, 1991). Equipment conditions and initial equilibration times were the same as those of the adsorption edge experiments. The DOC was added two hours prior to the addition of either As (V) or As (III). Sampling commenced four minutes after the addition of the arsenic species, and continued every four minutes during the first 0.5 h, and every eight minutes during the second 0.5h. After the first hour, sampling proceeded every 0.5 h. Samples were treated in the same manner as the samples for the adsorption edge experiments.

Results

The adsorption edges for As (V), As (III), humic acid peat (Hap), Suwannee River Fulvic Acid (FA), and citric acid (CA) on goethite are presented in Figure 1. We present this graph as a reference for the relative positions of the individual adsorption edges to each other.

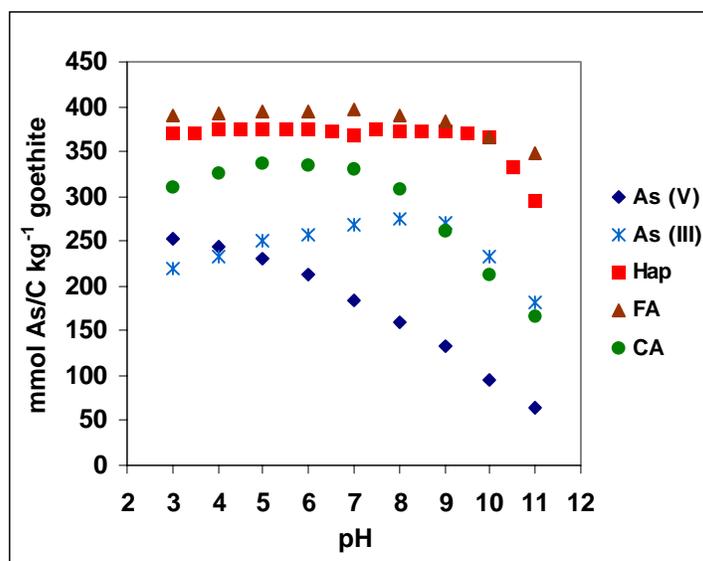


Figure 1: Adsorption edges of As (V), As (III), Hap, FA, and CA on α -FeOOH.

Arsenate and As (III) adsorption is typical of strong and weak oxy-acids with maximum adsorption near their respective pK_{a1} values ($pK_{a1As(V)} = 2.24$, $pK_{a1As(III)} = 9.29$) (Rubinson and Rubinson, 1998). Similar adsorption edges have been observed by Manning and Goldberg (1996) on goethite and gibbsite. Ligand exchange reactions with surface functional groups results in different surface complexes (e.g. monodentate vs. bidentate), which are also dependent on sorbate surface coverage (Fendorf, 1997). Arsenite adsorbs to goethite surfaces via ligand exchange reactions as well forming monodentate and bidentate complexes with mostly A-type hydroxyls and H-bonding with C-type (Sun and Doner, 1996).

The adsorption of organic acids is not as well defined but is assumed to be a dynamic interaction involving several mechanisms including ligand exchange reactions, H-bonding, and electrostatic interactions. Humic acid (peat) adsorption is complete by pH 9 and independent of pH below pH 9. Suwannee River Fulvic Acid (FA) adsorbs in a similar manner, while CA shows an adsorption maxima around pH 5. The citrate and Hap adsorption edges compare well with adsorption edges obtained by others (Geelhoed *et al.*, 1998; Schulthess and Huang, 1991). The adsorption of FA differs somewhat from that reported in the literature, showing an adsorption maxima at a higher pH value (e.g. pH 9). This may be attributed to differences in initial adsorptive concentrations. Filius *et al.* (2000) found that fulvic acid adsorption maxima on goethite are dependent on initial DOC concentration. At low initial coverage (75mg FA/ L), the adsorption maximum is reached at pH 9, however with increasing FA concentration, the adsorption maxima are at successively lower pH values (Filius *et al.*, 2000).

Arsenate adsorption in the presence of DOC

Only the addition scenario where DOC materials were added before As(V) are displayed (Figure 2), because there was no discernable difference between scenarios. Arsenate adsorption in the presence of DOC is reduced in the order of Hap > FA > CA. A sudden drop in adsorbed As (V) (33%) in the presence of Hap is observed at pH 8 and is maintained until pH 6, upon which the adsorption of As (V) gradually increases from a 30 % reduction to 13% reduction at pH 3. Similar results were obtained by others investigating the influence of humic acids on phosphate (PO_4^{3-}) adsorption on variably charged minerals (Fontes *et al.*, 1992; Sibanda and Young, 1986).

Arsenate adsorption in the presence of FA is noticeably reduced at pH 5 and continues to drop with decreasing pH (Figure 2). The percent reduction of As (V) adsorption to goethite in the presence of FA increases from 5 to 11 % as the pH decreases from 7 to 3. Similar results were obtained by Xu *et al.* (1988) who examined As (V) adsorption on alumina in the presence of FA (Xu *et al.*, 1988). We observed no effect of citric acid on As (V) adsorption to goethite. This is in contrast to Geelhoed *et al.* (1999) who observed a reduction in phosphate adsorption on goethite in the presence of citric acid. These results may be related to differences in adsorbent and adsorptive concentrations used in this study (Geelhoed *et al.*, 1998).

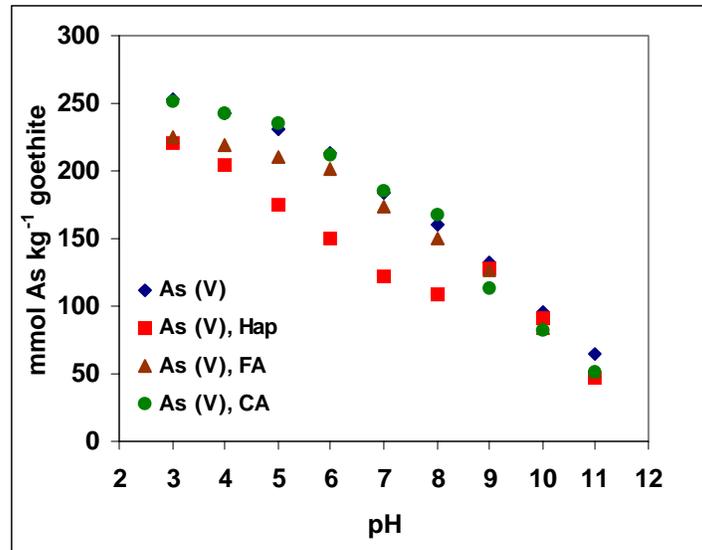


Figure 2: As (V) adsorption edges on α -FeOOH in the presence and absence of DOC: Hap, FA, and CA.

DOC adsorption in the presence of As (V)

The presence of As (V) reduces the adsorption of all DOC compounds investigated (Figure 3A - 3C). Humic acid adsorption is reduced by 30% between pH 6 and 11. This reduction in adsorption is consistent with the reduction in As (V) adsorption in the presence of Hap (32%). Below pH 6, a marked increase in Hap adsorption is observed. This increase may be attributed to interactions between COO^- functional groups on the organic acid and the surface and/or precipitation reactions of the humic acid in the increasingly acidic environment. Schulthess and Huang (1991) observed precipitation of humic acid in the presence of silica and aluminum oxides at pH values as high as 6 and this precipitation increased with decrease in pH.

Adsorption of FA was inhibited throughout the entire pH range by As (V). A slight increase in the adsorption of FA at pH values less than 6 may be attributed to increased surface interactions between COO^- and surface (OH) functional groups. Several researchers have pointed out the importance of COO^- functional groups in the adsorption process of natural organic matter (NOM) on variably charged surfaces (hematite, goethite, gibbsite) and the associated increase in adsorption at low pH (Evanko and Dzombak, 1999; Filius *et al.*, 2000; Gu *et al.*, 1994; Kaiser *et al.*, 1997; Varadachari *et al.*, 1997; Parfitt *et al.*, 1977). Citric acid adsorption was strongly inhibited by As (V) between pH 9 and 3. Similar results were observed by Geelhoed *et al.* (1998) for citrate adsorption on goethite in the presence of phosphate.

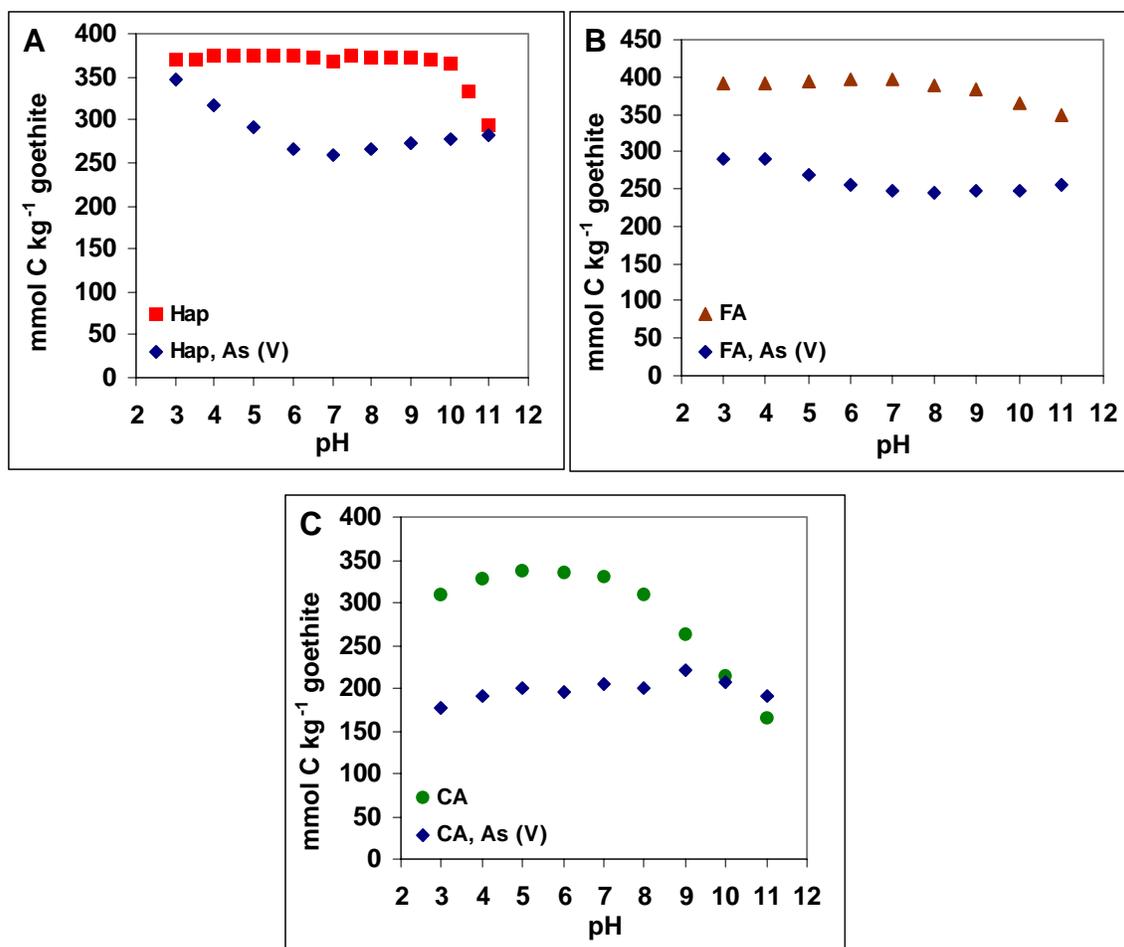


Figure 3: DOC adsorption edges on α -FeOOH in the presence and absence of As (V): (A) Hap, (B) FA, (C) CA.

