University of Naples Federico II
Faculty of Agriculture

Department of Soil, Plant, Environmental
and Animal Production Sciences

Ph.D. in Agrobiology and Agrochemistry
XXIV Cycle

Mobility and Phyto-Availability of Arsenic in Soil-Plant System and Decontamination Techniques of Arsenic Polluted Areas

Ph. D. dissertation by
Antonio Giandonato Caporale

Supervisor	Tutor	Coordinator
Prof. Antonio Violante	Dr. Massimo Pigna	Prof. Matteo Lorito

Academic years: 2008-2011
Naples, Italy

I would like to dedicate this Ph.D. dissertation to my dear father, an honest, right and loving man, who taught me that even the largest task can be accomplished if it is done with commitment and passion, one step at a time.

TABLE OF CONTENTS

ABSTRACT

With greater public awareness of arsenic (As) poisoning in animal and human nutrition, there has been a growing interest in developing regulatory guidelines and remediation technologies for mitigating As-contaminated ecosystems. Urgent action must be taken to reduce these impacts by providing access to safe water as a basic human right. Delaying mitigation will increase death and disease.

There are several treatment technologies available to reduce As concentrations in contaminated water but most of them are cost-prohibitive for small communities or developing countries, which are likely to face expensive and technically imposing challenges to meet the maximum contaminant level of 10 µg As L^{-1}. Several models show a wide range of costs for the different technologies, which can hinder their implementation to As-contaminated sources. For these reason, it is extremely important to investigate and promote new As remediation technologies able to remove As from contaminated areas in a cheap and safe way. It is therefore necessary to conduct researches on novel sorbents at low cost, easily synthesized, or even by-products coming from production processes, available for free or at very low price.

In the present work it was evaluated the sorption of arsenate on Al-Mg and Fe-Mg layered double hydroxides (easily reproducible anionic clays at low cost) as affected by pH and varying concentrations of inorganic (nitrate, nitrite, phosphate, selenite and sulphate) and organic (oxalate and tartrate) ligands, ii) the effect of residence time on the desorption of arsenate by these ligands and iii) the kinetics of arsenate desorption by phosphate.

The Fe-Mg-LDH sorbed nearly twice the amount of arsenate compared to the Al-Mg-LDH, due, in part, to its greater surface area and lower degree of crystallinity.

Moreover, the Fe-Mg-LDH sorbed more arsenate than phosphate, in contrast to the Al-Mg-LDH, which adsorbed more phosphate than arsenate, probably because of the greater affinity of arsenate than phosphate for Fe sites and, vice versa, the greater affinity of phosphate than arsenate for Al sites.

Arsenate sorption onto the samples decreased by increasing pH, due, maybe, to the high affinity of hydroxyl ions for LDHs and/or to the value of zero point charge (pzc) of two sorbents. The rate of decline in the amount of arsenate sorbed was, however, relatively constant, decreasing the fastest for the Fe-Mg-LDH compared to the Al-Mg-LDH.

The capacity of ligands to inhibit the fixation of arsenate followed the sequence: nitrate < nitrite < sulphate < selenite < tartrate < oxalate << phosphate on Al-Mg-LDH and nitrate < sulphate ≈ nitrite < tartrate < oxalate < selenite << phosphate on Fe-Mg-LDH. The inhibition of arsenate sorption increased by increasing the initial ligand concentration and was greater on Al-Mg-LDH than on Fe-Mg-LDH, evidently because arsenate anions have a stronger affinity for Fe than Al and for the presence in Fe-Mg-LDH of short-range-ordered materials on which arsenate forms very strong inner-sphere complexes not easily desorbable by competing ligands.

The longer the arsenate residence time on the LDH surfaces the less effective the competing ligands were in desorbing arsenate from sorbents. The effect of increasing residence time on desorbing arsenate was similar for all the ligands, for both LDHs. However, for the Al-Mg-LDH systems with phosphate, tartrate and oxalate, more arsenate was desorbed compared to the Fe-Mg-LDH systems for the same residence time. The amounts of arsenate desorbed by phosphate from the LDHs increased with time, being characterized by an initially very fast desorption reaction followed by a much slower desorption reaction until a plateau was reached. A greater percentage of arsenate was removed by phosphate from Al-Mg-LDH than from Fe-Mg-LDH, suggesting that the main difference between the two LDHs was in the amount of more easily desorbable arsenate.

In the present work, it was also studied the arsenate sorption by Fe- and Al-based drinking-Water Treatment Residual samples (by-products coming from drinking-water treatment plants) as a function of WTRs particles size at different initial As concentrations and solid:solution ratios (SSRs). This study was conducted in the Earth and Environmental Studies Department of the Montclair State University (Montclair, NJ, USA), in collaboration with Dr. Dybiendu Sarkar and his group of research. Specifically, it was studied the arsenate sorption capacity of four different sub-samples of Fe- and Al-based WTR, each characterized by a its own particles size: 1000-590 µm, 590-250 µm, 250-125 µm and < 125 µm.

Both WTR samples show a high affinity for arsenate. Anyway, the Al-WTR samples, characterized by a higher surface area (104.9 m^2 g^{-1}), were able to sorb much greater amounts of arsenate than the Fe-WTR, with a lower surface area (27.5 m^2 g^{-1}).

Al-WTR samples sorbed almost all arsenate loaded with solutions containing the lower concentrations of arsenate, at all SSRs, with no significant difference among different Al-WTR particles sizes. This considerable arsenate sorption capacity of the Al-WTR is probably due to the high external and internal specific surface area. With higher concentrations of arsenate in solution, arsenate sorption on Al-WTR were affected by SSRs and WTRs particles sizes. The greater the SSR, the higher the amounts of AsO_4 sorbed on Al-based WTR samples. The influence of particles size on the arsenate sorption capacity of the Al-WTR appeared evident with solutions containing higher arsenate concentrations, where, surprisingly, the biggest the Al-WTR particles the highest was the arsenate sorption capacity, whereas the smallest the Al-WTR particles the lowest the arsenate sorption capacity.

Fe-WTR sample showed a lower arsenate sorption capacity with respect to that of Al-WTR. However, the influence of Fe-WTR particles size on the arsenate sorption capacity was greatly pronounced when compared to that of the Al-WTRs. The smallest Fe-WTR particles were able to sorb much more arsenate than the bigger ones. The lower the arsenate concentration in solutions, the higher the difference in arsenate sorption capacity occurred among the smallest Fe-WTR particles size and the bigger ones. The influence of the SSRs on the arsenate sorption by different Fe-WTR particles also occurred and it was much more pronounced for the smallest Fe-WTR particles.

The implementation of decontamination systems of As-contaminated waters by providing for LDHs and/or WTRs use would be able to combine the lower costs of remediation and effective removal of the metalloid from them.

The presence of As in soils and/or groundwaters used for agricultural purposes, causes a strong abiotic stress to the cultivated plants, which manifests itself through the reduction of biomasses and, specially, yields, mostly non-tradable, both for the size that the high As-concentration. It is therefore desirable to identify and develop production techniques capable of limiting the mobility and phyto-availability of As in soil, through the stabilization of the metalloid on the more recalcitrant soil fractions. Incorporation of low-cost, widely available materials as compost into soil for As immobilization offers various potential advantages over other methods such as cost, simple methodology and low environmental impact. In the present work it was carried out an experiment on an edible plant, the bean *(Phaseolus vulgaris* L.), irrigated with different solutions containing arsenite and grown in a As-uncontaminated soil amended by increasing amounts of stabilized compost. The aims of this experiment were to: i) study the influence of the compost application on the mobility and phyto-availability of As in soil; ii) study the influence of the compost on the growth of the bean plants and their uptake of As from contaminated systems. Bean was selected as the test plant of this study, because this crop is grown in several As-contaminated areas and suffers from As toxicity.

Bean plants growth (roots, shoots and beans dry matter production) was significantly affected by As and compost treatments. Increasing As concentration in the irrigation water decreased markedly the dry biomass of bean plants, indicating the phytotoxic effect of As. The influence of compost application on bean plants growth was also significant, indicating the ameliorative influence of compost in alleviating the phytotoxicity of As. The major effect of compost application was realized on the bean yield, where the higher the amounts of compost application, the lower the decrease of bean yield occurred at increasing As concentration in irrigation solutions.

As a result of many negative effects on plants, As causes a reduction of the photosynthesis rate and damages the chloroplasts membranes and their structure. By increasing As concentration in irrigation water, in fact, bean leaves showed a decrease in both chlorophyll A and B concentration in leaves. However, by compost application there was an increase of both chlorophylls concentration.

Arsenic concentration in roots was higher than that in shoots and bean yield, in all experimental treatments. Indeed, bean plants showed a typical behavior of the plants sensitive to As toxicity, which usually tend to limit the As translocation from roots to shoots and yield. Moreover, the compost application reduced the As concentration in all tissues of the amended plants than those non-amended. A low As allocation in bean yield is definitely desirable, because a high content of As in edible part of the plant could cause contamination of the human food-chain, being beans a low-cost proteins source and a staple food in many Countries around the world.

Phosphorus (P) concentration in roots, shoots and bean yield significantly increased by compost application, particularly in the shoots and bean yield. The higher the compost application the higher the P concentration occurred in plant tissues, whereas the higher the As concentration in irrigation water, the lower the P concentration in roots, shoots and bean yield. Non-resistant plants can be made more resistant to As by raising their P status, as the P is taken more effectively compared to As.

The concentration of the free-fraction of As in soil samples (non-specifically sorbed As) decreased significantly by increasing amounts of compost application, whereas the higher the compost application the higher the concentration of specifically sorbed As by soil colloidal particles. Moreover, by increasing As concentration in irrigation solutions there was an increase of both concentrations of As non- and specifically sorbed in soil samples.

The use of a modern soil amendant as compost in the present work, in addition to improve bean plants growth and their nutritional status, has allowed to limit the As uptake by biomasses, through the immobilization of the metalloid, derived by irrigation water, on/in their humified organic macromolecules. Furthermore, the supply of nutrients through an organic fertilizer as compost falls within the context of organic farming, eco-friendly production system, which ensures the sustainability of the soil, improving its fertility.

CHAPTER 1 - INTRODUCTION

1.1 Arsenic

Arsenic (As) is the 33rd element of the periodic table of the chemical elements, belonging to group 15 (old group 5), its atomic number is 33 and while it is classified formally as a metalloid, meaning that it displays some properties of both a metal and a nonmetal, it is frequently also referred to as a metal and in the context of toxicology as a heavy metal (Mandal and Suzuki, 2002). Arsenic comes from the Greek word *arsenikos* which means male or masculine. It has been a known element since the ancient times. It was discovered by Albertus Magnus of Germany in 1250. This element is known for being poisonous however it was discovered that some of its compounds are also medicinal. One naturally occurring isotope of As exists, As-75. When heated, As does not melt, as most solids do, instead, it changes directly into a gas (sublimation). However, under high pressure, As can be forced to melt at about 814 °C. Arsenic has a density of 5.72 g cm^{-3}.

Arsenic is ubiquitous in nature and its abundance ranks 20th in the Earth's crust, 14th in seawater and 12th in the human body. Arsenic exists in nature in three allotropic forms, α (yellow), β (black), γ (grey), of the metallic state and in a number of ionic forms. It exists predominantly in nature as the oxyanion and its most common oxidation numbers are (+5), (+3) and (−3), in which the element is able to form both inorganic and organic compounds both in the environment and within the human body (Orloff et al., 2009). Arsenic binds covalently with most metals and nonmetals; in combination with other elements such as oxygen, sulfur and chlorine, the element is referred to as inorganic As and as combined with hydrogen and carbon as organic As.

Geochemical behavior of As is very similar to that of phosphorus (P), which is an important nutrient. An important difference between As and P (its neighbor in the periodic table) is the stability of their esters to hydrolysis. Adenosine triphosphate (ATP) is relatively stable whereas the corresponding compound formed with arsenate (AsO_4) is easily hydrolyzed thereby uncoupling oxidative phosphorylation; this accounts for the toxicity of AsO_4 in oxidative phosphorylation. Arsenite (AsO_3) has an affinity for sulfur and this probably accounts for its inhibition of a variety of enzymes such as pyruvate oxidase and 2-oxoglutarate dehydrogenase. It has been proposed that the tumorigenic potential of As compounds may be related to the ability of some of them to form free radicals (Yamanaka et al., 1996).

Since most As compounds lack colour or smell, the presence of As is not immediately obvious in food, water or air, thus presenting a serious human health hazard given the toxic nature of the element. Indeed, the very name As is synonymous with poison, in consequence of its long and nefarious history (Mandal and Suzuki, 2002).

Arsenic is found in rocks, soil, water, sediments, and air. It enters into the terrestrial and aquatic ecosystems through a combination of natural processes such as weathering reactions, biological activity, and volcanic emissions, as well as a result of anthropogenic activities. Excessive use of As-based pesticides and indiscriminate disposal of domestic (sewage) and industrial (timber, tannery, paints, electroplating, etc.) wastes, as well as mining activities, have resulted in widespread As contamination of soils and waterways. Arsenic in terrestrial and aquatic ecosystems attracts worldwide attention primarily because of its adverse impact on human health. The general population may be exposed to As from air, food, and water (Adriano, 2001; Sparks, 1995). Of the various sources of As in the environment, drinking water probably poses the greatest threat to human health (Smedley and Kinniburgh, 2002). People drinking As-contaminated water over prolonged periods often show typical arsenical lesions, which are a late manifestation of As toxicity. Arsenic has been unequivocally demonstrated to be both toxic and carcinogenic to humans and animals. Although trace levels of As have been shown to be beneficial in plant and animal nutrition (Leonard, 1991; Smith et al., 1998; USEPA, 1993), no comparable data are available for humans (Adriano, 2001), and elevated concentrations of As in the biosphere pose a significant threat to mankind.

Arsenic contamination of surface- and ground-waters occurs worldwide and has become a socio-political issue in several parts of the globe. For example, several million people are at risk from drinking As-contaminated water in West Bengal (India) (Chakraborti et al., 2002; Chatterjee et al., 1995) and Bangladesh (Smith et al., 2000). Scores of people from China (Wang, 1984), Vietnam (Berg et al., 2001), Taiwan (Lu, 1990), Chile (Smith et al., 1998), Argentina (Hopenhayn-Rich et al., 1998), and Mexico (Del Razo et al., 1990) are likely at risk as well.

The problem of As contamination in groundwaters of West Bengal and Bangladesh has been considered of calamitous proportion because a significant segment of the population is at high risk, with untold number already suffering from irreversible effects of As poisoning (Chatterjee et al., 1995).

Generally, As concentrations in uncontaminated soils seldom exceed 10 mg kg^{-1}. However, anthropogenic sources of As have elevated the background concentration of As in soils (Adriano, 2001). Indiscriminate disposal of industrial and mining wastes has led to extensive contamination of lands. Consequently, thousands of As-contaminated sites have been reported around the world (Eisler, 2004; ETCS, 1998; Smith et al., 1998; USEPA, 1997). The economic consequences of As contamination include loss of productivity, healthcare costs, and, most importantly, imposition of As contamination as a nontariff trade barrier, preventing export sales to some Countries.

With greater public awareness of As poisoning in animal and human nutrition, there has been growing interest in developing guidelines and remediation technologies for mitigating As-contaminated ecosystems. A range of technologies, including chemical immobilization and bioremediation, has been applied with varying levels of success either to completely remove As from the system or to reduce its biotoxicity. Phytoremediation, an emerging form of bioremediation technology that uses plants to remove or stabilize contaminants, may offer a low-cost and ecologically viable means for the mitigation of As toxicity in the environment.

1.1.1 Origin and sources of As contamination

A range of As compounds, both organic and inorganic, are introduced into the environment through geological (geogenic) and anthropogenic (human activities) sources. Small amounts of As also enter the soil and water through various biological sources (biogenic) that are rich in As (Figure 1; Mahimairaja et al., 2005).

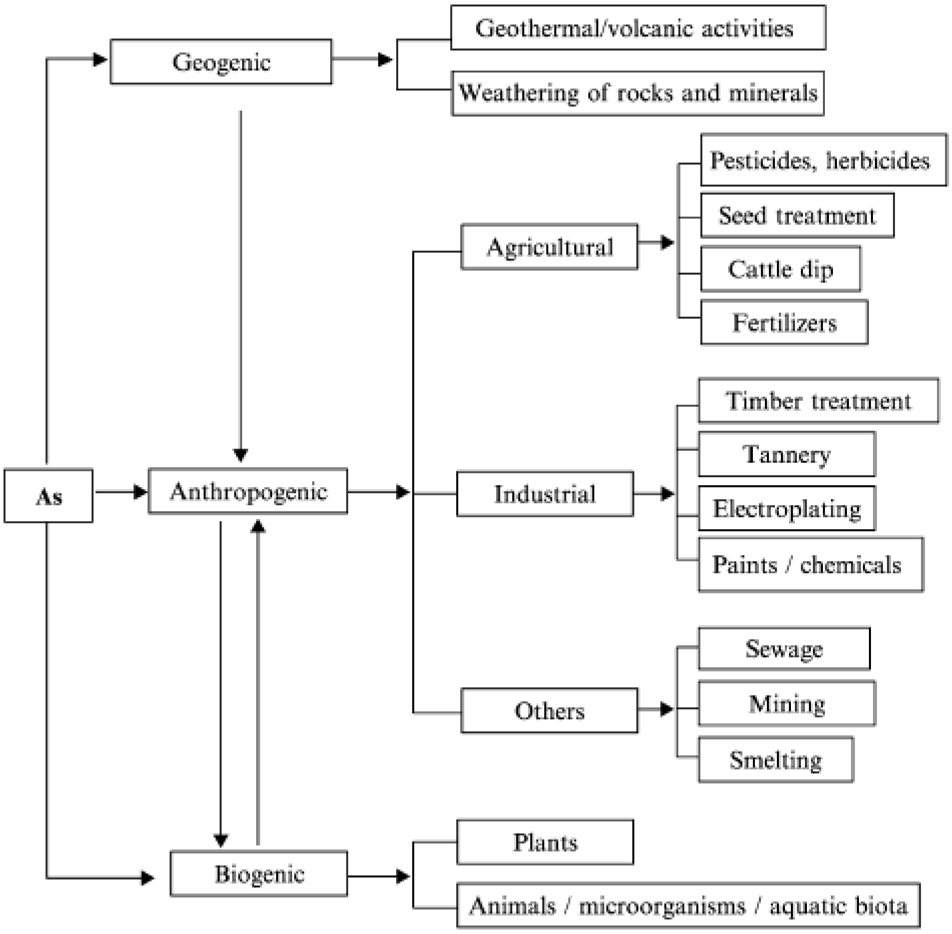


Figure 1 Major sources and routes of As in soil and aquatic ecosystems.

1.1.1.1 Geological sources

Arsenic is widely distributed in all geological materials at varying concentrations. An average concentration of 1.5 to 2.0 mg As kg^{-1} is expected in the continental crust of the earth. The mean concentrations of As in igneous rocks range from 1.5 to 3.0 mg kg^{-1}, whereas in sedimentary rocks range from 1.7 to 400 mg kg^{-1} (Smith et al., 1998).

Arsenic is widely distributed in a variety of minerals, but commonly occurs as arsenides of iron, copper, lead, silver, and gold, or as sulfides (Boyle and Jonasson, 1973; Reindel and Eikmann, 1986). It is a major constituent in more than 245 minerals (O'Neill, 1995). Realgar (As_4S_4) and orpiment (As_2S_3) are the two common As sulfides where As occurs in reduced form while As occurs in oxidized form in the mineral arsenolite (As_2O_3). loellingite ($FeAs_2$), safforlite (CoAs), niccolite (NiAs), rammelsbergite ($NiAs_2$), arsenopyrite (FeAsS), cobaltite (CoAsS), enargite (Cu_3AsS_4), gerdsorfite (NiAsS), glaucodot [(Co,Fe)AsS], and elemental As are other naturally occurring As-bearing minerals (Greenwood and Earnshaw, 1984).

Arsenic is released in the natural environment through natural processes such as weathering of rocks and minerals followed by subsequent leaching and runoff and volcanic eruptions and may be transported over long distances as suspended particulates through water or air. Therefore, the primary source of As in soil is the parent (or rock) materials from which it is derived (Yan-Chu, 1994). Geogenic contamination of As in soils and water has been reported in many parts of the world. One typical example is the extensive As contamination of groundwaters in Bangladesh and West Bengal in India.

Relatively high concentrations of naturally occurring As can appear in some areas as a result of inputs from geothermal sources or As-rich groundwaters (Smedley and Kinniburgh, 2002).

Arsenic concentration is usually higher in soil and shales than in earth crust because of its continuous accumulation during weathering and translocation in colloidal fractions. Arsenic may also be coprecipitated with Fe hydroxides and sulfides in sedimentary rocks. Therefore, Fe deposits and sedimentary Fe ores are rich in As, and the soils derived from such sedimentary rocks may contain as high as 20 to 30 mg As kg^{-1} (Zou, 1986). Arsenic in the natural environment occurs in soil at an average concentration of about 5 to 6 mg kg^{-1} (i.e., background level), but this varies among geological regions (Peterson et al., 1981).

Natural emission of As in the atmosphere is estimated to be around 2.8 gigagrams year^{-1} as dust and 21 gigagrams year^{-1} as volatile phases. These sources include windblown dust from weathered continental crust, forest fires, vegetation emissions, volcanoes, sea spray, hot springs, and geysers (Pacyna, 1986; Nordstrom, 2000). Volcanoes are also considered as a geogenic source of As to the environment with the total atmospheric annual emissions from volcanoes being estimated at 31,000 mg (Smith et al., 1998; Walsh et al., 1979). Emissions of As from volcanic eruptions vary considerably, as high as 8.9 gigagrams year^{-1} from Mount Saint Helens in the United States to about 0.04 gigagram year^{-1} from Poas in Costa Rica (Pacyna, 1986). Arsenic emission through volcanic eruptions is mostly in the form of dust, ca. 0.3 gigagram year^{-1} compared to nearly 0.01 gigagram year^{-1} as volatile forms (Lantz and Mackenzie, 1979).

Arsenic concentration in seawater is reported to be around 2.6 µg L^{-1} (Turekian, 1968), while rainwater derived from uncontaminated mass of oceanic air contains an average 19 ng As L^{-1} (Andreae, 1980). In natural lakes, levels of As range from 0.2 to 56 µg L^{-1} (Crecelius, 1975), but a level as high as 15 mg L^{-1} has been reported in Mono Lake, in California (Maest et al., 1992). River water contains low As, but a significant partitioning is observed among the As concentrations in the suspended particulates and the aqueous phase (Ferguson and Gavis, 1972). High levels of As are noted in both dissolved and particulate phases in rivers influenced by contamination from anthropogenic sources in Europe and North America (Seyler and Martin, 1991).

The cycling of As is caused by the interactions of natural water with bedrock, sediments and soils as well as the influence of local atmospheric deposition.

Weathering and leaching of geological formations and mine wastes result in elevated concentrations of As in natural waters in several areas. Mobility of As is constrained in the surface water because of the prevalence of oxic conditions. On the other hand, reducing conditions offered by the aquifers lead to the mobilization of As, thereby increasing the risk of groundwater contamination. Natural occurrence of As is widely reported in groundwater in several parts of the world, and the concentrations vary significantly depending on the redox characteristics of the groundwater and the lithological characteristics of the bedrock (Bhattacharya and Jacks, 2000; Bhattacharya and Welsh, 2000).

1.1.1.2 Anthropogenic sources

Arsenic is also being introduced into the environment through various anthropogenic activities. These sources release As compounds that differ greatly in chemical nature (speciation) and bio-availability. Mining, smelting, and ore beneficiation, pesticides, fertilizers, and chemical industries, thermal power plants using coal, wood preservation industries using CCA, and incinerations of preserved wood wastes contribute to significant influx of As to the environment (Tamaki and Frankenberger, 1992). The flue gases and particulate from smelters can contaminate nearby ecosystems downwind from the operation with a range of toxic metal(loid)s, including As (Adriano, 2001).

Global emissions of As in the atmosphere have been estimated to be 0.019 gigagram (0.012-0.026 gigagram), but in soil and aquatic environment, the estimated figures are 0.082 and 0.042 gigagram, respectively (Nriagu and Pacyna, 1988). However, there has been a substantial decrease in the atmospheric emission of As in Europe, from circa 0.005 gigagram in 1986 to 0.00031 gigagram in 1995 (Voldner and Smith, 1989; UN/ECE 1999).

Major sources of As discharged onto land originate from commercial wastes (~ 40 %), coal ash (~ 22 %), mining industry (~ 16 %) and the atmospheric fallout from the steel industry (~ 13 %) (Eisler, 2004; Nriagu and Pacyna, 1988). Arsenic trioxide (As_2O_3) is used extensively in the manufacturing of ceramic and glass, electronics, pigments and antifouling agents, cosmetics, fireworks, and Cubased alloys (Leonard, 1991). Arsenic is also used for wood preservation in conjunction with copper (Cu) and chromium (Cr), i.e., copper-chromium-arsenate (CCA).