Arsenite adsorption in the presence of DOC

There were no discernible differences between the addition scenarios for adsorption of As (III) in the presence and absence of Hap, FA, and CA, and therefore only one addition scenario is illustrated (DOC before As (III), Figure 4). Arsenite adsorption was decreased by all three organic acids in the order of CA > FA > Hap.

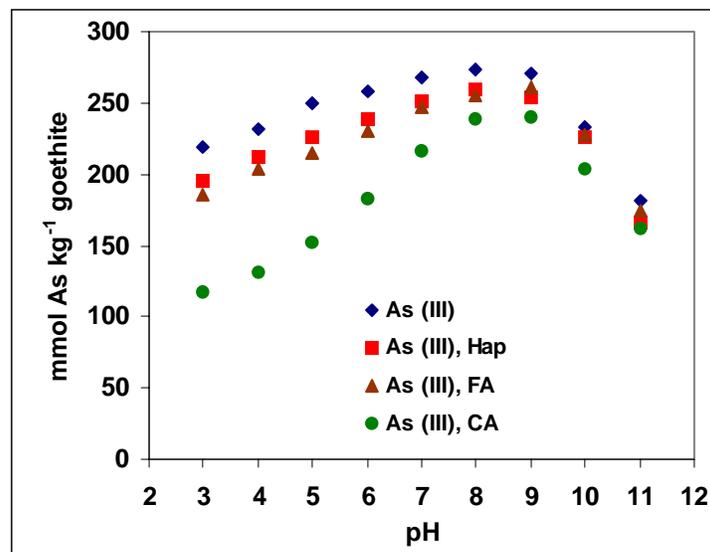


Figure 4: As (III) adsorption edges on α -FeOOH in the presence and absence of DOC: Hap, FA, and CA.

Humic and FA acids had little effect on As (III) adsorption from pH 11 to 9. However, a linear reduction of As (III) adsorption was observed in the presence of Humic acid (peat) and FA from pH 8 to pH 3. In the pH range from 8 to 3 Hap and FA reduced As (III) adsorption from 6 to 10% and 6 to 15%, respectively. In contrast citric acid reduced As (III) adsorption throughout the entire pH of the adsorption edge. Furthermore, this reduction in As (III) adsorption was most pronounced at pH values from 8 to 3, where As (III) adsorption was reduced from 13 to 46%.

DOC adsorption in the presence of As (III)

Arsenic (III) inhibited the adsorption of Hap and FA only at pH values of 6 and greater (Figure 5). In contrast CA adsorption was only inhibited at pH values from 7 to 9. This result is not unexpected, because the As (III) adsorption maximum is near its pK_{a1} (9) while below this pH, the affinity of As (III) for variable charge surface declines (Figure 1). Furthermore, one would expect less inhibition of CA adsorption, since this organic ligand was the strongest competitor with As (III) for the goethite surface. DOC adsorption decreased in the presence of As (III) in the order of Hap > FA > CA, which reflects the inhibition of As (III) adsorption in the presence of these DOCs: CA > FA > Hap.

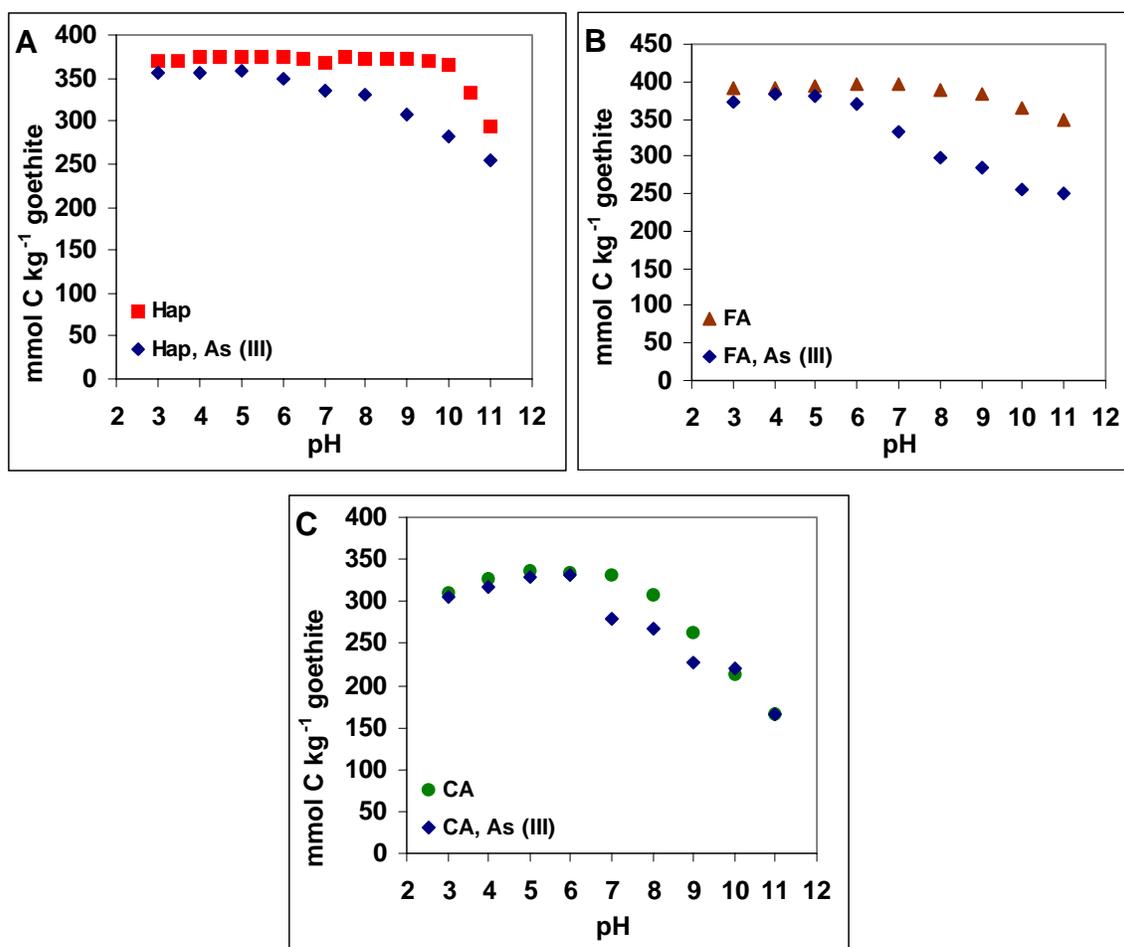


Figure 5: DOC adsorption edges on α -FeOOH in the presence and absence of As (III): (A) Hap, (B) FA, and (C) CA.

Kinetic Studies

The rate of the initial reaction (first 124 min) for As (V) adsorption is clearly controlled by the presence of DOCs on the surface, and as such, the initial reaction rate follows the order of As (V) > As (V)_{FA} > As (V)_{CA} > As (V)_{Hap} (Figure 6A). After 124 min, less As (V) was sorbed to the surface in the presence of Hap than in the presence of either FA or CA. Humic acid reduced As (V) adsorption by 27% (t = 124 min). Moreover, the initial adsorption reaction is inhibited more in the presence of CA than it is in the presence of FA. This result is in contrast to the adsorption edge data where fulvic acid inhibited As (V) adsorption to a greater extent than citric acid. This may be related to the type of surface complexes formed by the organic ligand and their relative affinity for the goethite surface. The relative strength of adsorption for an organic acid is dependent on its structural features, where the number of COO⁻ functional groups as well as their position relative to each other determines strength of adsorption (Evanko and Dzombak, 1999).

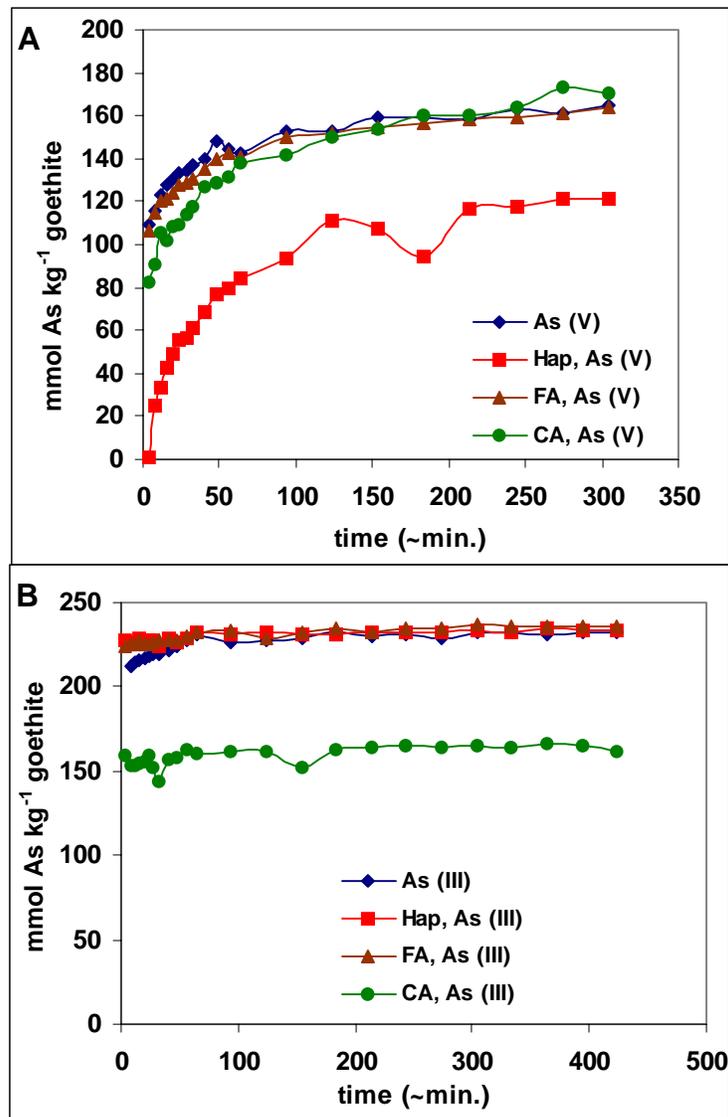


Figure 6: (A) As (V) and (B) As (III) adsorption on α -FeOOH over time in the presence and absence of DOC; α -FeOOH suspension concentration = 2.50g L^{-1} , $[\text{As (V)}] = 1.0\text{mM}$, $[\text{As (III)}] = 1.0\text{mM}$, $[\text{DOC}] = 1.0\text{mM C}$, $\text{pH}_{\text{As (V)}} = 6.50$, $\text{pH}_{\text{As (III)}} = 5.00$, background electrolyte = 0.01M NaNO_3 .

Compared to As (V) adsorption, the initial rate of As (III) adsorption was very fast and nearly complete within the first hour of the experiment (Figure 6B). In contrast to adsorption edge data, Hap and FA had no effect on As (III) adsorption. This may be related to differences in the experimental protocols between the kinetic study and the adsorption edge experiments. Additionally, the adsorption rate in the presence of fulvic and humic acids is faster than As (III) adsorption alone. The adsorption edge of arsenite is very similar to that of boric acid on variably charged surfaces due to the similar pKa1 values (9) (Rubinson and Rubinson, 1998; Su and Suarez, 1995). It has been shown that boric acid adsorbs to humic substances with adsorption maxima between pH 8.5 and 10

(Meyer and Bloom, 1997). Similar interactions between As (III) and FA and Hap may occur and may help to explain increased adsorption rates of As (III) on Hap or FA pre-equilibrated surfaces as well as the reduced effect on As (III) adsorption mentioned above. The reduction in As (III) adsorption in the presence of CA is similar to the one observed in the adsorption edges (45 vs. 40 %).