Mining and ore beneficiation. Because As is widely distributed in the sulfide ores of Pb, Zn, Au, and Cu, it is released during their mining and smelting processes. Elevated concentrations of As, as well as other metals such as Cd, Cu, Fe, Pb, Ni and Zn, are commonly encountered in the acid mine effluents. The principal source of As in mine tailings is the oxidation of arsenopyrite (FeAsS) following the reaction:

$$FeAsS\ (s) + 13Fe^{3+} + 8H_2O \leftrightarrow 14Fe^{2+} + SO_4^{2+} + 13H^+ + H_3AsO_4\ (aq)$$

Arsenopyrite can be oxidized by both O_2 and Fe(III), but the rate of oxidation by Fe(III) is faster than for pyrite (Rimstidt et al., 1994). The rate of this reaction was reported as 1.7 $\mu mol\ m^{-2}\ s^{-1}$, a reaction faster than a similar oxidation reaction for pyrite. Under extremely acidic environment, with a pH of about 1.5 and an aqueous As concentration at > 10 mmol L^{-1}, As precipitates as scorodite ($FeAsO_4 \cdot 2H_2O$) (Dove and Rimstidt, 1994). Under acidic conditions (pH < 3), AsO_4 may substitute sulphate in the structure of jarosite [$KFe_3(SO_4)_2(OH)_6$] in different mine wastes (Foster et al., 1998). Adsorption of As on $Fe(OH)_3$ surfaces was found to be the principal sink for As in studies of acid mine drainage (Webster et al., 1994). However, the adsorption of As by $Fe(OH)_3$ may be only transient as changes in redox conditions (Eh) and pH may result in dissolution of $Fe(OH)_3$ with consequent mobilization of As. Effluents and water in tailings ponds are often treated with lime to increase pH levels to stabilize the dissolved As and other metals as precipitates.

Agriculture. Over hundreds of years, inorganic arsenicals (arsenic trioxide, arsenic acid, arsenates of Ca, Cu, Pb and Na, and arsenites of Na and K) have been widely used in pigments, pesticides, insecticides, herbicides, and fungicides (Chisholm, 1972). At present, As is no longer used in agriculture in the developed Countries, but persistence of the residues of the inorganic arsenicals in soils is an issue of environmental concern (Smith et al., 1995). The use of horticultural pesticides, lead arsenate ($PbAsO_4$), calcium arsenate ($CaAsO_4$), magnesium arsenate ($MgAsO_4$), zinc arsenate ($ZnAsO_4$), zinc arsenite [$Zn(AsO_2)_2$], and Paris Green [$Cu(CH_3COO)_2 \cdot 3Cu(AsO_2)_2$] in orchards has contributed to soil As contamination in many parts of the world (Merry et al., 1983; Peryea and Creger, 1994). Soil contamination due to the use of organoarsenical herbicides such as monosodium methanearsonate (MSMA) and disodium methanearsonate (DSMA) was also reported (Gilmore and Wells, 1980; Smith et al., 1998). The use of sodium arsenite ($NaAsO_2$) to control aquatic weeds has contaminated small fish ponds and lakes in several parts of United States with As (Adriano, 2001). Arsenic contamination in soil was also reported due to the arsenical pesticides used in sheep and cattle dips to control ticks, fleas, and lice (McBride et al., 1998; McLaren et al., 1998).

Studies by Kenyon et al. (1979) and Aten et al. (1980) have indicated elevated concentrations of As in vegetables grown in soils contaminated by lead arsenate used as an insecticide in apple orchards. The recalcitrant nature of arsenical herbicides has, however, been observed in agricultural soils particularly around old orchards (Bishop and Chrisholm, 1962). Biomethylation of As (Challenger, 1945; Challenger et al., 1954) is a mechanism through which a significant quantity of methylarsines may be released into the atmosphere following the application of As compounds to the soil. A relatively faster production of dimethyl- and trimethylarsines has been reported from grasslands treated with methylarsenic compounds while grass treated with sodium arsenite indicated slow release of methylarsene into the atmosphere.

Industries that manufacture As-containing pesticides and herbicides release As-laden liquid and solid wastes that, upon disposal, are likely to contaminate soil and water bodies. For example, indiscriminate discharge of industrial effluents from the manufacturing of Paris Green (copper acetoarsenite, an arsenical pesticide) resulted in the contamination of soil and groundwater in residential area of Calcutta, India (Chatterjee et al., 1999). Similarly, in New Zealand, timber treatment effluent is considered to be the major source of As contamination in aquatic and terrestrial environments (Bolan and Thiyagarajan, 2001). Continuous application of fertilizers that contain trace levels of As also results in As contamination of soil, thereby reaching the food chain through plant uptake (McLaughlin et al., 1996).

Wood Preservation. The use of CCA and other As-based chemicals in wood preservation industries has caused widespread contamination of soils and aquatic environments (Carnö, 1983; Bergholm and Dryler 1989; Bergman, 1991; Bhattacharya et al., 1995; Bhattacharya et al., 1996). CCA had attained wide-scale industrial application as a wood preservative owing to biocidic characteristics of Cu(II) and AsO_4. The preservative chemical used for pressure impregnation comprises a waterbased mixture of dichromic acid ($H_2Cr_2O_7$), arsenic acid (H_3AsO_4), and Cu(II) as divalent cation at variable proportions (Jacks and Bhattacharya, 1998). Chromium is used to bind As and Cu into the cellular structure of the wood. Fixation of CCA is dependent on the transformation of Cr(VI) to Cr(III), a reaction that is dependent on the temperature and water content of the wood. Cr(III) forms insoluble complexes with both As and Cu (Ryberg and Haugen, 1992). Further stabilization of these complexes takes place after complete fixation of the As and Cu in the wood tissues and minimizes the risk of leaching of the CCA components from the processed wood. Among the active ingredients of CCA wood preservatives, As is most mobile and toxic to a broad range of organisms, including human beings.

Studies around an abandoned wood preservation site at Konsterud, Kristinehamns Community in Central Sweden (Bhattacharya et al., 1995; Bhattacharya et al., 1996) revealed soil As concentrations between 10 and 1,067 mg kg^{-1}, and the order of abundance for metal contaminants was found to be As > Zn > Cu ≥ Cr. Sediments in a drain adjacent to the cemented impregnation platform contained an average 632 mg As kg^{-1}. Arsenic concentrations in the reference soils (119 mg kg^{-1}) were lower than in the contaminated area, but exceeded the level of As in average glacial till (Koljones, 1992). Analyses of water in a stream found As concentration of 238 µg L^{-1} (Bhattacharya et al., 1995). Groundwater contamination must therefore be considered as an imminent risk close to wood preservation sites, and especially at older sites where precautions against spills and material handling were not taken adequately.

Coal Combustion and Incineration of Preserved Wood Products. Coal combustion not only releases gaseous As into the atmosphere, but also generates fly and bottom ash containing varied amounts of As. Disposal of these materials often leads to As contamination of soil and water (Beretka and Nelson, 1994).

Combustion of high-As-bearing coals is known to be a principal pathway of As emission in the Guizhou province of southwestern China (Zheng et al., 1996). Open coal-burning stoves used for drying chili peppers have been the principal cause of chronic As poisoning in a population of nearly 3,000. Fresh chili peppers have less than 1 mg As kg^{-1}, while chili peppers dried over high-As coal fires were reported to contain more than 500 mg As kg^{-1} (Zheng et al., 1996). Consumption of other tainted foods, ingestion of kitchen dust containing as high as 3,000 mg kg^{-1} As, and inhalation of indoor air polluted by As from coal combustion are the other causes of chronic As poisoning.

A possible pathway for exposure through air particulates is the incidental use of preserved wood in open fires, indoors or outdoors. Incineration of CCA impregnated wood from a sawmill was found to be a source of As contamination to the environment (Aggett and Aspell, 1980). The content of As in air particulates from open fires was found to exceed the German air quality standards by 100-fold (Bringezu et al., 1990). The ashes, spread on lawns or vegetable cultivations, pose further risk to human health. In addition, tobacco smoke is another source of As emission in the indoor environment. It is interesting to note that mainstream cigarette smoke contains 40-120 ng As per cigarette (USEPA, 1994).

1.1.1.3 Biogenic redistribution

Biological sources contribute only small amounts of As into soil and water ecosystems. However, plants and micro- and macroorganisms affect the redistribution of As through their bioaccumulation (e.g., biosorption), biotransformation (e.g., biomethylation) and transfer (e.g., volatilization).

Arsenic accumulates readily in living tissues because of its strong affinity for proteins, lipids and other cellular components (Ferguson and Gavis, 1972).

Aquatic organisms are particularly known to accumulate As, resulting in considerably higher concentrations than in the water in which they live (i.e., biomagnification). Upon disposal or consumption they subsequently become a source of environmental contamination. Arsenic could be transferred from soil to plants and then to animals and humans, involving terrestrial and aquatic food chains. For example, poultry manure addition is considered to be one of the major sources of As input to soils. In the Delaware-Maryland-Virginia peninsula along the eastern shore of the United States, 20-50 mg of As is introduced annually to the environment through the use of As compounds (e.g., Roxarsone, ROX) in poultry feed (Christen, 2001). However, in many situations the soil-plant transfer of As is low (Smith et al., 1998) and it is important to recognize that metal(loid)s loading through manure application may overestimate their actual net accumulation in soil, as a substantial portion of the metal(loid)s in manure originate in crop uptake and are therefore being recycled within a production system (Bolan et al., 2004).

1.1.2 Arsenic distribution in soil

In soils, As forms a variety of inorganic and organic compounds (Vaughan, 1993). Arsenic forms solid precipitates with Fe, Al, Ca, Mg and Ni. A number of studies involving solid phase speciation have shown that As is prevalent mostly in the oxalate fractions associated with amorphous and crystalline Fe and Al oxides, indicating the strong affinity of As for these soil components (Wenzel et al., 2001). The soluble As concentration in soil is largely determined by redox conditions, pH, biological activity, and adsorption reactions. The adsorption and mobility of As in soil are affected more strongly by the presence of PO_4 ion than any other anions. Arsenic is subject to both chemical and biological transformations in soils, resulting in the formation of various species.

In soil, As occurs both as inorganic [AsO_3 and AsO_4] and as organic forms. Trivalent As can exist as arsenous oxide (As_2O_3), arsenious acid ($HAsO_2$), arsenite ($H_2AsO_3^-$, $HAsO_2^{2-}$, AsO_3^{3-}) ions, arsenic trichloride ($AsCl_3$), arsenic sulfide (AsS_3), and arsine (AsH_3). Pentavalent As commonly occurs as arsenic pentoxide (As_2O_5), orthoarsenic acid (H_3AsO_4), metaarsenic acid ($HAsO_3$), and arsenate ($H_2AsO_4^-$, $HAsO_4^{2-}$, AsO_4^{3-}) ions. The presence of different forms of organic As, such as monomethylarsonic acid [MMA, $CH_3AsO(OH)_2$], dimethylarsenic acid [DMA, $(CH_3)_2AsO(OH)$], trimethylarsine oxide [$(CH_3)_3AsO$], methylarsine (CH_3AsH_2), dimethylarsine [$(CH_3)_2AsH$] and trimethylarsine [TMA, $(CH_3)_3As$], has also been observed in contaminated soil (Gao and Burau, 1997).

The most common forms of As in the soils are the inorganic oxyions of AsO_3 and AsO_4. In contaminated soils, generally AsO_4 predominates over AsO_3. Arsenite is more toxic and relatively mobile in contaminated soils, whereas AsO_4 is relatively less toxic. Both AsO_3 and AsO_4 compounds are highly soluble in water and may change valency states depending on the pH and redox conditions. Masscheleyn et al. (1991) studied the influence of redox potential and pH on As speciation and solubility in a contaminated soil. They observed that alterations in the oxidation state of As, as influenced by redox potential and pH, greatly affected its solubility in soil. At oxic redox levels (500-200 mV), As solubility was low and the major part (65-98 %) of the As in soil solution was present as AsO_4. At alkaline pH, the reduction of AsO_4 to AsO_3 released substantial proportions of As into solution. Under moderately reducing conditions (0-100 mV), As solubility was controlled by the dissolution of Fe oxyhydroxides. At an anoxic redox level of -200 mV, soluble As increased 13-fold as compared to an oxic redox level of 500 mV. The apparent slow kinetics of the AsO_4 to AsO_3 transformation and the high concentrations of Mn indicate that, under reducing conditions, As solubility could be controlled by the $Mn_3(AsO_4)_2$ phase.

Both inorganic and organic species of As undergo various biological and chemical transformations in soils, including adsorption, desorption, precipitation, complexation, volatilization, and methylation (Figure 2; Mahimairaja et al., 2005). The most thermodynamically stable species of AsO_3 (i.e., H_3AsO_3 and $H_2AsO_4^-$) and AsO_4 (i.e., $HAsO_4^{2-}$) occur over the normal soil pH range of 4.0 to 8.0.

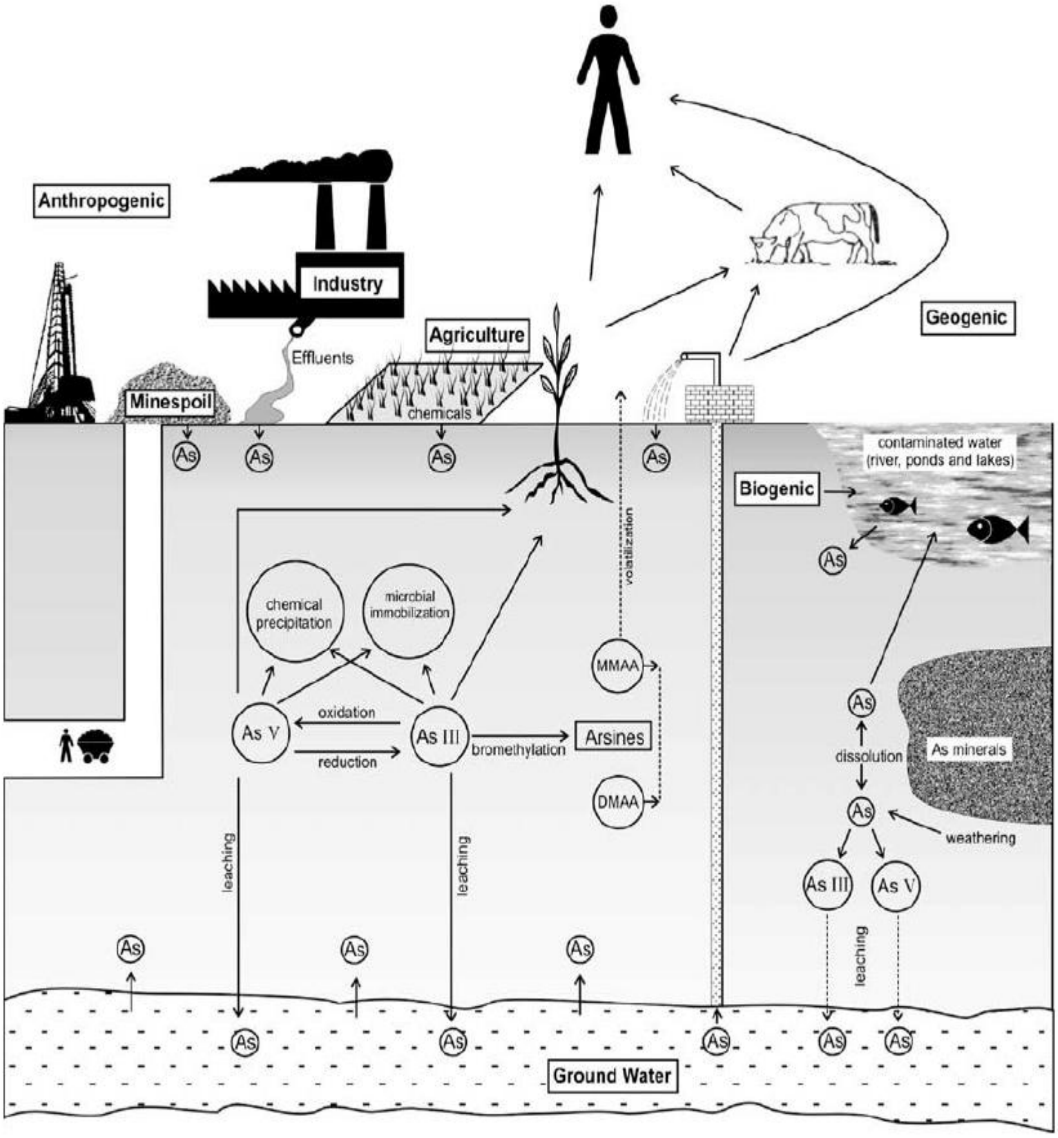


Figure 2 Arsenic dynamics in contaminated soil and aquatic ecosystems.

1.1.3 Arsenic distribution in the aquatic environment

Arsenic in an aquatic environment is distributed in both the aqueous solution and sediments. Elevated concentrations of As in natural waters are usually associated with As-rich sedimentary rocks of marine origin, weathered volcanic rocks, fossil fuels, geothermal areas, mineral deposits, mining wastes, agricultural use, and irrigation practices (Korte and Fernando, 1991).

Uncontaminated waters usually contain less than 0.001 µg As L^{-1}. In contaminated areas, however, high levels of As have been reported in water bodies. It would be noted that considerable variation in As concentration exists within the same geological area as reported by different researchers. The World Health Organization (WHO, 2004; USEPA, 2006) recommends that the As concentration in drinking water not exceed 10 µg L^{-1}.

As discussed earlier, one of the principal causes of high As concentrations in subsurface waters is the reductive dissolution of hydrous Fe oxides and/or the release of adsorbed As (Smedley and Kinniburgh, 2002). Deuel and Swoboda (1972), proposed that the release was primarily due to reduction (and dissolution) of ferric arsenates instead of changes in the As speciation.

The high As in groundwater can be associated with reducing conditions, resulting from the presence of dissolved organic carbon, particularly in alluvial and delta environments. The groundwater of the Bengal basin is the most notable example. While the exact mechanisms responsible for this remain uncertain, it is possible that both reductive dissolution and desorption of As from oxides and clay play an important role in elevating As concentration (Smedley and Kinniburgh, 2002).

A significant proportion of As in aquatic environment is derived from the sediments, and the relative distribution of As in water and sediments depends mainly on the nature and amounts of sediments.

Arsenic in river sediments is highly variable, ranging from 32.8-42.7 mg kg^{-1} (Australia) (Taylor, 1996) to 8,700-156,100 mg kg^{-1} (New Zealand) (Robinson et al., 1995). The As-rich sediments act as a buffer in maintaining the As concentration in water bodies, thereby controlling the dynamics and bioavailability of As in the aquatic environment.

Arsenic is stable in four oxidation states (+5, +3, 0, −3) under the Eh conditions that occur in aquatic systems. At high Eh values (mostly exist in oxygenated waters), arsenic acid species (i.e., H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-}) are stable. At mildly reducing conditions, arsenious acid species (i.e., H_3AsO_3, $H_2AsO_3^-$ and $HAsO_3^{2-}$) become stable (Korte and Fernando, 1991). The speciation of As in aquatic environment is critical in controlling the adsorption/desorption reactions with sediments.

Adsorption to sediment particles may remove AsO_4 from contaminated water, as well as inhibiting the precipitation of As minerals such as scorodite ($FeAsO_4 \cdot 2H_2O$) that control the equilibrium aqueous concentration (Foster et al., 1997).

Under the aerobic and acidic to near-neutral conditions (typical of many aquatic environments), AsO_4 is adsorbed very strongly by oxide minerals in sediments. The highly nonlinear nature of the adsorption isotherm for AsO_4 in oxide minerals ensures that the amount of As adsorbed is relatively large, even when dissolved aqueous concentrations of As are low. Such adsorption occurring in natural environments protects water bodies from widespread As toxicity problems. Adsorption of As species by sediments are as follows: $AsO_4 > AsO_3 >$ DMA (Smedley and Kinniburgh, 2002).

In As-contaminated sediments, Clement and Faust (1981), found that a significant portion of the As was bound in organo-complex forms and indicated that adsorption-desorption equilibrium must be considered as well as the redox effects in examining the dynamics of As in aquatic environment.

As pH increases, especially above pH 8.5, As desorbs from the oxide surfaces, thereby increasing the concentration of As in solution. Desorption of As from As-contaminated sediments at high pH is the most likely mechanism for the development of groundwater As problems under the oxidizing conditions (Robertson, 1989; Smedley et al., 2002). These adsorption and desorption reactions of As in the aquatic environment have not been studied in detail under varied ecological conditions and therefore require greater attention.

Arsenic undergoes a series of biological transformations in the aquatic environment, yielding a large number of compounds, especially organo-arsenicals. Certain reactions, such as oxidation of AsO_3 to AsO_4, may occur both in the presence and in the absence of microorganisms, whereas other reactions, such as methylation, are not thermodynamically favorable in water and can occur only in the presence of organisms. In neutral oxygenated waters, AsO_4 is the thermodynamically favored form, whereas AsO_3 is stable under reducing conditions (Ferguson and Gavis, 1972).

Some bacteria and marine phytoplankton are capable of reducing AsO_4 to AsO_3 or oxidizing AsO_3 to AsO_4 (Andreae, 1977). Biological reduction of AsO_4 to AsO_3 reportedly occurs most easily at a pH between 6.0 and 6.7 (Korte and Fernando, 1991).

The reduction of AsO_4 to AsO_3 has been attributed to biological components of the river ecosystem. This biotransformation has been reported to occur in various aquatic systems, mediated by bacteria (Johnson, 1972; Myers et al., 1973) and algae (Andreae and Klumpp, 1979; Sanders and Windom, 1980; Sanders 1983). MMA and DMA are the common organo-arsenicals in river water. Methylated As species could result from direct excretion by algae or microbes or from degradation of the excreted arsenicals or more complex cellular organo-arsenicals. Methylation may play a significant role in the mobilization of As by releasing it from the sediments to aqueous environment. The presence of organo-arsenicals in river sediments is evidence that methylation occurs in the sediments (Anderson and Bruland, 1991). The rate of methylation/demethylation reactions and the consequent mobilization of arsenicals are affected by adsorption by sediments and soils.

Primary producers such as algae take up AsO_4 from solution and reduce this to AsO_3 prior to methylation of the latter to produce MMA and DMA; the methylated derivatives are then excreted. This may be considered to represent a detoxification process in respect to the organism involved. Arsenic is taken up by algae due to its chemical similarity to PO_4. Although the detoxification of As by microorganism can be achieved through methylation, the element may be of significant toxicity to phytoplankton and periphyton communities in marine environments.

Both macro- and microorganisms accumulate As in their tissues. Concentrations in organisms may be considerably higher than in the water in which they live, but unlike mercury (Hg), there is little, if any, concentration upward through the food chain (i.e., bioaugmentation). The toxicity of As to aquatic organisms is similar to its effects on terrestrial life, i.e., AsO_4 is much less toxic than AsO_3 (Ferguson and Gavis, 1972).

Arsenate can replace PO_4 uptake in PO_4-deficient waters and can then be accumulated by algae. In a study of As accumulation in the food chain, it has been reported that most of the As accumulated by algae was in a non-methylated form, which was bound strongly to protein or polysaccharides in the algal cell (Maeda et al., 1990). Such transformation can be stimulated by adding nutrients. Microbial formation of volatile arsine or other volatile-reduced compounds may play a role in the discharge of As to the atmosphere. Arsenite can be reduced and methylated to DMA, which can be further methylated or reduced and may eventually volatilize (Korte and Fernando, 1991).

1.1.4 Toxicity to plants

Arsenic contamination of soil and water poses a serious threat to plants and animals. Plants and microorganisms are known to accumulate As in their tissues and exhibit a certain degree of tolerance. However, at high concentrations, As is toxic to nearly all forms of life.

Bio-toxicity is mostly determined by the nature and bio-availability of As species present in the contaminated habitat. An average toxicity threshold of 40 mg kg^{-1} has been established for crop plants (Sheppard, 1992).

At high concentrations, As in plants inhibits plant metabolic processes, such as photosynthesis through interference of the pentose-PO_4 pathway, thereby inhibiting growth and often leading to death (Marques and Anderson, 1986; Tu and Ma, 2002). Arsenite penetrates the plant cuticle to a greater degree than AsO_4 and generally results in the loss of turgor (Adriano, 2001).

Arsenic is accumulated mainly in the root system, to a lesser extent in the above-ground organs and causes physiological disorders (Wells and Gilmor, 1997). Biomass production and yields of a variety of crops have been shown to reduce significantly at high concentrations of As in soils (Carbonell-Barrachina et al., 1997). For example, significant yield reductions of barley (*Hordeum vulgare* L.) and ryegrass (*Lolium perenne* L.) have been reported with the application of only 50 mg As kg^{-1} soil (Jiang and Singh, 1994).

Plant uptake of As is greatly influenced by its species in soil. Arsenic has already been discussed, different species have different solubility and mobility, thereby differing in their bio-availability to plants. Marin et al. (1992) reported that the order of As availability to rice (*Oryza sativa* L.) is as follows: AsO_3 > MMA > AsO_4 > DMA. They observed that upon absorption, DMA is readily translocated to the plant shoots, whereas AsO_3, AsO_4 and MMA accumulate primarily in the roots. While the application of AsO_4 and DMA did not affect rice growth, both AsO_3 and MMA were found to be phytotoxic to rice. Burlo et al. (1999) noted that both MMA and DMA in tomato plants (*Lycopersicon esculentum* Mill.) had a greater upward translocation than AsO_3 and AsO_4.

In general, the accumulation of As in the edible parts of most plants is low (O'Neill, 1995), which is attributed to a number of reasons, including (Wang et al., 2002): i) low bioavailability of As in soil; ii) restricted uptake by plant roots; iii) limited translocation of As from roots to shoots; iv) phyto-toxicity and subsequent premature plant death at relatively low As concentrations in plant tissues. Apart from chemical forms, it has been shown that the phytotoxicity of As varies with the soil conditions. For example, Reed and Sturgis (1963) reported that As inhibits rice plant growth more strongly under submerged soil conditions than under upland soil conditions, because AsO_4 is reduced to AsO_3, which is more soluble and more toxic to plants in submerged soil. Arsenic phytotoxicity is expected to be greater in sandy soils than in other soil types, as the former soils generally contain low amounts of Fe and Al oxides and silicate clays, which have been implicated in the adsorption of As from soil solution (Sheppard, 1992; Smith et al., 1998).

The antagonistic and synergistic effects of various nutrient anions also determine the phytotoxicity of As to some extent. For example, Davenport and Peryea (1991) reported a reduction of As uptake by plants with the application of PO_4, which was attributed to PO_4 ion-induced inhibition of AsO_4 uptake by plant roots. In contrast, Woolson (1973) observed that a PO_4 application increased As availability and As uptake by plants, which was attributed to the PO_4 ion-induced release of AsO_4 to the soil solution.