Discussion

Arsenate adsorption in the presence of DOC

The equilibrium and kinetic experiments demonstrated that equimolar concentrations of DOC can influence As (V) adsorption on goethite surfaces. Hap substantially reduced (30%) As (V) adsorption on goethite at pH values less than 9. In contrast FA only reduced As (V) adsorption at pH values less than 6 while CA only reduced As (V) adsorption in the kinetic studies at times less than 120 minutes. While this data demonstrates that DOC can reduce As (V) adsorption on goethite, it does not explain the difference observed between the different organic materials.

The adsorption mechanism(s) of organic acids on variably charged surfaces of aluminum (Al) and iron (Fe) oxides have been examined by a number of researchers (Evanko and Dzombak, 1999; Fontes *et al.*, 1992; Geelhoed *et al.*, 1998; Gu *et al.*, 1994; Parfitt *et al.*, 1977; Schulthess and Huang, 1991; Sibanda and Young, 1986; Stevenson, 1994; Varadachari *et al.*, 1997). Proposed mechanisms include; (i) anion exchange (electrostatic interaction), (ii) ligand exchange-surface complexation, (iii) hydrophobic interactions, (iv) entropy effects, (v) hydrogen bonding, and (vi) cation bridging (Evanko and Dzombak, 1999; Fontes *et al.*, 1992; Geelhoed *et al.*, 1998; Gu *et al.*, 1994; Parfitt *et al.*, 1977; Schulthess and Huang, 1991; Sibanda and Young, 1986; Stevenson, 1994; Varadachari *et al.*, 1997). It has been proposed that physicochemical characteristics of organic acids, as well as those of mineral surfaces lead to energetic differences, which result in different combinations of the above adsorption mechanisms. The dominant adsorption mechanism is likely the one in which the organic acid forms the most stable association with the mineral surface. Many researchers have confirmed that ligand exchange reactions occur between mineral surfaces and organic acids, where the strength of adsorption is controlled by the density and relative position of COO⁻ groups (Evanko and Dzombak, 1999; Gu *et al.*, 1994; Kaiser *et al.*, 1997; Parfitt *et al.*, 1977). This may provide some insight as to why we saw an effect with Hap, however it contradicts the minimal effect of FA and CA, which each have higher COO⁻ functional group densities than Hap. Therefore, the interaction of COO⁻ groups and the surface cannot be solely responsible for the observed reduction in As (V) adsorption. A different functional group content as well as other adsorption mechanisms may be responsible for the reduction in As (V) adsorption in the presence of Hap. Fontes *et al.* (1992) examined the association of micro-crystalline goethite and humic acid in oxisols of Brazil and found considerable quantities of HA at depths up to 200 cm. This DOC was observed to effectively compete with phosphate for adsorption sites (Fontes *et al.*, 1992). Infrared spectra in this study showed that COO⁻ were deprotonated and bonding thorough these groups to the goethite surface was suggested. Gu *et al.* (1994) examined the adsorption of humic acid on hematite using Fourier Transformed Infrared Spectroscopy (FTIR) and heat of

adsorption. The results indicated that both COO^- and OH groups are involved in ligand exchange reactions with the surface (Gu *et al.*, 1994). Similar results and conclusions were obtained by Schulthess and Huang (1991) and Parfitt *et al.* (1977) who examined the adsorption of humic and fulvic acids on silicon, imogolite, aluminum oxides, and goethite (Parfitt *et al.*, 1977; Schulthess and Huang, 1991). Parfitt *et al.* (1977) suggested that the observed adsorption of humic acid was not fundamentally different from that of fulvic acid in neutral solutions. Therefore, strong interactions may be formed between organic acids and mineral surfaces with non-carboxyl organic functional groups. These strong associations are likely due to acidic phenol and catechol functional groups on the organic acid and occur at alkaline pH values due to the $\text{pK}_{\text{a}1}$ values of phenol and catechol functional groups ($\text{pK}_{\text{a}1}$ catechol = 9.34, $\text{pK}_{\text{a}2}$ catechol = 13.24; $\text{pK}_{\text{a}1}$ phenol = 9.98) (Evanko and Dzombak, 1999; Gu *et al.*, 1994; Rubinson and Rubinson, 1998). Filius *et al.* (2000) examined fulvic acid adsorption on goethite and proposed strong outer sphere adsorption of phenolic OH groups via H-bonding, where the H^+ ion served as a proton bridge satisfying the charge on a goethite O^- and the O^- of the fulvate molecule.

We believe that the abundance of similar alkaline functional groups on Hap (catechol and phenol) may play a dominant role in its adsorption to goethite. Furthermore we believe that this may be responsible for the decrease in As (V) adsorption to goethite by means of competition for surface functional groups. The adsorption of Hap on goethite over As (V) is favored by the relative affinity of Hap for the surface at alkaline and neutral pH values. Oxy-acids such as As (V) and orthophosphate bind preferentially at low pH values near their $\text{pK}_{\text{a}1}$ value, which is 2.24 for As (V) (McBride, 1994). Additionally, we believe that there exists an electrostatically unfavorable field around the adsorbed Hap molecule, which is at least in part generated by COO^- functional groups not involved in the adsorption process, that prevents As (V) from approaching the surface and undergoing a ligand exchange reaction. This is in part supported by our kinetic data, which shows no increase in adsorption of As (V) over time in the presence of Hap. Finally, some of the adsorption of the Hap molecule will be governed by physical adsorption (van der Waals forces), especially in the lower pH region when Hap becomes more hydrophobic. Hence a physical separation between the surface and As (V) is also maintained by the size of the organic acid.

The minimal effect of FA and CA on the adsorption of As (V) to goethite is unexpected, since researchers have observed a competitive effect between phosphate and similar organic anions. Moreover this has been shown to be enhanced by a short chain length and an increase in the density of COO^- functional groups (Geelhoed *et al.*, 1998; Schulthess and Huang, 1991; Struthers and Sieling, 1950). Our results are in contrast to the findings of Geelhoed *et al.* (1998), Schulthess and Huang (1991) or Struthers and Sieling (1950) and may be attributed to differences in adsorptive and adsorbent loading. The small effect that we do see in the presence of FA at low pH values and citric acid in the kinetic study at times less than 120 minutes demonstrates the importance COO^- functional groups. At low pH values, FA may form polydentate surface bonds, which can effectively compete with As (V) for surface sites. This is in part supported by our measurements which show a ~ 12% decrease in As (V) adsorption at pH 3 and increase in FA adsorption of ~ 12 % over the pH range from 6 to 3. Filius *et al.* (2000) investigated the adsorption of fulvic acid to goethite and fit experimental results to the CD-MUSIC model. The authors propose outer-sphere adsorption of FA at high pH involving phenolic

groups and inner-sphere adsorption at low pH involving primarily carboxyl groups (Filius *et al.*, 2000). The affinity constant for the ligand exchange of COO^- of the FA molecule and the surface is however very small and takes place only as a contribution of strong electrostatic attraction between the protonated surface OH and the negatively charged carboxylate groups of FA. In the presence of As (V), which strongly reduces the point of zero charge of goethite, ligand exchange reactions between carboxylate functional groups of FA and the surface will only take place to a very small degree. A similar electrostatic repulsive effect may also be responsible for the lack of CA adsorption to goethite at low pH and the concurrent unaltered As (V) adsorption in the presence of CA.

Arsenite adsorption in the presence of DOC

Arsenite adsorption on goethite was reduced in the presence of all organic acids. However, unlike As (V), citric acid inhibited As (III) adsorption more than FA and Hap. We believe that this is related to the pKa of the organic acids, where those with the lowest pKa values are preferentially adsorbed. Arsenite is a weak acid, whose pK_{a1} value is 9.29, and whose surface activity on goethite is maximized at alkaline pH values (see Figure 1 or 3) (Rubinson and Rubinson, 1998). Similarly maximum adsorption for Hap and FA is also achieved at alkaline pH, however, the dynamic interactions between the surface and the organic acid (whether ligand exchange, electrostatic attraction or van der Waals forces) appear to be weaker than those of As (III) and the surface. This is supported by a reduction in Hap, FA, and CA adsorption in the presence of As (III) in the pH region of 11 to 6, (Figures 3 and Figure 4A-4C). As the pH drops, the affinity of the neutral As (III) oxy-acid declines and the adsorption of Hap, FA and CA increases and the presence of As (III) has little effect on their adsorption. In essence, As (III) is desorbed or replaced from the goethite surface as the surface activity of the organic acids increase. The surface activity of the organic acids (ligand exchange) depends on chain length, and COO^- functional group density, and decreases in the order that we have observed: $\text{CA} > \text{FA} > \text{Hap}$ (Geelhoed *et al.*, 1998; Schulthess and Huang, 1991). Factors of chain length and COO^- group density (and their relative position to each other) are however only relevant when the oxy-acid they compete with for the mineral surface is a weaker acid. Hence we see increased efficacy in reducing As (III) adsorption, but not As (V) adsorption.

We made two interesting observations. First, the extent to which As (III) inhibits DOC adsorption ranks $\text{FA} > \text{HA} > \text{CA}$. This may seem contradictory at first to As (III) adsorption data, however is in good agreement with the proposed functional group distribution of HA, which we assume to be higher in phenolic and catecholic OH groups. Since phenol and catechol OH as well as As (III) have similar pKa values between 9 and 10, greater competition for surface sites would be expected from Hap than from FA at neutral to alkaline pH values. Second, it is interesting to note that in the kinetic work concerning As (III), the rate of the adsorption reaction for As (III) in the presence of FA and HA was greater than when As (III) was by itself. The order of the rate of reaction ($\text{mmol As (III) kg}^{-1} \text{ goethite min}^{-1}$) for the first 1.0 hr or so is $\text{As (III)}_{\text{Hap}} > \text{As (III)}_{\text{FA}} > \text{As (III)} > \text{As (III)}_{\text{CA}}$. The adsorption of arsenite is very similar to that of boric acid on variably charged surfaces due to the similar pK_{a1} values (9) (Rubinson and Rubinson, 1998; Su and Suarez, 1995). It has been shown that boric acid also adsorbs to humic

substances with an adsorption maximum between pH 8.5 and 10 (Meyer and Bloom, 1997). A similar retention mechanism may exist between As (III) and Hap or FA, and may hence help to explain slightly greater rates of As (III) adsorption on either Hap or FA pre-equilibrated goethite surfaces.

Conclusion

The effect of Hap, FA, and CA on As (V) or As (III) adsorption on goethite was examined using pH adsorption edges and kinetic studies. Arsenate adsorption was reduced in the order of Hap > FA > CA, while As (III) adsorption was reduced in the order of CA > FA > Hap. The efficacy with which an organic acid may reduce As adsorption is species dependent and follows the principle of maximum surface activity. As such, stronger oxy-acids, like As (V) are out-competed by weaker organic acids like Hap, whose abundant phenolic OH and catecholic OH functional group content is able to compete for surface sites on goethite and create an electrostatically unfavorable field around the adsorbed humic acid molecule. The efficacy of chain length, carboxyl group density, and relative position of COO⁻ functional groups is not sufficient to interfere significantly with As (V). The slight effects of FA on As (V) adsorption on goethite are ascribed however to the presence of an abundant carboxyl functional group content, which is likely to form polydentate bonds between the surface and FA. Furthermore, the affinity constant for chemisorption of carboxylate groups on FA is low and inner sphere complexes are only formed at low pH values, because of strong electrostatic attraction between the fulvate molecule and the positively charged functional groups on goethite (Filius *et al.*, 2000). Since sorbed As (V) lowers the point of zero charge of variably charged surfaces, such strong electrostatic forces may have been absent which may prevent most of the carboxylate groups on FA from undergoing ligand exchange with the surface. For weaker acids (e.g. As (III)) increased acidity of the organic acid increases its surface activity, and in association with factors of chain length, COO⁻ density, and relative positioning, is able to compete for surface sites with As (III). The small influence of Hap and FA on As (III) adsorption and their effect on the rate of As (III) adsorption suggests that there may be similar interactions as occur between boric acid and humic acid.