The biochemical responses of plants to As stress are insufficiently studied (Hartley-Whitaker et al., 2001). Arsenic is not a redox metal. Nevertheless, there is significant evidence that exposure of plants to inorganic arsenic does result in the generation of ROS, which is connected with As valence change, a process that readily occurs in plants (Flora, 1999; Lynn et al., 1998). ROS can directly damage proteins, amino acids and nucleic acids and cause peroxidation of membrane lipids (Dat et al., 2000). To combat these effects, enzymatic and nonenzymatic antioxidants are mobilized to quench ROS.

The ability of specific plants to survive in polluted soils has been related to a variety of mechanisms of metal tolerance or detoxification, which includes chelation, compartmentalization, biotransformation and cellular repair (Gonzaga et al., 2006). There has been evidence that the ease of reducing AsO_4 to AsO_3 is a strategy that hyperaccumulator plants use to accumulate large amounts of As without developing toxicity symptoms (Ma et al., 2001). Although AsO_3 is more phytotoxic than AsO_4, once reduced AsO_3 becomes less toxic within the plant due to the formation of AsO_3-thiol complexes (-SH) and As-phytochelatins (Schmoger et al., 2000; Schat et al., 2002; Reina et al., 2005).

Most plants do not accumulate enough As to be toxic to animals and humans. Growth reductions and crop failure are the main consequences of soil As contamination (Walsh and Keeney, 1975). Thus the major hazard for animal and human systems is derived from direct ingestion of As-contaminated soil or water (Smith et al., 1998).

1.1.5 Risk to humans and animals

Drinking water is the most important source of dietary intake of As by animals and humans (Fitz and Wenzel, 2002). However, food also forms a source of As exposure (Adriano, 2001). The occurrence of inorganic As in drinking water has been identified as a source of risk for human health even at relatively low concentrations. As a consequence, more stringent safer limits for As in drinking water have been proposed (Wenzel et al., 2001).

Soluble As compounds are rapidly absorbed from the gastrointestinal tract (Hindmarsh and McCurdy, 1986). Several studies in humans indicate that both AsO_3 and AsO_4 are well absorbed across the gastrointestinal tract (USDHHS, 2000). Studies involving the measurement of As in fecal excretion in humans indicated that almost 95 % of oral intake of AsO_3 is absorbed (Bettley and O'Shea, 1975). This was supported by studies in which urinary excretion in humans was found to account for 55-80 % of daily intakes of AsO_3 or AsO_4 (Buchet et al., 1981; Crecelius, 1977; Mappes, 1977). It has also been reported that both MMA and DMA are also well absorbed (75-85 %) across the gastrointestinal tract (Buchet et al., 1981).

When air containing As dusts is breathed in, the majority of the dust particles settle onto the lining of the lungs (Chen et al., 2006). Very little internal exposure to As occurs via the material passing through the skin into the body, and so there is little risk of As poisoning posed by this route.

The majority of As enters the body in the trivalent inorganic form AsO_3 via a simple diffusion mechanism (Cohen et al., 2006). Once absorbed, simultaneous partial oxidation of AsO_3 to AsO_4 and partial reduction of AsO_4 to AsO_3 occur, yielding a mixture of AsO_3 and AsO_4 in the blood. Only a small amout of pentavalent inorganic As can cross cell membranes via an energy-dependent transport system, after which it is immediately reduced to trivalent As.

The AsO_3 may undergo enzymatic methylation primarily in the liver to form MMA and DMA, but the rate and relative proportion of methylation production vary among animal species. Most As is promptly excreted in the urine as a mixture of AsO_3, AsO_4, MMA, and DMA, and relatively smaller amounts are excreted in the feces. Some As may remain bound to tissues, depending on the rate and extent of methylation.

Monomethylarsonic acid may be methylated to DMA, but neither MMA nor DMA is demethylated to yield AsO_3 or AsO_4. Arsenic may accumulate in skin, bone, and muscle and its half-life in humans is between 2 and 40 days (USDHHS, 2000). Arsenic is toxic to the majority of organ systems, the most sensitive target organ being the kidney (Cohen et al., 2006). The extent of As poisoning depends on various factors such as dose, individual susceptibility to As and the age of the affected individuals (Figure 3). While chronic As exposure affects the vascular system and causes hypertension and cardiovascular disease, acute As toxicity may cause cardiomyopathy and hypotension.

Figure 3 Tipical symptoms of arsenicosis: spotted keratosis, melanosis, dolsal keratosis, hyper pigmentation, hyper keratosis and gangrene.

Arsenite inhibits pyruvate dehydrogenase by binding to the sulfydryl groups of dihydrolipoamide, resulting in a reduced conversion of pyruvate to acetyl coenzyme A (CoA), while both citric acid cycle activity and production of cellular ATP

are decreased (Bergquist et al., 2009). Arsenite inhibits numerous other cellular enzymes through sulfydryl group binding. It also inhibits the uptake of glucose into cells, gluconeogenesis, fatty acid oxidation and further production of acetyl CoA. Significant to oxidative stress is that AsO_3 inhibits the production of glutathione, which protects cells against oxidative damage (Miller et al., 2002).

In part, the toxicity of AsO_4 is due to its conversion to AsO_3, from which the toxic effects proceed as outlined above. At a more significant and specific level, AsO_4 emulates PO_4 and replaces PO_4 in glycolytic and cellular respiration pathways (Hughes, 2002). Uncoupling of oxidative phosphorylation occurs because the normal high-energy PO_4 bonds are not formed; e.g. in the presence of AsO_4, adenosine diphosphate (ADP) forms ADP-AsO_4 instead of ATP with the absence of the high-energy ADP-PO_4 bonds (Jomova et al., 2011).

The metabolism of inorganic As involves a two-electron reduction of AsO_4 to AsO_3, mediated by glutathione, followed by oxidative methylation to form pentavalent organic As (Figure 4; Hughes, 2002).

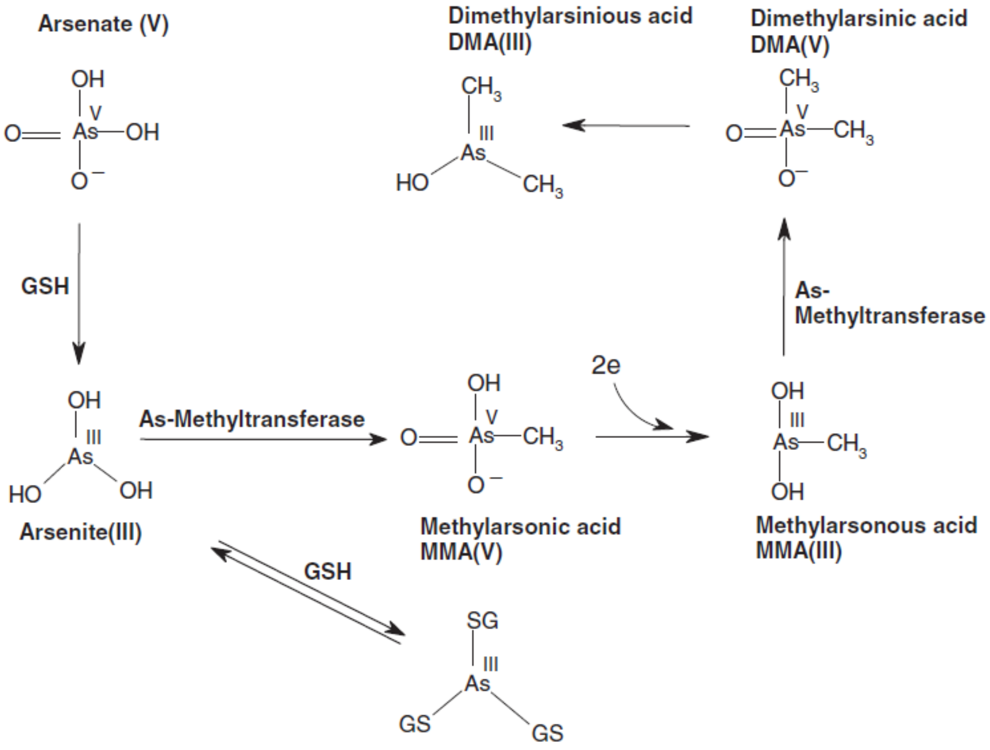


Figure 4 The metabolism of inorganic As.

Teratogenic effects of As in chicks, golden hamsters, and mice have been reported. Arsenic does not appear to be mutagenic in bacterial and mammalian assays, although it can induce chromosomal breakage, chromosomal aberration, and chromatid exchange. Studies have shown that As may be an essential element at trace concentrations for several animals such as goats, rats, and poultry, but there is no evidence that it is essential for humans (USEPA, 1988). The acute toxicity of As compounds in humans is a function of their rate of removal from the body. Arsine is considered to be the most toxic form, followed by AsO_3, AsO_4 and organic As compounds (MMA and DMA). Lethal doses in humans range from 1.5 mg kg^{-1} (diarsenic trioxide) to 500 mg kg^{-1} of body weight (DMA). Acute As intoxication associated with the ingestion of contaminated well water has been reported in many Countries.

The most common neurological effect of long-term As toxicity is peripheral neuropathy and the gastrointestinal effects are manifested by toxic hepatitis accompanied by increased levels of liver enzymes. The single most characteristic effect of long-term exposure to As is a pattern of skin changes, including hyperkeratosis (a darkening of the skin and appearance of small “corns” or “warts” on the palms, soles, and torso). A small number of the “corns” may ultimately develop into skin cancer (USDHHS, 2000).

Early symptoms of As poisoning in humans include abdominal pain, vomiting, diarrhea, muscular pain and weakness, with flushing of the skin (Armstrong et al., 1984; Cullen et al., 1995; Moore et al., 1994). These symptoms are often followed by numbness and tingling of the extremities, muscular cramping and the appearance of an erythematous rash. Further symptoms may appear within a month, including burning paraesthesias of the extremities, hyper/hypopigmentation (mottled or multicolor skin), Mee’s lines on fingernails and progressive deterioration in motor and sensory responses (Fennell and Stacy, 1981; Murphy et al., 1981).

Acute oral As poisoning at doses of 8 mg As kg^{-1} and above have been reported to affect the respiratory system (Civantos et al., 1995). A number of studies in humans have shown that As ingestion may lead to serious effects on the cardiovascular system (Cullen et al., 1995). Anemia and leukopenia were also found to be the common effects of As poisoning in humans resulting from prolonged oral exposure at doses of 0.05 mg As kg^{-1} day^{-1} or more (Armstrong et al., 1984; Mazumder et al., 1988; Saha et al., 2003). Studies have also revealed hepatic effects of As poisoning (USDHHS, 2000), as indicated by swollen and tender liver with elevated levels of hepatic enzymes in blood (Armstrong et al., 1984).

It has been reported that while As is toxic by itself, it also interacts with Se, resulting in excretion of their mutual metabolite (Gailer et al. 2000). This confounding excretion of Se can be a health concern as Se, an essential micronutrient, supports antioxidation, chemoprevention and immune-competence and low Se status is found with occurrence of illnesses such as diabetes (Can et al. 2005), some cancers (Clark et al. 1996), viral infections (Beck et al. 1994) including poliovirus (Broome et al. 2004), HIV (Baum et al. 2000), and avian H5N1 influenza.

1.1.6 Risk management of As in contaminated environments

Risk management of contaminated sites includes source reduction, site remediation and environmental protection (Figure 5; Mahimairaja et al., 2005). Selection of optimal risk management strategies requires consideration of core objectives such as technical practicability, feasibility, and cost effectiveness of the strategy and wider environmental, social, and economic impacts. Arriving at an optimal risk management solution for a specific contaminated site involves problem identification, development of problem solving alternatives (i.e., remediation technologies) and management of the site.

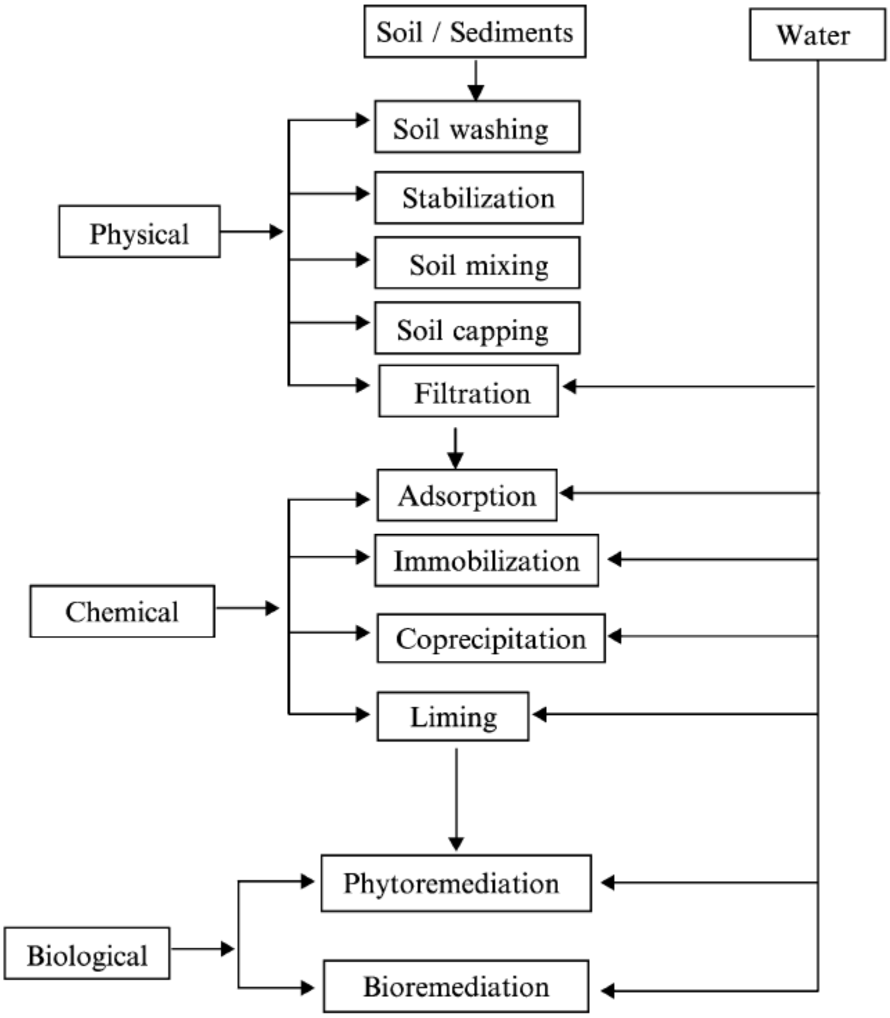


Figure 5 Viable remediation technologies for As-contaminated soil/sediment and aquatic ecosystems.

1.1.6.1 Remediation of As-contaminated soils

Remediation of As-contaminated soil involves physical, chemical, and biological approaches (Figure 6), that may achieve either the partial/complete removal of As from soil or the reduction of its bioavailability in order to minimize toxicity (Mahimairaja et al., 2005). A large variety of methods have been developed to remediate As-contaminated soils. The selection and adoption of these technologies depend on the extent and nature of As contamination, type of soil, characteristics of the contaminated site, cost of operation, availability of materials and relevant regulations.

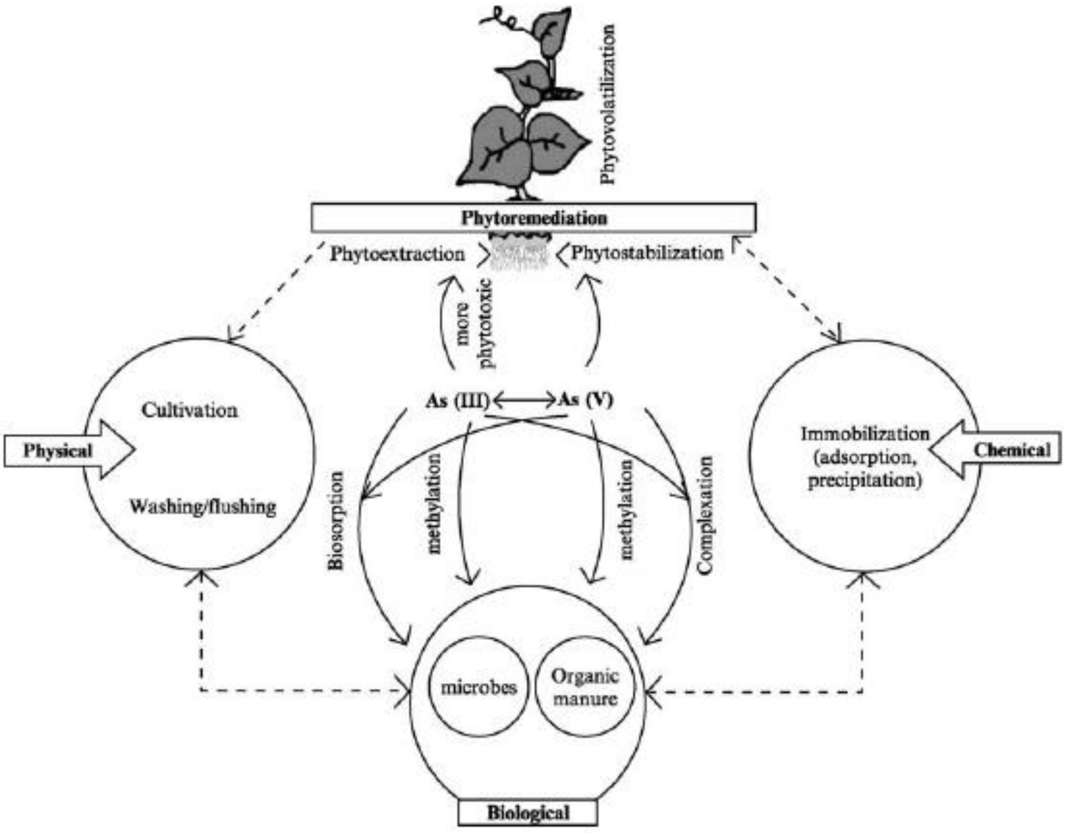


Figure 6 Conceptual integrated approach for remediation of As-contaminated soil.

1.1.6.1.1 *Physical remediation*

Major physical *in situ* treatment technologies to remediate As-contaminated soils include capping, soil mixing, soil washing and solidification.

The simplest technique for reducing the toxic concentration of As in soils is mixing the contaminated soil with uncontaminated soil. This results in the dilution of As to acceptable levels. This can be achieved by importing clean soil and mixing it with As-contaminated soil or redistributing clean materials already available in the contaminated site. Another dilution technique, especially in cultivated soils, relies on deep ploughing, during which the vertical mixing of the contaminated surface soil with less contaminated subsoil reduces the surface contamination, thereby minimizing the potential for As uptake by plants and ingestion of As by grazing animals. However, in this method the total concentration of As in soil will remain the same.

Soil washing or extraction has also been used widely for the remediation of metal(loid)-contaminated soils in Europe (Tuin and Tels, 1991) and this method may be applicable for As-contaminated soils to some extent.

The success of soil washing largely depends on speciation of As present in the contaminated soils, as it is based on the desorption or dissolution of As from the soil inorganic and organic matrix during washing with acids and chelating agents. Although soil washing is suitable for off-site treatment of soil, it can also be used for on-site remediation using mobile equipment. However, the high cost of chelating agents and choice of extractant may restrict their usage to only small-scale operations (Mahimairaja et al., 2005).

Arsenic-contaminated soil may be bound into a solid mass by using materials such as cement, gypsum, or asphalt. However, there are issues associated with the long-term stability of the solidified material. Capping the contaminated sites with clean soil is used to isolate contaminated sites as it is less expensive than other remedial options (Kookana and Naidu, 2000). Such covers should obviously prevent upward migration of contaminants through the capillary movement of soil water. The depth of such cover or cap required for contaminated sites should be assessed carefully.

1.1.6.1.2 Chemical remediation

Remediation, based on chemical reactions, is becoming increasingly popular largely because of a high rate of success. A number of methods have been developed mainly involving adsorption, immobilization, precipitation, and complexation reactions. However, such methods are often expensive for the remediation of large areas. Two approaches are often used in the chemical remediation of metal(loid)-contaminated soils: (i) immobilization of metal(loid)s using inorganic and organic soil amendments in order to reduce their bio-availability and (ii) mobilization of metal(loid)s and their subsequent removal through plant uptake (phytoremediation) or soil washing. Chemical immobilization is achieved mainly through adsorption/precipitation of As in contaminated sites through the addition of soil amendments (Mahimairaja et al., 2005).

The mobilization of metal(loid)s in soils for plant uptake and leaching to groundwater can be minimized by reducing their bio-availability through chemical and biological immobilization (Bolan et al., 2004). There has been interest in the immobilization of metal(loid)s using a range of inorganic compounds such as lime, P fertilizers (e.g., PO_4 rocks) and alkaline waste materials, and organic compounds such as biosolids and compost (Basta et al., 2001; Knox et al., 2000). Depending on the source, the application of P compounds can cause direct adsorption of As onto these materials, promote As complex formation, or induce desorption of As through competition. This method is considered more economical and less disruptive than the conventional remediation option of soil removal (Bolan et al., 2003a).

Immobilization of As may be achieved by (i) changing the physical properties of the soil so that As is more tightly bound and therefore becomes less bioavailable; (ii) chemically immobilizing As either by sorption onto a mineral surface or by precipitation as a discrete insoluble compound; and/or (iii) mixing the contaminated soil with uncontaminated soil, thereby increasing the number of As-binding sites (Naidu et al., 2003).

A number of organic and inorganic amendments are known to immobilize a range of metal(loid)s including As by chemical adsorption. These include ion-exchange resin, ferrous sulphate, silica gel, gypsum, clay minerals such as bentonite, kaolin, zeolite, green sand, Al and Fe-based layered double hydroxides and liming materials. These materials are naturally occurring and nontoxic with a large specific surface area and a significant amount of surface charge. The use of naturally occurring clay minerals as adsorbents is a novel method for the remediation of metal(loid)-contaminated soils (Minato et al., 2000). The advantages of clay minerals application are their high efficiency for retention of metal(loid)s in soils, low cost, and easy application.

Boisson et al. (1999) assessed the effectiveness of soil additives in reducing contaminant mobility. Although the addition of hydroxyapatite decreased the mobility of metals such as Cd and Pb, it increased the mobility of As mainly due to PO_4/AsO_4 competition for the sorption sites. Therefore, the use of hydroxyapatite at multimetal(loid)-contaminated sites requires careful attention.

Liming is increasingly being used as an important soil management practice in reducing the toxicity of certain metal(loid)s in soils (Bolan et al., 2003a). Lime addition to As-contaminated soil induces the formation of $CaH(AsO_4)_2$, thereby reducing the soluble As in the soil solution for plant uptake and leaching. However, the solubility product of this compound is greater than that for Fe and Al arsenates, which are readily formed in most soils. For this reason, liming is not practiced widely to overcome As toxicity in soils (Jones et al., 1997), although liming has been reported to increase the immobilization of As (Bothe and Brown, 1999) and to decrease the plant uptake of As (Jiang and Singh, 1994; Tyler and Olsson, 2001).

1.1.6.1.3 Biological remediation

1.1.6.1.3.1 Bioremediation

Because As undergoes biological transformation in soil, appropriate microorganisms may be used for the remediation of As contaminated soils. Existing and developing *in situ* bioremediation technologies may be grouped into the following two broad categories (NRC, 1997):

i. Intrinsic bioremediation is where the essential materials required to sustain microbial activity exist in sufficient concentrations that naturally occurring microbial communities are able to degrade the target contaminants without the need for human intervention. This technique is better suited for remediation of soils with low levels of As over an extensive area;

ii. Engineered bioremediation relies on various approaches to accelerate *in situ* microbial degradation rates. This is accomplished by optimizing the environmental conditions by adding nutrients and/or an electron donor/acceptor, thus promoting the proliferation and activity of existing microbial consortia. It is favored for highly contaminated localized sites.

Three approaches could be used in the bioremediation of As-contaminated soils:

Bioaccumulation. Microorganisms exhibit a strong ability to accumulate (bioaccumulation) As from a substrate containing very low concentrations of this element. Bioaccumulation is activated by two processes, namely biosorption of As by microbial biomass and its by-products and physiological uptake of As by microorganisms through metabolically active and passive processes. Factors such as soil pH, moisture and aeration, temperature, concentration and speciation of As, soil amendments, and rhizosphere are known to influence the process of bioaccumulation of As in microbial cells. While a number of bacterial and fungal species have been known to bioaccumulate As, some algal species (*Fucus gardneri* and *Chlorella vulgaris*) are also known to accumulate As (Granchinho et al., 2001; Maeda et al., 1985).

Microbial redox reactions. Heterotrophic bacteria have been found to oxidize toxic AsO_3 in soils and sediments to less toxic AsO_4 and thus could play an important role in the remediation of contaminated environment (Wakao et al., 1988). Because AsO_4 is strongly adsorbed onto inorganic soil components, microbial oxidation could result in the immobilization of As. Strains of *Bacillus* and *Pseudomonas* spp. (Frankenberger and Losi, 1995) and *Alcaligenes faecalis* (Phillips and Taylor, 1976) and *Alcaligenes* spp. (Osborne and Ehrlich, 1976) were found capable of oxidizing AsO_3 to AsO_4.

Methylation of As. A variety of microbes could transform inorganic As into its metallic hydride or methylated forms. Due to their low boiling point and/or high vapor pressure, these compounds are susceptible for volatilization and could easily be lost to the atmosphere (Braman and Foreback, 1973). Methylation is considered a major biological transformation through which As is volatilized and lost.

Methanogenic bacteria, commonly present in sewage sludge, freshwater sediments, and composts, are capable of methylating inorganic As to volatile DMA. Arsenate, AsO_3, and MAA can serve as substrates in DMA formation. Inorganic As methylation is coupled to the CH_4 biosynthetic pathway and may be a widely occurring mechanism for As removal and detoxification (Frankenberger and Losi, 1995). In addition to bacteria, certain soil fungi also are able to volatilize As as methylarsine compounds, which are derived from inorganic and organic As species.