Our research suggests that DOC may influence the potential bioavailability of As in natural systems. The ability of DOC to influence As bioavailability will depend on many factors including the type of DOC species, the oxidation state of As, and the type of mineral surface present. Additional research is necessary to further elucidate reaction mechanisms and to evaluate the effect of DOC on As transport in whole soils. In highly weathered soils such as the oxisol and ultisol orders, the retention of As (V) or As (III) may be reduced in the presence of DOC species.

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Chapter 4

Adsorption of Arsenate and Arsenite on Ferrihydrite in the Presence and Absence of Dissolved Organic Carbon (DOC)

Abstract. The adsorption of As (V) and As (III) on synthetic 2-line ferrihydrite in the presence and absence of a peat humic acid (Hap), Suwannee River Fulvic Acid (FA) or citric acid (CA) was investigated. Previous work with goethite has demonstrated the ability of DOC materials to reduce As (V) and As (III) adsorption. In this study, a batch technique was used to examine the adsorption of arsenic (III and V) and DOCs on ferrihydrite in the pH range from 3 to 11. The results obtained demonstrated that As (V) adsorption on ferrihydrite was reduced only in the presence of CA. Arsenate reduced the adsorption of all organic acids except Hap. Both FA and CA reduced As (III) adsorption on ferrihydrite, while Hap had no effect. Fulvic and citric acid adsorption on ferrihydrite was reduced in the presence of As (III), however, adsorption increases of FA and CA were observed at lower pH, which is consistent with a decrease in As(III) adsorption. The peat humic acid had no effect on As (III) adsorption, and we believe that the adsorption process of Hap and As (III and V) on ferrihydrite are independent of each other. The observed differences between this study and the study on goethite are believed to be an intricate function of ferrihydrite's surface characteristics, which affects the mechanisms of surface adsorption and hence the affinity of organic acids such as Hap, FA, and CA for the ferrihydrite surface. As such, the adsorption of DOCs to ferrihydrite are assumed to be energetically less favorable and to occur with a fewer number of ligands, resulting in lower surface coverage of weaker bond strength. Additional factors for the observed differences are discussed. This work demonstrates the importance of the solid phase in adsorption processes and functional group composition, as noticeable differences are observed in comparison to a crystalline Fe-oxide solid phase.

Introduction

The potential bioavailability of As in the environment may be affected by the presence or absence of naturally occurring organic molecules, which may compete with As for sorption sites (Grafe *et al.*, 2000; Xu *et al.*, 1988). Research has demonstrated that As adsorption to mineral surfaces may be reduced in the presence of oxyanions such as PO_4^{3-} , SO_4^{2-} , and MoO_4^{2-} (Manning and Goldberg, 1996). Furthermore, organic acids have been shown to decrease phosphate adsorption on goethite and other soil constituents surfaces (Fontes *et al.*, 1992; Geelhoed *et al.*, 1998; Gu *et al.*, 1994; Sibanda and Young, 1986). However, there is relatively little information examining the role of dissolved organic carbon on the adsorption behavior of As species.

Recently, we have demonstrated that As (V) and As (III) adsorption to goethite is reduced in the presence of humic acid peat (Hap), Suwannee River Fulvic Acid (FA), and citrate (Grafe *et al.*, 2000). The reduction in As adsorption in the presence of DOC may be a function of the surface activity of the functional groups present on the DOC material. For example, humic acid peat, whose functional group content shows a higher phenol OH group content reduced As (V) adsorption more than citric acid, whose functional group content is composed of three COO^- groups as well as one OH group ($\text{pK}_a > 12$). In

contrast, As (III) adsorption was greatly reduced by CA at lower pH values as the As (III) affinity for the surface decreased, and that of CA increased.

Overall, the adsorption of As (V) on goethite was reduced in the order of Hap > FA > CA, and that of As (III) in the order of CA > FA > Hap. Kaiser et al. (1997) demonstrated that the adsorption of DOC materials on ferrihydrite may be more physical in nature, while DOC adsorption on goethite was more chemical in nature. Hence the overall weaker adsorption of DOC materials on ferrihydrite likely influences its competitiveness for surface sites with As (III and V).

Unlike goethite, ferrihydrite is an amorphous iron oxide whose random assembly of primarily dioctahedral Fe-octahedra results in an increased number of A and C-type functional groups (Manceau, 1995; Waychunas *et al.*, 1993). Several researchers have pointed out that As (V) and As (III) adsorption will take place preferentially on A-type hydroxyl groups of iron oxides (Manceau, 1995; Sun and Doner, 1996; Waychunas *et al.*, 1993). Moreover, As (V) and As (III) differ in their use of adjacent B- and C-type hydroxyls, while As (III) binds preferentially with doubly coordinated C-type hydroxyls and As (V) with triply coordinated B-type hydroxyls (Sun and Doner, 1996). The surface structural differences between goethite and ferrihydrite therefore warrant a closer examination of their effect on competitive adsorption reactions between As and other competing ligands such as organic acids.

The objectives of this research were to establish the competitive nature between As species and dissolved organic carbon (Hap, FA, or CA) on a non crystalline iron oxide (i.e. ferrihydrite). Secondly, we wanted to introduce As (V) transport data from column studies using ferrihydrite-coated sand previously aged with a leonardite humic acid.

Materials and Methods

Adsorbent Preparation

A 2-line ferrihydrite ($\text{Fe}_5\text{OH}_8 \cdot 4\text{H}_2\text{O}$) (rapid hydrolysis) was prepared by dissolving 40.4 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.1 mole Fe) in 800ml of deionized water in a 1L plastic beaker. The pH was adjusted to 7 – 8 with 5M NaOH while rigorously stirring the mixture. After the suspension settled over night, the clear supernatant was siphoned off, and the remaining suspension slurry was rapidly dialyzed changing deionized water several times every day, until the electrical conductivity of the dialysis bath was nearly equal to that of deionized water. A freeze-drying step followed until aggregates in the sample cylinders broke apart freely when slightly shaking the cylinders.

The specific surface area was $253 \text{ m}^2 \text{ g}^{-1}$, as determined by a five-point N_2 Brunauer-Emmett-Teller (B.E.T.) gas adsorption isotherm method. X-ray diffraction (XRD) analysis and thermo-gravimetric analysis (TGA) verified the identity of 2-line ferrihydrite and were consistent with those present in (Schwertmann and Cornell, 1991) and showed no traces of either hematite or goethite.

Ferrihydrite coated sand was prepared for the column study using sand from T.J. Baker (LOT H37720). The sand was washed with 0.10M HCl, rinsed with double deionized water, and dried prior to coating. Four 100g samples of previously cleaned and

dried sand were measured into 250ml ceramic evaporation dishes. Each 100g sand sample received 8.08g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 50ml of double deionized water. Following that 12ml of 5M NaOH were added to each suspension and mixed well. Suspension pH was adjusted to 7.5 with appropriate amounts of either 5M NaOH or 6M HCl. The sand-ferrihydrite mixture is then allowed to dry in an oven at 40°C overnight. After drying, the sand was rewetted with double deionized water, and dried again in the oven at 40°C. After the sand was completely dry, the sand was transferred to a 53micrometer stainless steel sieve and washed until all salts and indiscrete particles were removed. This point was determined when the effluent was clear in color. The coated sand was then dried again in the oven at 40°C (Amacher, 1999).

Adsorption Edges

Adsorption edges were conducted to examine the function of pH on As and DOC sorption on 2-line ferrihydrite. The adsorption of arsenate/ arsenite and DOCs was examined as a function of pH (3-11) in a background electrolyte solution of 0.01M NaNO_3 at a constant adsorbate (1.0mM) and adsorbent concentrations (1.0g ferrihydrite L^{-1}). An appropriate quantity of N_2 purged ferrihydrite suspended in 0.01M NaNO_3 was added to 500 ml Teflon lined flat-bottomed, water-jacketed reaction vessel (500 ml). The reaction vessel was covered with a removable glass lid containing entry ports for a mechanical stirrer, pH electrode, N_2 gas, burette tip, and pipette and allowed to fully hydrate overnight. The pH was adjusted to 11.00 using a Brinkmann Metrohm® 718 Stat Titrino and the drop-wise addition of 0.10M NaOH. Each adsorption edge was kept well stirred with the aid of a mechanical stirrer (Cafamo RZR-2000) spinning at 300 rev. min^{-1} . All experiments were conducted at 298° K \pm 0.1° K and 1 atm pressure under a N_2 environment to eliminate CO_2 influences.

After a minimum of 12 hours, appropriate volumes of adsorptives were added to the suspension. Adsorptives for the adsorption edges were obtained from prepared stock solutions (0.10M AsV and 0.10M AsIII) prepared from sodium salts. All DOC stock solutions were prepared using background electrolyte of 0.01M NaNO_3 . A peat humic acid solution of 0.01MC was prepared by placing required amounts of dry humic acid in the background electrolyte at pH 8. The background electrolyte was previously purged with nitrogen for 20 minutes before the addition of the peat humic acid. While dissolving, the pH was maintained at 8.00, and the system was continuously purged with nitrogen. The total acidity of the Hap is 9.95mmolc g^{-1} (Personal communication, P. Bloom, 2000). Suwannee River Fulvic Acid stock solution was prepared (0.01M carbon) in a similar manner at pH 7. A citric acid stock solution (0.01M carbon) was prepared by dissolving an appropriate quantity of sodium citrate salt in 0.01M NaNO_3 at pH 7. The total acidity of Suwannee River Fulvic Acid has been reported to be 13.9 and 14.2 mmolc g^{-1} (Yates and von Wandruszka, 1999). Suwannee River Fulvic Acid and peat humic acid were obtained from the International Humic Substances Society (IHSS). The total acidity of CA can be calculated from its formula weight and the assumption that only COOH are active in the pH range of 3 to 11. The total acidity is then 15.62 mmolc g^{-1} .

Adsorption edges were conducted in duplicate and employed three consecutive addition scenarios for the adsorbates. The first scenario saw the addition of DOC species

before the arsenic species, the second scenario had the arsenic species added before the DOC species, and the final scenario saw a simultaneous addition of the adsorptives. After the addition of each adsorptives, the pH was titrated back to 11.00 and was allowed to equilibrate for a minimum of two hours.

The suspension pH was lowered in half or full pH units from pH 11.00 to 3.00 using the pH-stat and 0.10 M HNO₃. After two hours of minimum equilibration time, a sample was removed from the reaction vessel. For As (V), As (III) and DOC edges, 12.00ml aliquots were removed using a Rainin[®] automated digital pipet and filtered through a 0.10 µm Gelman metrical membrane into previously acid-washed polypropylene test tubes. The 12.00 ml aliquot was divided into equal 6 ml samples for the analysis of arsenic (As) and total organic carbon (TOC). For the competitive adsorption edges, aliquots of 18.00 ml were taken for each adsorptive. The 18.00 ml aliquots were divided again into equal volumes of 6ml for As analysis, As (V) speciation, and TOC analysis. Arsenic was measured using a Spectro[®] inductively coupled plasma atomic emission spectrometer (ICP-AES). Samples containing any of the DOC materials were analyzed using a Phoenix[®] 8000 Carbon Analyzer.

Arsenic Speciation

Arsenate speciation was done using a colorimetric assay by (Cummings *et al.*, 1999). Samples were mixed with appropriate amounts of 25mM HCl and reagent mix to give a final volume of 3ml in a 4ml plastic cuvette. The reagent mix consists of four equal amounts of potassium antimony tartrate (0.544g/L), ammonium molybdate (24g/L), sulfuric acid (269.2ml conc. sulfuric acid/L), and ascorbic acid (43.2g/L). The reagent mix was prepared fresh for every analysis within 2 hours prior to the assay. Arsenate standards of 0, 250, 500, 750, and 1000µM were prepared from stock solutions of known concentrations. Standards and samples were placed into water bath of 351 ±1°K for exactly 10 min, immediately removed and placed in an ice bath for 5 min. Arsenate was speciated using a Beckmann Coulter DU-640[®] spectrophotometer using a wavelength (λ) of 640nm. Any observed difference between As content established by ICP-AES and the colorimetric technique was considered a reduction of As (V) to As (III). No such observations were made. To determine potential interference from the organic acids, we prepared samples of known As (V) concentration in a background of the respective organic acid, and followed the procedure outlined above. No significant interference could be noted from the presence of Hap, FA, or CA.

Column Study

Two columns from Soil Measuring SystemsTM were used. The inner diameter of the columns was 2.7cm and the length of the columns was 7.6cm. This gives each column a total volume of 43.55cm³. Each column was uniformly packed with 67.2 grams of ferrihydrite coated sand, which resulted in a bulk density of the solid fraction of 1.54g cm⁻³, and porosity equaling to 0.42. One pore volume was thus equal to 18.29cm³. Each column was attached to a fraction collector that was set up such that each test tube would collect 130 drops of solution, which corresponds to 8 ml. All solutions were passed

through the columns at a flow rate of $0.4775 \text{ ml min}^{-1}$. All solutions passing through the columns were at a pH of 6.5, and were prepared in a background of 0.01 M CaCl_2 . Columns were primed overnight by saturating the sand with 0.01 M CaCl_2 prior to applying any of the adsorbates. The first column then received 18 pore volumes of $1.0 \text{ mM Leonardite}$ solution followed up by enough CaCl_2 (8 pore volumes until break-through of the DOC solution was achieved). Subsequently, we passed 1.0 mM As(V) solution through the column, followed by enough CaCl_2 until break-through of the As(V) occurred. For the second column (after priming with 0.01 M CaCl_2), we passed a 100 ppm KBr solution through the column followed by enough CaCl_2 until break-through of the KBr solution occurred. Potassium bromide serves as an inert background electrolyte or conservative tracer. Finally, four pore volumes of As(V) (1.0 mM As(V)) were passed through the column, followed up by enough CaCl_2 to obtain break-through of As(V). We analyzed for Br^- colorimetrically using a Lachat QuickChem ion analyzer (Lachat Instruments, Milwaukee, WI USA) to develop a breakthrough curve (BTC) for Br^- . Arsenic was measured by ICP and Leonardite was measured using a TOC analyzer (Phoenix 8000, Tekmar-Dohrmann). The BTCs for As and Leonardite were compared to that of Br^- to determine the relative sorption of each species.

Results

The pH adsorption edges for As(V), As(III), humic acid peat (Hap), Suwannee River Fulvic Acid (FA), and citric acid (CA) on ferrihydrite are presented in Figure 1. We present this graph as a reference for the relative positions of the individual adsorption edges.

Arsenite and As(V) adsorption is typical of a weak and strong oxy-acid with maximum adsorption near their respective $\text{pK}_{\text{a}1}$ values ($\text{pK}_{\text{a}1\text{As(III)}} = 9.29$, $\text{pK}_{\text{a}1\text{As(V)}} = 2.24$) (Rubinson and Rubinson, 1998). Similar adsorption edges have been observed by (Manning and Goldberg, 1996) and (Grafe *et al.*, 2000) on gibbsite and goethite, respectively. Arsenate adsorption involves ligand exchange reactions with the surface functional groups that results in different surface complexes (e.g. monodentate vs. bidentate) which depends on surface coverage (Fendorf, 1997). Arsenite adsorbs to goethite surfaces via ligand exchange reactions as well, forming monodentate and bidentate complexes with mostly A-type hydroxyls and H-bonding with C-type hydroxyls (Sun and Doner, 1996). Adsorption of As(III), As(V), and all DOC species is greater 2 to 3 times on ferrihydrite than on goethite, and the relative positioning of the adsorption maximum along the pH scale (Grafe *et al.*, 2000). We attribute these differences to an increase in reactive functional groups on the ferrihydrite surface relative to that on the goethite surface. The functional group density of goethite is $5.73 \mu\text{mol sites m}^{-2}$, while that of ferrihydrite is $16.8 \mu\text{mol sites m}^{-2}$ (Dzombak, 1990). Similar adsorption edges were observed by (Pierce and Moore, 1982).

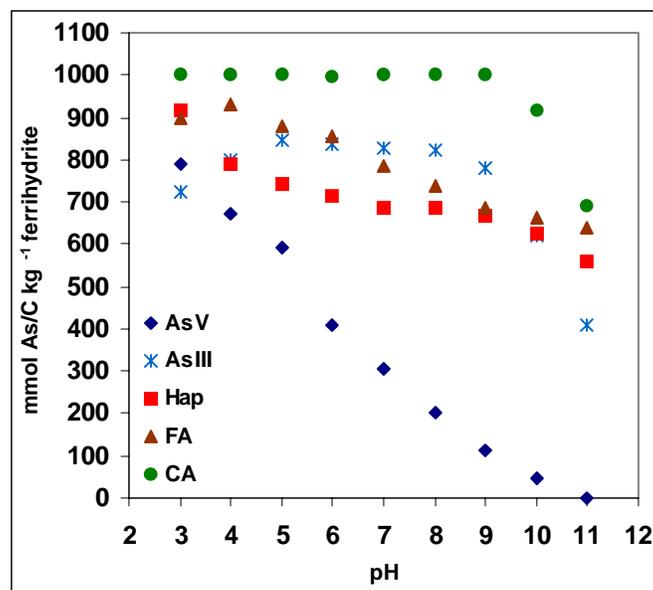


Figure 1: Adsorption edges of As (V), As (III), Hap, FA, and CA on ferrihydrite ($\text{Fe}_5\text{OH}_8\cdot 4\text{H}_2\text{O}$).

The adsorption of organic acids is not as well defined but is assumed to be a dynamic interaction of several mechanisms between organic functional groups (mainly COOH and OH) and the surface including ligand exchange reactions, H-bonding, and electrostatic interactions. Humic acid (peat) adsorption increases from pH 11 to 9 and levels off between pH 7 and 6. From pH 6 to 3, a noticeable increase in Hap adsorption can be observed, however, one should be cautious to interpret this increase as solely as an adsorption reaction. Schulthess and Huang (1991) showed that humic acid precipitation may occur as early as pH 6 and will increase with decreasing pH (Schulthess and Huang, 1991). Humic acid (peat) adsorption on ferrihydrite is markedly different from that on goethite, where Hap adsorption plateaus between pH 3 and 9, and decreases above pH 9 (Grafe *et al.*, 2000).

Suwannee River Fulvic Acid (FA) adsorption on ferrihydrite is S-shaped from pH 3 to 11 with an adsorption maximum near pH 4. Similar adsorption behavior has been observed by Filius *et al.* (2000) for a soil fulvic acid on goethite at a surface loading of 300 mg L^{-1} (Filius *et al.*, 2000). Citrate adsorption on ferrihydrite increases strongly from pH 11 to and 9 and then remains nearly constant from pH 8 - 3. This adsorption behavior is different from what Geelhoed *et al.*, 1998 and Grafe *et al.*, 2000 observed on goethite and may be related to the reactive functional group density increase on ferrihydrite.

Kaiser *et al.* (1997) compared the adsorption of dissolved organic matter (DOM) and a fulvic and humic acid mixture (acidified humic substance = AHS) on illite, gibbsite, goethite and ferrihydrite, but saw no differences in the amount of adsorbed C per Kg of adsorbent. However the sorption capacities of goethite was approximately $3 \text{ mol carbon Kg}^{-1}$ less than that of ferrihydrite, which indicated that the sorption capacity for DOM and AHS at the experimental loading rates had not been reached.

Arsenate Adsorption in the Presence of DOC

Only the addition scenario where DOC materials were added before As(V) are shown (Figure 2), because there was no discernable difference between scenarios. Arsenate adsorption is inhibited by CA, while no effect is observed in the presence of Hap or FA. These observations are contrary to our parallel study with goethite, where Hap and FA inhibited As (V) adsorption on goethite, but where citrate had no effect at the same adsorbate loading ($1.00 \text{ mmol As or C } 250\text{m}^{-2}$) (Grafe *et al.*, 2000). Citric acid most effectively inhibited As (V) adsorption between pH 5 and 3 (17% to 20%, respectively). Geelhoed *et al.* (1998) observed a similar inhibition of phosphate adsorption on goethite in the presence of citrate.

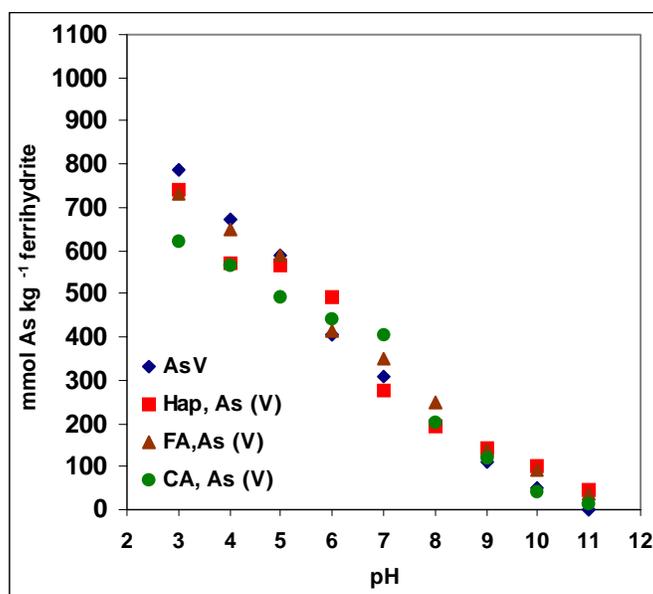


Figure 2: As (V) adsorption edges on ferrihydrite ($\text{Fe}_5\text{OH}_8 \cdot 4\text{H}_2\text{O}$) in the presence and absence of DOC: Hap, FA, and CA.

DOC Adsorption in the Presence of As (V)

Humic acid (peat) adsorption in the presence of As (V) was not affected and maintained an s-shaped curve over the entire pH range tested (Figure 3A). Since we did not observe an inhibition of As (V) adsorption, we expected to see a reduction in humic acid (peat) adsorption, however, this was not the case. In contrast, FA and CA adsorption on ferrihydrite is inhibited by As (V) (Figure 3B and 3C, respectively). Fulvic acid adsorption decreased between pH 8 to 3, while citric acid adsorption decreased between pH 3 to 6. The adsorption edge of CA on ferrihydrite is dissimilar to that obtained by Geelhoed *et al.*, 1998 and Grafe *et al.*, 2000, but increased inhibition of CA adsorption at low pH is consistent with the aforementioned studies.