1.1.6.1.3.2 Phytoremediation

Phytoremediation is considered a subset of bioremediation that employs plants and their associated root-bound microbial community to remove, contain, degrade, or render environmental contaminants harmless (Raskin et al., 1997; Robinson et al., 2003). This terminology applies to all plant-influenced biological, chemical, and physical processes that aid in the remediation of contaminated medium (Cunningham and Lee, 1995). It involves soil-plant systems in which metal(loid)s-accumulating plants are grown in contaminated sites. It is considered an economically feasible and environmentally viable technology for remediating metal(loid)-contaminated systems. The effectiveness of this technology is, however, variable and highly site dependent.

In phytoremediation, plants are exploited as a bio-pump that use the energy of the sun to remove water and contaminants from the soil to the aboveground portion and return some of the products of photosynthesis back into the root zone in the form of root exudates involved in the (im)mobilization of contaminants. Transpiration is the driving force for phytoremediation.

By removing water from the medium, plants help reduce erosion, runoff, and leaching, thereby limiting the movement of contaminants off-site. Some contaminants are taken up in the transpiration stream, where they may be metabolized, and may be eventually volatilized. By removing excess water from the soil profile, plant roots may also create an aerobic environment where metal(loid) mobility is reduced and biological activity is enhanced. Plants stimulate microbiological activity in the roots zone by providing a carbon source from roots exudates and decaying root materials (Robinson et al., 2003). Phytoremediation technologies have been grouped into various categories that include phytostabilization, rhizofiltration, and phytoextraction (Cunningham et al., 1995).

In phytostabilization, transpiration and roots growth are used to immobilize contaminants, including As by reducing leaching, controlling erosion, creating an aerobic environment in the roots zone, and adding organic matter to the substrate that binds As. It involves the establishment of metal(loid)-tolerant vegetation on the contaminated site that is left in perpetuity. The stabilization of As in the roots zone could be achieved through the addition of organic matter as well as soil amendments.

In rhizofiltration, the roots can be used to adsorb or absorb metal(loid)s, which are subsequently removed by harvesting the whole plant. In this case, metal(loid) tolerance and translocation of the metal(loid)s to aerial parts are largely irrelevant.

In phytoextraction, plants can be grown on contaminated soil and the aerial parts [and the metal(loid)s they contain] harvested. In this case, plants need to be tolerant only if the soil metal(loid) content is very high, but they need to accumulate very high concentrations in their aerial parts. Phytoextraction involves repeated cropping of plants until the metal(loid) concentration in the soil has reached the acceptable (targeted) level. Certain plants, termed “hyperaccumulators” (Brooks et al., 1977), accumulate an inordinate concentration of metal(loid)s in their aboveground biomass. These plants may even accumulate metal(loid)s that are nonessential and often toxic to plants. The minimum concentration of As required for a plant to be classified as a hyperaccumulator of As was set at 1000 mg kg^{-1} (0.1%) on a dry weight basis (Ma et al., 2001). The hyperaccumulation of metal(loid)s involves uptake of the soluble metal(loid) species by the root system, translocation to the aerial parts, and storage in a nontoxic form in the aerial portions. At present there are about 400 species of known terrestrial plants that hyperaccumulate one or more of several metal(loid)s (Robinson et al., 1995).

Ma et al. (2001) discovered an As-hyperaccumulating plant, Chinese brake fern (*Pteris vittata* L.), which accumulates large amounts (23,000 mg kg^{-1} dry weight basis) of As from soils. The unique property of As hyperaccumulation by the Chinese brake fern is of great significance in the phytoremediation of As-contaminated soils. Therefore, the potential of this fern for phytoremediation of As-contaminated soil was assessed by Tu et al. (2002). Results have shown that the Chinese brake accumulated huge amounts of As from soil and that its As concentration increased with the growth period. Another silver fern, *Pityrogramma calomelanos* (L.), has also been reported to hyperaccumulate As up to 8,350 mg kg^{-1} dry mass from soil containing 135 mg kg^{-1} (Francesconi et al., 2002). It occurs in tropical and subtropical regions of the world and is widely distributed in Thailand where it favors open, high rainfall areas.

Phytoremediation has several advantages over other remediation and metal(loid) extraction technologies. The cost involved in phytoremediation is much lower than other technologies, such as soil removal, capping, and ex situ cleansing. Other advantages include the ultimate fertility of the cleaned site, the high public appeal of “green” technology and the possibility of producing secondary products that offset the cost of the operation or even produce a small profit. However, some of the basic plant physiological processes, such as low biomass production and shallow root growth, nonetheless limit the scope of phytoremediation. Only surface contamination can be removed or degraded and the cleanup is restricted to areas that are amenable to plant growth. Most importantly, it may take a long time for site remediation to be effective. Phytoremediation can only be used if it meets environmental regulation during the operation as well as its end point.

1.1.6.2 Removal of As from aquatic environments

Because most cases of As toxicity in humans have resulted from the consumption of As-contaminated water, there have been intensive research efforts in developing technologies aimed at stripping As from water. A plethora of methods suitable for the removal of As from water at both household and community levels are currently available. These methods are primarily based on: i) removal of solid-phase As through coagulation, sedimentation, or filtration; ii) removal of solution-phase As through ion exchange, osmosis, or electrodialysis; iii) oxidation of AsO_3 to AsO_4 and its subsequent removal through adsorption and/or precipitation; iv) biosorption using microorganisms; v) rhizofiltration using aquatic plants.

1.1.6.2.1 Physicochemial methods

Filtration, adsorption, and chemical precipitation are the most common physicochemical methods used for stripping As from water. While the particulate As in water can be removed by simple filtration, the aqueous As can be removed through adsorption or precipitation followed by filtration.

Filtration. Most of the domestic drinking water treatment systems for As removal involve filtration. For example, the "Pitcher filter" involving porous ceramics (Neku and Tandukar, 2003) and sand filters (Yokota et al., 2001) have been found to be effective in stripping As from water. Seidel et al. (2001) noticed that the porous nanofiltration anion-exchange membrane removed about 90 % of AsO_4 present in water at a concentration of 316 μg L^{-1}. Although this technology could achieve a high degree of As removal, it involves a high initial investment and high operation and maintenance costs.

Adsorption. A number of compounds, including Al and Fe salts and minerals, activated alumina, Fe-coated sand and ion-exchange resins are used to adsorb As. In most geologic environments, Fe_2O_3 carries a positive surface charge that preferentially adsorbs As. Similarly, $Al(OH)_3$ and silicate clays also adsorb large amounts of As.

The adsorption of As by Al-rich and Fe rich minerals, affected by pH, residence time, etc., was widely studied (Violante and Pigna, 2002; Violante et al, 2005; Violante et al, 2006; Pigna et al., 2006; Violante et al, 2007; Violante et al., 2009). A class of anionic clays known as LDHs have shown great potential to efficiently remove As from aqueous systems (Cavani et al., 1991) (a wide description of LDHs is reported below in the section 1.2). The effect of competing anions on AsO_4 sorption/desorption on/from Al or Fe oxides has been extensively studied (Violante and Pigna, 2002; Violante et al., 2005; Pigna et al., 2006; Violante et al., 2008; Goh and Lim, 2010; Zhu et al., 2011), while only a few studies have examined the effect of competing anions (e.g., phosphate, carbonate, sulphate, fluoride, chloride, bromide, nitrate) on the efficiency of LDHs to remove As from aqueous systems (You et al., 2001a; Violante et al., 2009).

Arsenic removal from aquatic contaminated system by Al- and Fe-drinking Water Treatment Residuals (amorphous masses of Al- and Fe-hydroxides, removed from the raw water during water purification process for drinking purposes) was also studied

(Makris et al., 2006; Makris et al., 2007; Makris et al., 2009; Nagar et al., 2010) (as discussed below in the section 1.3).

Hlavay and Polyak (1997) developed and tested novel adsorbents for As stripping. Porous support materials were granulated using Al_2O_3 and/or TiO_2 and then $Fe(OH)_3$ was freshly precipitated onto the surface of these particles. The resulting $Fe(OH)_3$-impregnated porous adsorbent was dried at room temperature and packed into an ion-exchange column. These columns were found to remove > 85 % of As in water. The AsO_3 ions can primarily be sorbed by chemical reaction on the surface of $Fe(OH)_3$. Das et al. (1995) demonstrated the practical application of the adsorption technique in stripping As by developing a simple household device to remove As from groundwater used for drinking and cooking purposes. The system consists of a filter, tablet, and two earthen or plastic jars. The tablet contains Fe(III) salt, an oxidizing agent, and activated charcoal. The filter is made of mainly purified fly ash with binder.

Precipitation. Arsenate can be removed by precipitation/coprecipitation using Fe and Al compounds. Gulledge and O'Connor (1973) achieved a complete removal of AsO_4 from water using $Fe_2(SO_4)_3$ at a pH range of 5.0 to 7.5. Hydrolyzing metal salts such as $FeCl_3$ and alum [$Al_2(SO_4)_3$] have been shown to be effective in stripping As by coagulation. Shen (1973) removed As from drinking water by dosing with chlorine (Cl_2) and $FeCl_3$. Oxidation of AsO_3 to AsO_4 by Cl_2 and the subsequent removal by precipitation were considered the mechanisms involved in this process. One of the advantages in chemical precipitation method is that this can be used at both household and community levels. The materials are readily available and generally inexpensive.

However, a problem of disposal of toxic sludge exists and it also requires trained operators.

1.1.6.2.2 Biological methods

Phytoremediation using aquatic plants. Phytoremediation of As-contaminated waters may be readily achieved by the use of aquatic plants because unlike soil, most of the As in water is available for plant uptake. In the case of soils, the plant must first solubilize the metal(loid)s in the rhizosphere and then should have the ability to transport it to the aerial tissue (Brooks and Robinson, 1998). The use of freshwater vascular plants for the removal of metal(loid)s from water has been long established. Rhizofiltration usually involves the hydroponic culture of plants in a stationary or moving aqueous environment wherein the plant roots absorb metal(loid)s from the water (Brooks and Robinson, 1998). Ideal plants for rhizofiltration should have extensive root systems and be able to remove metal(loid)s over an extended period.

Microbial Removal of As. Bio-sorption and biomethylation are the two important processes by which metal(loid)s, including As, are removed from water using microorganisms. Bio-sorption is one of the promising technologies involved in removing As from water and wastewater. Several chemically modified sorbents have been examined for their efficiency in removing metalloids. Genetically engineered microorganisms (e.g., *Escherichia coli*) that express a metal(loid)-binding protein (i.e., metallothionein) and a metal(loid)-specific transport system have been found to be successful in their selectivity for accumulation of a specific metal(loid) in the presence of a high concentration of other metal(loid)s and chelating agents in solution (Chen and Wilson, 1997). Loukidou et al. (2003) examined the potential of *Penicillum chrysogenum*, a waste by-product from antibiotic production, for the removal of AsO_4 from wastewaters.

Methylation is the most reliable biological process through which As can be removed from aquatic medium. Certain fungi, yeasts and bacteria are known to methylate As to gaseous derivatives of arsine. Commercial application of biotransformation of metal(loid)s in relation to the remediation of metal(loid)-contaminated water was documented by Bender et al. (1995).

1.2 The Layered Double Hydroxides (LDHs)

Layered double hydroxides (LHDs), also called anionic clays, display unique physical and chemical properties surprisingly close to the properties of clay minerals. The general terms hydrotalcite-type (HT) compounds is also widely used, probably due to the fact that most of its characterizations have been carried out on hydrotalcite (a Mg, Al hydroxycarbonate), and that it can be easily and inexpensively synthesized. The name LDH is derived from the early works of Feithnecht, who called these compounds *Doppelschichtstrukturen* (double sheet structures), hypothesizing a structure with intercalated hydroxide layers. This hypothesis was refuted many years later on the basis of single crystal XRD analysis, which showed that all the cations are placed in the same layer, with the anions and water molecules located in the interlayer region (Del Hoyo, 2007).

LDHs are a class of two-dimensional nanostructured anionic clays. The structure of LDHs can be described as a positively charged brucite-like sheets [e.g., brucite, $Mg(OH)_2$], where a fraction of the divalent cations coordinated octahedrally by hydroxyl groups have been isomorphously replaced by trivalent cations, giving positively charged sheets. The net positive charge is compensated by anions in the interlayer region between the brucite-like sheets. Some hydrogen-bonded water molecules may occupy the free space in this interlayer region (Cavani et al., 1991; Li and Duan, 2005; Evans and Duan, 2006). The structure of LDHs and a typical octahedral unit are shown in Figure 7 (Goh et al., 2008). The basal spacing (c') is the total thickness of the brucite-like sheet and the interlayer region. The octahedral units of M^{2+} or M^{3+} (sixfold coordinated to OH^-) share edges to form infinite sheets. These sheets are stacked on top of each other and are held together by hydrogen bonding.