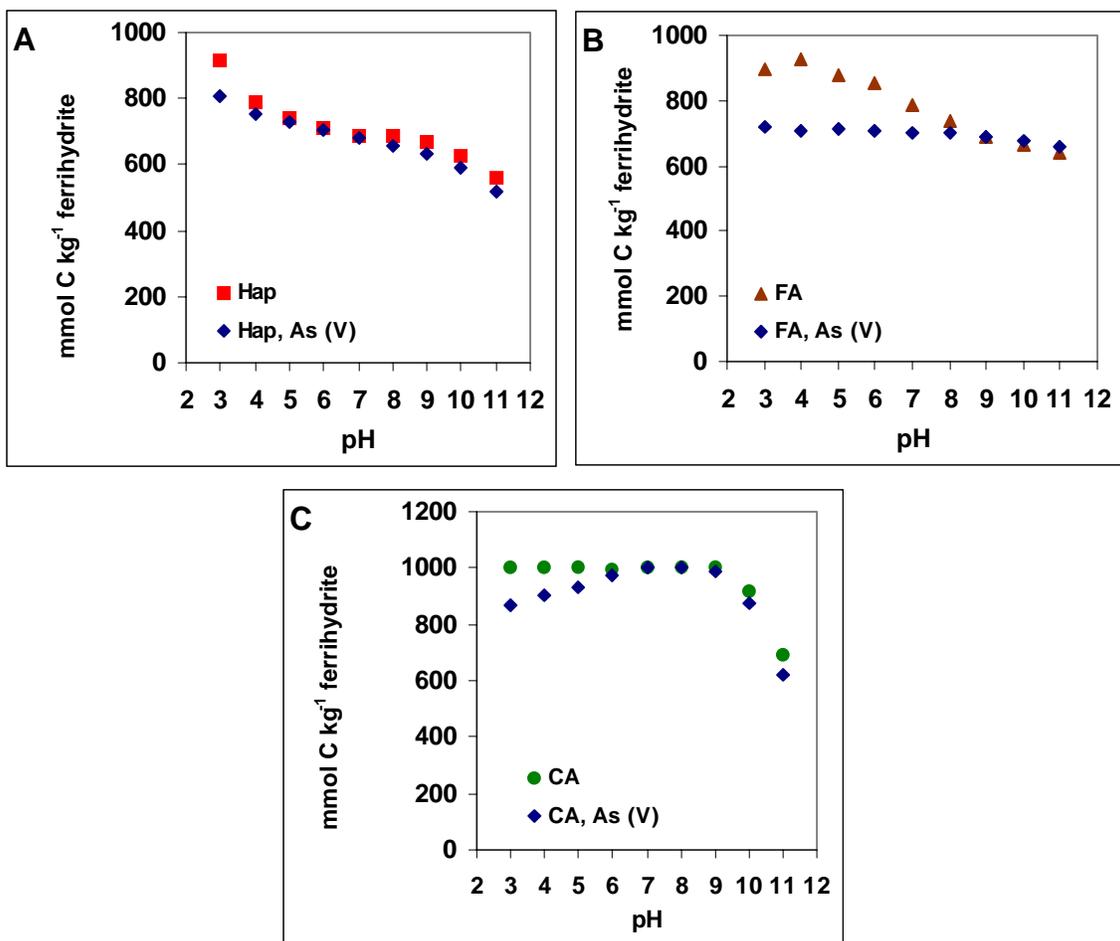


Figure 3: DOC pH adsorption envelopes on $\text{Fe}_5\text{OH}_8 \cdot 4\text{H}_2\text{O}$ in the presence and absence of As (V): (A) Hap, (B) FA, (C) CA.

Arsenite Adsorption in the Presence of DOC

There were no discernible differences between the addition scenarios for adsorption of As (III) in the presence and absence of Hap, FA, and CA, and therefore only one addition scenario is illustrated (DOC before As (III), Figure 4).

Fulvic and citric acid inhibited As (III) adsorption, while Hap had no effect on As (III) adsorption on ferrihydrite. Arsenite adsorption decreased linearly from pH 7 to 3 in the presence of FA and CA. At pH 3, fulvic and citric acid inhibited As (III) adsorption by approximately 9% and 13%, respectively. Arsenite adsorption was also inhibited between pH 11 and 7 in the presence of CA. This appears unusual, because in this pH range both the ferrihydrite surface and CA should be mostly negatively charged and hence repulsion should occur, while As (III) sorption should be more favorable as the pK_{a1} of As (III) is approximately 9.29.

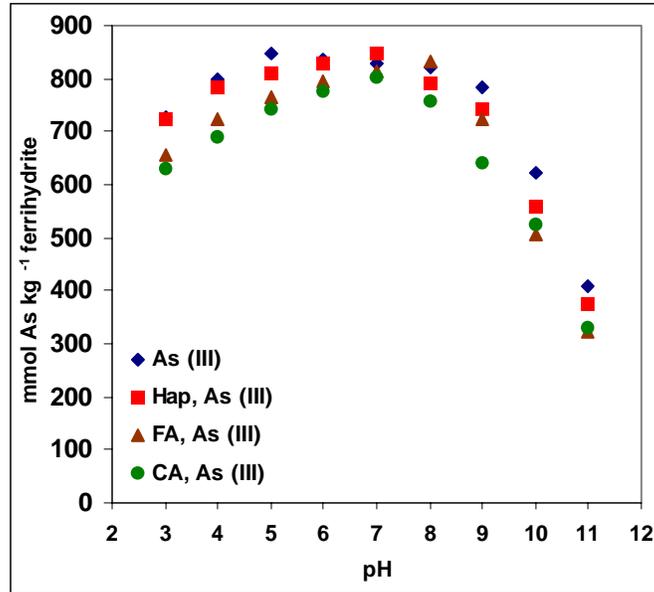


Figure 4: As (III) pH adsorption envelopes on $\text{Fe}_5\text{OH}_8\cdot 4\text{H}_2\text{O}$ in the presence and absence of DOC: Hap, FA, and CA.

The inhibition of As (III) adsorption is similar to what we observed previously on goethite. In the presence of FA, As (III) adsorption on goethite decreased by approximately 15%. In the presence of CA, however, a much greater inhibition of As (III) adsorption (40 to 45%) on goethite had been observed (Grafe *et al.*, 2000). However, the inhibitory effect of Hap on As (III) adsorption previously observed on goethite is absent on ferrihydrite.

DOC Adsorption in the Presence of As (III)

Similar to the Hap – As (V) system (Figure 3A), As (III) did not affect Hap adsorption (Figure 5A). Increased Hap adsorption in the pH range of 3 to 5 should be regarded cautiously, because of coincidental precipitation reactions (Schulthess and Huang, 1991). It appears that the adsorption mechanisms of Hap and As (III) (and As (V)) are non-interfering.

FA and CA adsorption was inhibited by As (III) in ferrihydrite suspension (Figure 5B and 5C, respectively). Fulvic acid adsorption on ferrihydrite decreased in the presence of As (III) from pH 9 to 4 (Figure 5B). In this pH range, the adsorption of FA dropped by ca. 12%. Fulvic acid adsorption follows a near linear increase as pH drops in the presence and absence of As (III) and maximizes at pH 3.

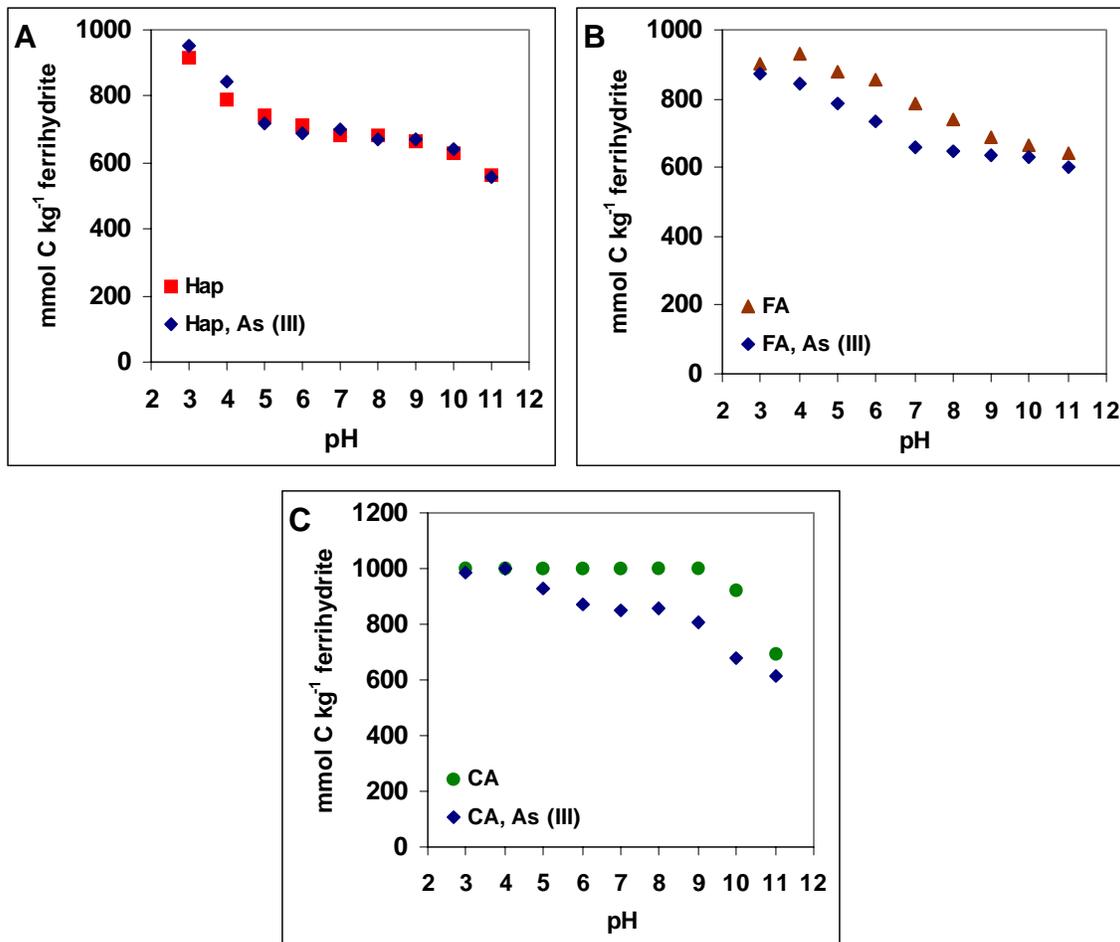


Figure 5: DOC pH adsorption envelopes on $\text{Fe}_5\text{OH}_8 \cdot 4\text{H}_2\text{O}$ in the presence and absence of As (III): (A) Hap, (B) FA, (C) CA.

Similarly, As (III) inhibited CA adsorption on ferrihydrite by 17% from pH 10 to 6 (see Figure 5C). From pH 10 to 8, CA adsorption increased and remained unaltered until pH 6 – 5, when CA adsorption increased again and reached an adsorption maximum near pH 4. From pH 7 to 3, the inhibition of As (III) adsorption on ferrihydrite by FA or CA is in good agreement with the simultaneous adsorption increases of the respective organic acid.

Column Study

The retention of the eluents on ferrihydrite coated sand as a function of applied pore volumes followed the order of $\text{Br}^- < \text{leonardite} < \text{As (V)} \sim \text{As (V)}$ after leonardite (Figure 6). The graph clearly demonstrates that the greatest retention occurs for As (V) (~ 12 pore volumes) regardless of previous treatment with leonardite (~ 8 pore volumes). This is consistent with batch studies that demonstrated that Hap had no effect on As (V) adsorption on ferrihydrite.

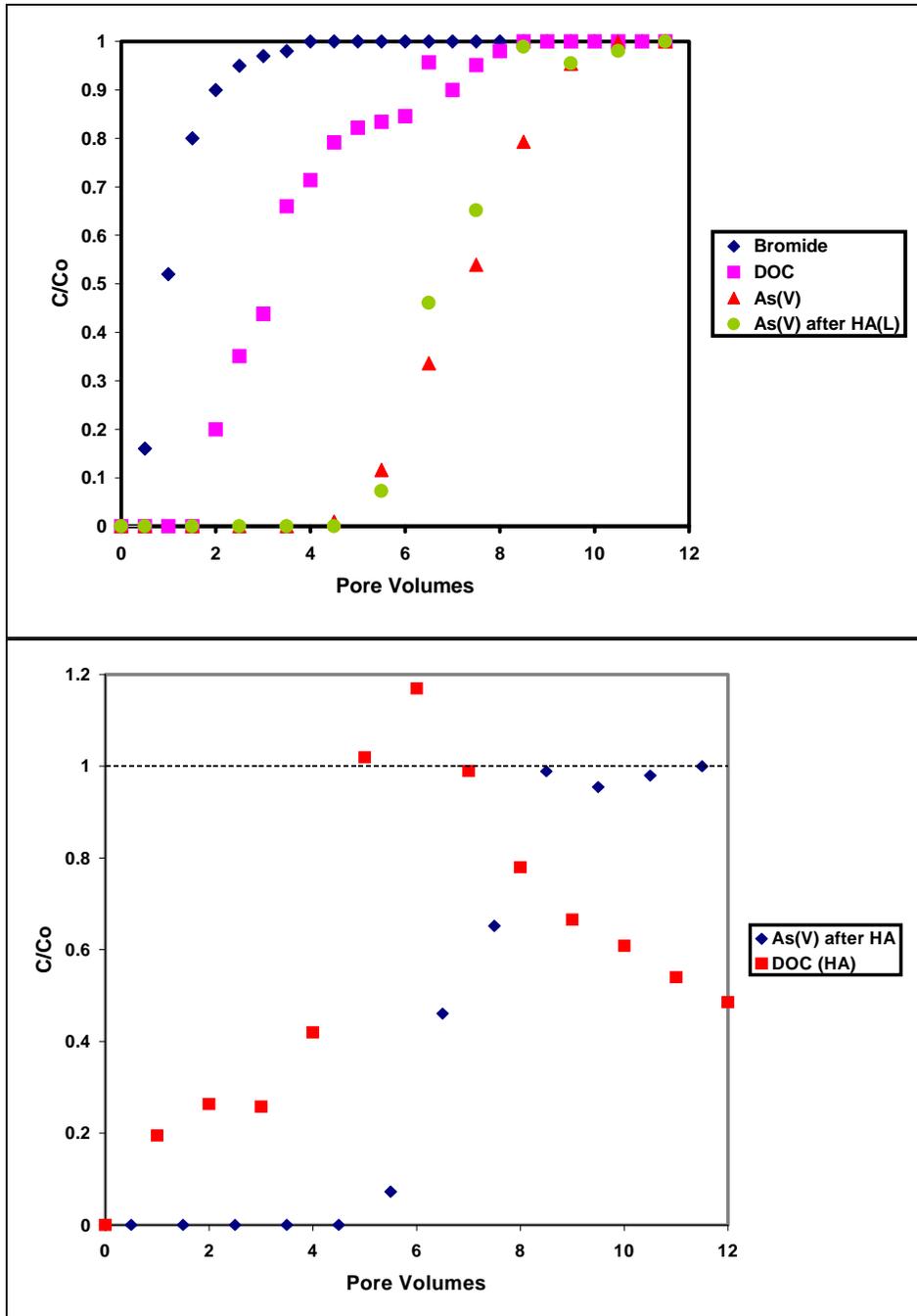


Figure 6: Eluted Fractions as a function of applied pore volumes.

Discussion

Arsenate

The adsorption of As (V) on ferrihydrite is inhibited by CA, while FA and Hap had no effect. These results stand in contrast to those obtained on goethite (Grafe *et al.*, 2000), where Hap and FA inhibited As (V) adsorption while CA had no effect. Hence the ability of DOC materials to decrease As (V) adsorption on ferrihydrite ranks in the order CA > FA ~ Hap which is the reverse order of the results obtained with goethite. These results demonstrate the significance of the solid phase in adsorption and competitive adsorption processes between As and DOC species.

The ability of CA to inhibit As (V) adsorption is generally in good agreement with the results of other researchers. Geelhoed *et al.* (1998) suggest that the adsorption of citrate to goethite is a combination of bidentate surface complexes of two COO⁻ groups and hydrogen bonding by the remaining COO⁻ group, which effectively competes with phosphate for surface sites at low pH. Similar results were obtained by other researchers who showed that relative functional group positioning on the organic acid and overall (small) molecular size increase competitiveness (Evanko and Dzombak, 1999; Struthers and Sieling, 1950). However, it remains unclear why CA was effective in inhibiting As (V) adsorption on ferrihydrite but not on goethite.

In contrast to CA, the fulvic and humic acids used in this experiment were not able to inhibit As (V) adsorption. This may be related to the functional group composition and the affinity and adsorption mechanism on ferrihydrite. Ferrihydrite is an amorphous iron oxide whose random assembly of primarily dioctahedral Fe-octahedra results in an increased number of A and C-type functional groups in comparison to crystalline Fe-oxyhydroxides (e.g. goethite) (Manceau, 1995; Waychunas *et al.*, 1993). Sun and Doner (1996) and Waychunas *et al.* (1995 & 1993), used a combination of spectroscopic techniques to examine the local bonding structure of As (V) on goethite and ferrihydrite surfaces. All researchers observed the formation of different surface complexes, which were dependent on surface coverage. Arsenate tetrahedra preferentially undergo ligand exchange reactions with A-type hydroxyls of Fe-octahedra, forming bidentate binuclear, bidentate mononuclear, and / or at low mole As/Fe ratios also monodentate surface complexes (Fendorf, 1997; Sun and Doner, 1996; Waychunas *et al.*, 1993). H-bonding of a third oxygen with an adjacent B-type OH is thermodynamically favorable for As (V) tetrahedra in bidentate coordination, as less strain is imposed on the Fe crystal (Sun and Doner, 1996; Waychunas *et al.*, 1993). Therefore the change in adsorbent phase from goethite to ferrihydrite energetically favors the adsorption of As (III and V). In contrast to 5.73 $\mu\text{mol sites m}^{-2}$ for goethite, ferrihydrite has a surface functional group density of 16.8 $\mu\text{mol sites m}^{-2}$. The surface functional group increase is reflected in two to threefold adsorption increases of all adsorbates on ferrihydrite relative to their adsorption on goethite (Grafe *et al.*, 2000). Moreover, shape changes of Hap and FA adsorption edges are observed with differing adsorbents, while those of As (V) and As (III) remain similar (Grafe *et al.*, 2000). We believe that such a change in the shape of adsorption edges signifies a change in adsorption mechanisms or an alteration of functional group involvement in the adsorption process(es) of DOC materials.

Kaiser et al. (1997) investigated the adsorption of dissolved organic matter (DOM) and acidified humic substances (AHS, containing humic and fulvic substances) on goethite and ferrihydrite using ^{13}C -nuclear magnetic resonance (^{13}C -NMR) and diffuse reflectance Fourier-transform infrared (DRIFT) spectroscopy. The researchers demonstrated that the adsorption capacity for DOM and AHS were higher on ferrihydrite (7.1 and 7.8 mol C Kg⁻¹, respectively) than on goethite (4.0 and 4.5 mol C Kg⁻¹, respectively). Dissolved organic matter or AHS adsorption on goethite and ferrihydrite applied at equal adsorptive concentrations were the same regardless of adsorbent, which signified that DOM/ AHS surface coverage was higher on goethite than on ferrihydrite. Moreover, the intensity of DRIFT bands of protonated carboxyl groups in the spectra of DOM and AHS sorbed onto goethite indicated that the number of ligands involved in the adsorption reaction were higher on goethite compared to ferrihydrite. This occurred despite a closer arrangement of DOM or AHS molecules on the goethite surface. The authors concluded that the formation of polydentate complexes was favored on goethite, but not on ferrihydrite (Kaiser *et al.*, 1997). The researchers also demonstrated that the intensity increases of COO⁻ bands indicated the importance of these functional groups in adsorption reactions on ferrihydrite as well as on goethite. In contrast, an increase in the intensity of phenolic bands was observed on goethite but not ferrihydrite, indicating their importance in adsorption on goethite. Furthermore, a greater intensity of carbohydrate bands for reactions on ferrihydrite suggests that DOM and AHS adsorption processes on ferrihydrite preferentially involves these carbohydrate rather than phenolic groups (Kaiser *et al.*, 1997). In a similar study employing surface complexation modeling (CD-MUSIC) Filius et al. (2000) proposed an adsorption mechanism for a soil fulvic acid on goethite. Their results suggest that fulvic acid adsorbs via a strong outer sphere adsorption of phenolic OH groups via H-bonding occurred, where the hydrogen ion served as a proton bridge satisfying charge on goethite $-\text{O}^-$ and fulvate $-\text{O}^-$ functional groups. Due to this weak electrostatic interaction one would expect that As (V) would out-compete FA for adsorption on Fe-oxide surfaces. Moreover, in the presence of adsorbed As (V), which strongly reduces the point of zero charge of variably charged surfaces, ligand exchange reactions between COO⁻ groups of FA and functional groups of the surface should therefore be even less favorable.

The results of Kaiser et al. (1997) and Filius et al. (2000) help to explain the observed differences of As (V) adsorption on goethite and ferrihydrite in the presence of all three DOC materials. First, DOC adsorption to ferrihydrite is energetically less favored than to goethite, resulting in weaker surface associations. Second, of all organic functional groups, COO⁻ groups are more involved in adsorption processes on goethite and ferrihydrite than phenolic groups (phenol-OH) and or carbohydrate functional groups (carbohydrate-OH). Hence, As (V) adsorption on ferrihydrite is least favored in the presence of CA, whose functional group content is composed of three COO⁻ groups. Third, the relative importance of phenol groups in the adsorption process to ferrihydrite and goethite explains why Hap with a higher phenol and catechol functional group content was effective in reducing As (V) adsorption on goethite but not on ferrihydrite. Finally, the increased involvement of carbohydrate functional groups demonstrates the increased physical interactions between organic acids and the ferrihydrite surface. Moreover, hydroxyl functional groups on carbohydrate structures occur in a saturated carbon setting, where the dissociation of the OH is thermodynamically unfavorable

(Stevenson, 1994). Hence FA and Hap were ineffective in competing with As (V) for surface sites.

Our column study provides further evidence that humic acids weakly adsorb to ferrihydrite coated surfaces, as prior aging with leonardite did not effect the number of pore volumes required to achieve As (V) breakthrough on a ferrihydrite coated sand packed column. A lack or reduced involvement of phenol-OH in the adsorption process on ferrihydrite explains why Hap did not inhibit As (V) adsorption on ferrihydrite, but was very effective on goethite, where phenol-OH / surface interactions are more prevalent (Grafe *et al.*, 2000).

Arsenite

Arsenite adsorption on ferrihydrite is reduced in the pH range from 7 to 3 in the presence of FA with a concurrent increase in FA and CA adsorption. Arsenite adsorption on goethite involves bidentate surface complexes preferentially with A-type OHs of the surface, and a hydrogen bonding between the remaining functional group and a neighboring C-type OH on the adsorbent surface (Sun and Doner, 1996). Several researchers have pointed out that ligand exchange reactions between COO⁻ groups of organic acids and surface OHs is one of the major adsorption mechanisms for organic acids such as fulvic and humic acids, as well as for citric acid (Evanko and Dzombak, 1999; Filius *et al.*, 2000; Fontes *et al.*, 1992; Geelhoed *et al.*, 1998; Gu *et al.*, 1994; Kaiser *et al.*, 1997; Parfitt *et al.*, 1977; Sibanda and Young, 1986; Varadachari *et al.*, 1997). Exchange reactions of ligands will take place preferentially at their pK_a values, because deprotonated functional groups are required for ligand exchange. Therefore As (III) adsorption on variably charged surfaces will take place preferentially at pH 9.29 (pK_{a1} of H₃AsO₃) (Rubinson and Rubinson, 1998) and COO⁻ adsorption of organic acids will take place at lower pH values (pK_{a1} – 3 of CA are: 2.24, 4.49, and 6.93, respectively). Therefore, As (III) adsorption on ferrihydrite becomes energetically less favorable as pH drops, while that of FA and CA increases. The above explanation explains the observed decrease in As (III) adsorption on ferrihydrite in the presence of FA and CA. The decrease in As (III) adsorption in the presence of FA or CA, however, cannot be ascribed merely to the presence of COO⁻ functional groups, because we should see a small effect with Hap. Abundance and the density of COO⁻ functional groups as well as the relative position of functional groups to each other appear to play an equally important role in the formation of surface complexes and hence in competitive reactions for surface sites (Evanko and Dzombak, 1999; Gu *et al.*, 1994). This would also explain the greater As (III) adsorption inhibition with CA compared with FA.

We also observed a shift in the adsorption maximum of As (III) on ferrihydrite compared to goethite (pH 7 vs. pH 9) (Figure 1). Other researchers have observed similar results, which may be explained by the higher functional group density of ferrihydrite compared to goethite (Pierce and Moore, 1982). It may also explain why CA and FA were less effective in reducing As (III) adsorption on ferrihydrite than on goethite. On goethite, As (III) adsorption was reduced by 10, 15, and 46% at pH 3 (for the presence of Hap, FA, and CA, respectively), while on ferrihydrite As (III) adsorption at pH 3 was inhibited only by 0, 9, and 13% (Hap, FA, and CA, respectively). Additional explanation for this reduction is given by Kaiser *et al.* (1997), who showed that DOM and AHS

adsorption to ferrihydrite (rather than goethite) involves less ligand functional groups. Therefore, the adsorption strength of Hap, FA, and CA on ferrihydrite is expected to be lower compared to goethite and may therefore may not be able to compete as effectively with As (III).

Arsenite adsorption on ferrihydrite was also inhibited by FA and CA between pH 11 and 7. This is unusual, because in this pH range both the ferrihydrite surface and FA/CA should be mostly negatively charged and hence repulsion should prevail, while As (III) adsorption should be more favorable as the pK_{a1} of As (III) is approximately 9.29. Considering the individual adsorption of CA and As (III) on ferrihydrite (Figure 1), we observe approximately 1.2 to 1.7 times greater CA adsorption than As (III) adsorption. In the presence of CA, As (III) adsorption is approximately 1.2 times smaller than in the absence of CA (Figure 4). Inhibition of As (III) adsorption between pH 11 and 8 by FA may be due to an increased affinity of FA for the surface by electrostatic attraction of protonated amine sites in the FA structure and the negatively charged ferrihydrite surface. Furthermore, carbohydrates partitioning to the surface may physically block adsorption sites on ferrihydrite (Kaiser *et al.*, 1997).

Arsenite adsorption on ferrihydrite was not inhibited by Hap, and likewise Hap adsorption on ferrihydrite was not inhibited by As (III). This is similar to what we observed for the As (V)–Hap system on ferrihydrite. However, this is in contrast to what was observed for the As (III)–Hap system on goethite (Grafe *et al.*, 2000). We believe that the same reasons provided in the As (V)-Hap system are valid to explain why As (III) adsorption was not altered in the presence of Hap and vice versa.

Conclusion

The adsorption of As (V) and As (III) on ferrihydrite in the presence of Hap, FA, and Ca has been discussed. The adsorption of As (V) was inhibited at low pH only by CA, while FA and Hap did not inhibit As (V) adsorption on ferrihydrite. In contrast, As (III) adsorption on ferrihydrite was inhibited only by FA and CA from pH 7 – 3 as well as from pH 11 to 8. These results stand in contrast to those obtained earlier on goethite (Grafe *et al.*, 2000).

The observed differences observed between goethite and ferrihydrite can be explained as follows:

1. DOC adsorption on ferrihydrite is energetically less favorable, and results in a lower surface coverage with fewer ligands associating with the surface (Kaiser *et al.*, 1997). The bond strength between DOCs (FA and Hap) and the ferrihydrite surface is hence weaker.
2. Of all DOC functional groups, COO^- groups are likely to be the most involved in the adsorption process. Moreover, the relative density and positioning of these functional groups on the organic acid as well as their size are important in competitive adsorption processes. Hence we observe an effect with CA but not with FA (Evanko and Dzombak, 1999; Kaiser *et al.*, 1997; Struthers and Sieling, 1950).
3. The affinity constant of ligand exchange reactions between the fulvate molecule and the goethite surface according to the CD-MUSIC model of Hiemstra and van Riemsdijk (1996) was shown to be low. Furthermore, ligand exchange reactions occur only due to strong electrostatic attractions between the fulvate molecule and the

positively charged surface OHs (Filius *et al.*, 2000). Arsenate though is known to lower the point of zero charge of variably charged surfaces, hence making ligand exchange reactions between the fulvate molecule and the ferrihydrite surface less likely.

4. Hap had no effect on the adsorption of As (V), because phenol groups are not likely to interact with a ferrihydrite surface as much as they do with a goethite surface (Kaiser *et al.*, 1997).

5. Associations between the ferrihydrite surface and the DOC increasingly involves carbohydrate functional groups, which form weaker H-bonds and other physical interactions with the ferrihydrite surface, which are out-competed by As (V) (Kaiser *et al.*, 1997).

6. Citric acid and FA decreased As (III) adsorption to smaller extent, due to a greater surface activity of As (III) with decreasing pH, but also for reasons mentioned above under 'Two' and 'Four'.

7. We observed no effect of Hap on As (V) or As (III) adsorption and vice versa. We believe that the adsorption processes of As and Hap on ferrihydrite are independent and may occur non-interferingly in the presence of each other.

It has been demonstrated that the ability of soluble organic carbon (Hap, FA or CA) to inhibit arsenic adsorption is in part a function of the adsorbent phase. Only very little is known about the strength of adsorption of soluble organic matter on various geologic material, however, the adsorption strength and the underlying mechanisms of adsorption may control the potential bioavailability of As in the environment and possibly that of other oxyanions such as phosphate, molybdate, and sulfate. The results of this study therefore warrant further investigation of DOC adsorption on other common soil constituents such as Al-oxides and oxyhydroxides, 1:1, and 2:1 clay minerals.

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Chapter 5

Conclusion

Plants have toxic threshold limits at which, when exceeded, the plant's normal metabolic functions are severely impaired and may ultimately lead to the plant's death. The real danger however lies in the fact that edible plants may accumulate As to such levels, which are toxic to animals and humans alike, without showing significant stress symptoms, which would hence exclude the crop from harvest. Therefore, the As tolerant food crop poses real danger to life, because we do not have any visual signs any more that would indicate that the plant contains high levels of a toxic substance.

When the establishment of a plant cover is in question, one should keep in mind that seeds have different As tolerance levels than their maturing plant counterparts. Smaller seeds appear to have lower thresholds to As than larger seeds. Once established, plants of higher root area appear to have a greater tolerance to As by diffusing the induced stress over a greater surface area, thereby lowering the negative effects.

In any case, all plants produce and exude organic acids and all plants eventually die. Their corpses will decay to organic acids and in turn attract microbes, which also produce and exude organic acids. Such organic acids include amongst others, humic and fulvic acids, as well as citric acid.

We have demonstrated that organic ligands (Hap, FA, and CA) compete with As (III and V) for surface sites on goethite and ferrihydrite, thereby increasing the bio-available fraction of the total As present. The local mineralogy influences the extent and degree of competition between organic acids and As (III and V). Ferrihydrite will retain more As (III and V) than goethite under the experimental conditions that we dictated. This is in part a function of the ability of the organic acid to react with the surface. DOC adsorption on goethite is more chemical in nature, while adsorption to ferrihydrite is more physical in nature. As a result, the chemisorbing As molecule out-competes its organic competitors.

We need to identify the adsorption mechanism and strength of organic acids to most or all soil inorganic constituent surfaces in order to evaluate their competitiveness for surface sites with respect not only to As (III and V), but also to phosphate, molybdate, borate, silicate, sulfate and many other environmentally critical substances. Spectroscopic techniques (IR, NMR, XANES) provide an excellent tool base to follow up on some of the suggested mechanisms with which DOCs compete with inorganic ligands for surface sites. Finally, time resolved studies are needed to elucidate the long term fate of adsorbed As (III and V), as organic matter is added freshly to soils every year due to the natural cycling of plant materials.

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Objective

The objective is to inform interested parties of my current and past academic/ professional activities and to fulfill the requirements of the VPI&SU electronic thesis.

Academics

Bachelor of Science: Virginia Polytechnic Institute & State University, Crop and Soil Environmental Science Dept., GPA 3.79 / 4.00, May 1998.

Master of Science: Virginia Polytechnic Institute & State University, Crop and Soil Environmental Science: Soil Plant Chemistry, GPA: 3.80/ 4.00, December 2000.

Previous Research: **Heavy Metals**

(VPI&SU and Utah State University)

- Competitive Adsorption between Humic Acids and Arsenic Species on Iron Oxides
- Effects and Distribution of Arsenic Species on Radishes and Lettuce Growing in a Hydroponic Growth Medium

Current Research:

(University of Delaware)

- quick exafs experiments to monitor adsorption reactions of Ni(II), Pb(II), and As (V) on pyrophyllite.

Previous Employment

September 2000-
current

University of Delaware:

- Graduate Research Assitant in the Soil Chemistry Group of Dr. Sparks

August 1998 –
December 1999

VPI& SU:

- Teaching Assistant to the following courses:
 - Soil Environmental Chemistry (Fall 98)
 - Clay Mineralogy (Spring 99)
 - Soil Survey & Taxonomy (Fall 99)

May-July 1994-1997

BASF Ukraina:

1. Developed and translated Farm Inquiry Questionnaires for the Ukraine from templates generated by BASF farm 'Limburger Hof'.
2. Supported Ukrainian sovchos (state run farm) in assessing current and future assets (soil productivity, crop production, animal husbandry, mechanical and stationary commodities).
3. Sales Manager (temporary) for BASF Chemical Products: supervised contractual and transport logistics for BASF clientele.

**Previous
Employment
continued**

4. BASF Agro: conducted an intensive analysis of the pesticide market in the Ukraine.

October 93 – May 94

Kiev Institute for Agriculture and Technology:

- Taught English and German conversational courses

**Extracurricular
Activity**

*Made in Germany/
Austria
(VPI&SU)*

Club President (1998 to 2000)

*Council of
International Student
Organizations
(VPI&SU)*

1. **Member at Large** (1997/98)
2. **Public Relations** (1996/97)
 - Organized with coworkers the International Week Event at VPI&SU encompassing a budget of \$15, 000;
 - Published and edited the International Week Newspaper 1997;
 - Liaison between the international student body and university administrative and support groups;
 - Modified and amended Bylaws of the organization.

*Phi Beta Delta
(VPI&SU)*

Vice President for International Students (1996, 1997)

- Initiated with coworkers the foundation for the first international honor society at VPI&SU.
- Acted as vice president for the first term of office.
- Recipient of the first International Service Award from Phi Beta Delta (1999)

*International
Undergraduate
Association
(VPI&SU)*

1. **Secretary** (1995)
2. **Board Member** (1996)
 - Reinitiated the IUA in the spring of 1995 with fellow coworkers;
 - Provided support services for newly arriving international undergraduate students;
 - Convinced the university to institutionalize a pick-up service for international students.

**Computer/ Software
Skills**

- Experience with both Macintosh and PC
- Software: Windows (3.1, 95, 98), Word, Excel, SAS, PowerPoint, PhotoShop, PageMaker.

Languages

German (native)	English (lingua academia)
Russian (semi-fluent)	French (9 years: high school/ Gymnasium)
Spanish (learner)	

Vitae

1974: born in Ludwigshafen/ Rh., Germany
 1976-1979: Moscow, USSR
 1980-1987: Speyer, Germany
 1987-1991: Karachi, Pakistan
 1991-1993: Herman Lietz- Schule Spiekeroog, Germany

1993-1997: Kiev, Ukraine; Blacksburg, VA
1998- present: Blacksburg, VA; Baven, Germany.

Nationality: German