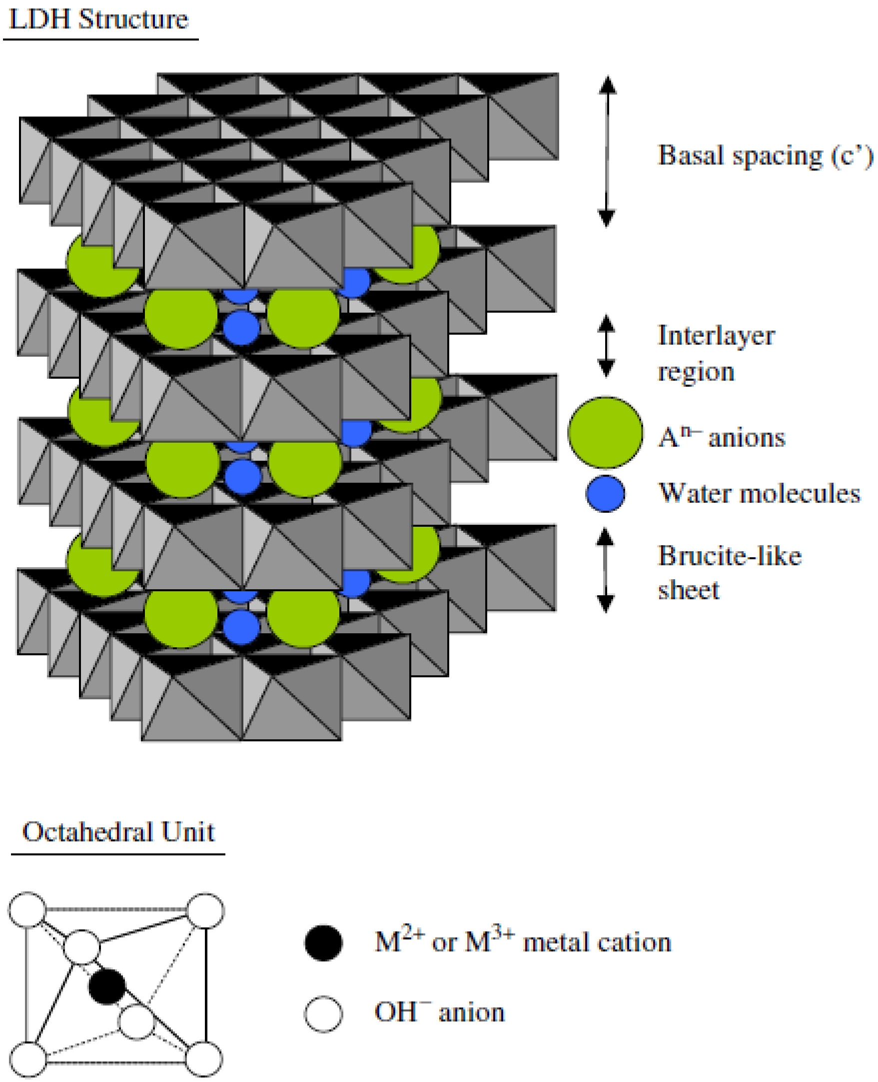


Figure 7 Schematic representation of the LDH structure.

However, it must be pointed out that the terms HT compounds or anionic clays also are not generally accepted, taking into account that in the first case the term refers strictly to a specific mineral and that these compounds do not fulfill some clay requirements, for example, the very small particle size (Cavani et al., 1991).

LDHs can be represented by the general formula $[M^{2+}_{1-x} M^{3+}_{x} (OH)_6]^{x+} [(A^{n-})_{x/n} m H_2O]^{x-}$, where x is the molar ratio $M^{3+}/(M^{2+}+ M^{3+})$, taking values between 0.20 and 0.33, while M^{2+} and M^{3+} are divalent (Ca, Mg, Co, Fe, Cu, Ni, Mn) and trivalent metal cations (Al, Fe, Cr), respectively, and A is an interlayer anion (e.g., Cl, NO_3, ClO_4, CO_3, SO_4) of valence n. They are composed of positively charged brucite-like sheets and the positive charges are balanced by intercalation of anions in the hydrated interlayer regions, analogous to the cationic clays whose negative charge of the aluminosilicate layers are counterbalanced by cations (Miyata, 1975; Cavani et al., 1991; Costantino et al., 1995; Ulibarri et al., 2001; Lazaridis et al., 2002). The LDHs have relatively weak interlayer bonding and, as a consequence, the original anions sorbed in the interlayer are easily exchanged with many inorganic and organic anions by simple ion exchange methods.

The most interesting properties of these layered double hydroxides may be summarized as follows:

(A) High specific surface area (100 ± 300 m^2 g^{-1}).

(B) Homogeneous dispersion of the metal ions thermally stable also at reducing conditions, with formation of very small and stable metal crystallites. Impregnation procedures for the preparation of metal catalysts normally cannot achieve such a high degree of metal dispersion.

(C) Synergetic effects between the elements, due to the intimate dispersion which favors, for example, the development of unusual basic or hydrogenating properties. It is worth noting that basic properties depend significantly on the composition and the calcination temperature.

(D) “Memory effect”, which allows reconstruction under mild conditions (after calcination until 500 °C) of the original structure by contact with solutions containing various anions.

(E) Good anion exchange capacities.

LDHs are also relatively simple and economical to synthesize by coprecipitation methods under laboratory conditions (Miyata, 1975; Cavani et al., 1991; Vaccari, 1998), thus they can be produced in large quantities. The simplest and most commonly used method is coprecipitation. In this method, aqueous solutions of M^{2+} and M^{3+} containing the anion that is to be incorporated into the LDHs are used as precursors, of which Mg and Al are the most frequently used metal precursors. In order to ensure simultaneous precipitation of two or more cations, it is necessary to carry out the synthesis under conditions of supersaturation.

Synthetic layered double hydroxides, as such or, mainly, after thermal decomposition, find many industrial applications and probably more will be found in the future in unexpected areas.

Although the available literature data on layered double hydroxides is significantly less extended than that for clay minerals, in recent decades, layered double hydroxides have attracted substantial attention due to their potential use in many applications. LDHs have been studied in a wide range of important areas, i.e. catalysis, photochemistry, electrochemistry, polymerization, magnetization, biomedical science, and environmental application (Cavani et al., 1991; Newman and Jones, 1998; Rives, 2001; Li and Duan, 2005; Evans and Duan, 2006). LDHs could be also used in pharmaceutical formulations and for new drug delivery systems in biomedical science (Rahman et al., 2004).

Moreover, LDHs have been used as heat retention additives in plastic films (Evans and Duan, 2006), flame retardants (Shi et al., 2005; Wang et al., 2005), stabilizing agents for polymers (Van Der Ven et al., 2000; Lin et al., 2005), and precursors to magnetic materials (Sugimoto, 1999).

There has also been considerable interest in using LDHs to remove environmental contaminants since environmental pollution has emerged as an important issue in the recent decades. Significant progress has been achieved in the research and development of LDHs' application in environmental protection, such as their use as environmental catalysts in removing organic and inorganic wastes (Corma et al., 1997; Shannon et al., 1997; Kannan, 1998; Kannan and Swamy, 1999; Palomares et al., 1999, 2004; Pérez-Ramìrez et al., 1999; Rahman et al., 2004).

Indeed, increasing interest has recently been diverted to evaluating the ability of LDHs to remove inorganic contaminants such as oxyanions (e.g. arsenite, arsenate, chromate, phosphate, selenite, selenate, borate, nitrate, etc.) and monoatomic anions (e.g. fluoride, chloride, bromide, and iodide) from aqueous solutions by the process of adsorption and ion exchange. This is because LDHs have exhibited a great potential to efficiently remove harmful oxyanions. In addition to the large surface area and high anion exchange capacity of LDHs, their flexible interlayer region that is accessible to various anionic species as well as polar molecular species is another important feature promising their high removal efficiencies of contaminants. Several factors that play important roles in the adsorption process, such as pH, competitive anions, temperature, LDH particle size, etc.

The pH effect on the oxyanion adsorption by LDHs is dependent on the types of oxyanions and the types of LDHs. In general, the adsorption of oxyanions such as arsenate, chromate, phosphate, and selenite by LDHs tends to decrease with increasing pH, with a few exemptions reported in the published literature. The surface of the LDHs is negatively charged when $pH < pH_{pzc}$. Therefore, in the higher pH range, the oxyanions will be repelled by the LDH surface. For $pH < pH_{pzc}$, the LDH surface is positively charged, favoring adsorption of the oxyanions. However, at a very low pH, i.e. $pH \ll pH_{pzc}$, the stability of the LDH structures is impaired and this decreases the oxyanion adsorption. At a higher pH ($pH \gg pH_{pzc}$), the oxyanion adsorption may be affected due to the increasing competitive effect of OH ions for adsorption on LDHs (Goh et al., 2008).

There are many published literature reporting the effect of competitive anions on oxyanion adsorption by LDHs, and the anion affinity or anion intercalation capability of LDHs (Goswamee et al., 1998; You et al., 2001a, b; Das et al., 2004, 2006; Tezuka et al., 2004; Kiso et al., 2005; Yang et al., 2005, Violante et al., 2009). The effect of competing anions on AsO_3 adsorption by LDHs was found to reduce in the order phosphate > sulphate > carbonate > fluoride > chloride >bromide > nitrate (You et al., 2001a), while the interfering effects of competing anions on AsO_4 adsorption by LDHs were reported to follow the order carbonate > phosphate > sulphate > chloride (Kiso et al., 2005) and phosphate > (bicarbonate and carbonate) > sulphate > nitrate (Yang et al., 2005). Yang et al. (2005) observed that the competing ions had stronger effect on the AsO_4 adsorption on the uncalcined LDHs than on the calcined LDHs.

A change in temperature will change the equilibrium capacity of the adsorbent for particular adsorbate. Usually, the adsorbate uptake decreases with increasing temperature due to the exothermic nature of the simple adsorption reaction. The AsO_4

adsorption on both calcined and uncalcined LDHs was reported as an exothermic process (Yang et al., 2005).

The nature of the LDHs precursor metals, including different combinations of the metals, atomic ratio of the metals, metal-metal distance in the brucite-like sheet, etc. and the crystallinity of LDHs can significantly influence the adsorption of guest oxyanions. It is generally believed that the oxyanion adsorption by LDHs can be enhanced by increasing the anion exchange capacity of the LDHs. This may be achieved by incorporating more trivalent cations or higher valent cations in the brucite-like sheet, which can subsequently increase its net positive charge in the brucite-like sheet (layer charge). The charge and species of the interlayer anion can also affect the adsorption of guest oxyanions.

Another key factor affecting the oxyanion adsorption by LDHs is the calcination during the synthesis of LDHs. When LDHs were thermally decomposed below 200 °C, only surface water and interstitial water were lost; between 250 and 450 °C, both carbon dioxide and water from the dehydroxylation were lost (Sato et al., 1986). At 450-500 °C, calcined LDHs would lose their layer structure and form highly active composite metal oxides with high thermal stability, large surface area, basic properties, small crystal size, and high stability against sintering even under extreme conditions (Li et al., 2005). This calcined product can reconstruct its original layer structure with rehydration and sorption of various anions. The calcination temperature is the key parameter to be controlled in this process. It must be high enough to eliminate most of the carbonate anions, since their presence will inhibit significant incorporation of guest oxyanions, but is low enough to permit the layer reconstruction. The differences in behavior between calcined and uncalcined LDHs may be linked to several reasons: i) increased surface area of the calcined products (Carja et al., 2005; Yang et al., 2005); ii) increased porosity as a result of the calcinations process (Lazaridis et al., 2001; Carja et al., 2005); iii) fewer carbonate anions in the interlayer of the calcined LDHs than in the uncalcined LDHs (Yang et al., 2005).

A few studies have reported that decreasing the particle size of the LDHs has a dramatic effect on the oxyanion adsorption rate but not on the oxyanion adsorption capacity (Lazaridis et al., 2004; Yang et al., 2006). The experiment by Yang et al. (2006) showed that AsO_4 adsorption capacity was independent of the LDH particles size (ranging from 53 to 300 µm). The relatively higher adsorption rate with smaller adsorbent particle may be attributed to the fact that smaller particles yield large surface area and require shorter intra-particle diffusion time to reach sorption equilibrium.

1.3 The drinking-Water Treatment Residuals (WTRs)

Drinking-WTRs are the waste material, resulting from the treatment of surface- or ground-water with Al and Fe salts. Drinking-WTRs are primarily amorphous masses of Fe, Al hydroxides, or $CaCO_3$, that also contain sediment, activated carbon and polymer removed from the raw water during water purification process for drinking purposes (Elliott and Dempsey, 1991). Potable water production is usually achieved with the use of three methods; sedimentation-flocculation, ion exchange and reverse osmosis. Sedimentation-flocculation is the most conventional water treatment method, which makes use of metal salts combined with synthetic polyelectrolytes such as surfactants and polymers. Addition of Fe, Al, or Ca salts to raw water removes colloids, color, sediment and contaminants from surface and groundwater supplies intended for potable water use. Depending of the metal salt used, the resulting WTRs are referred to as Al-WTRs (use of Al salt), Fe-WTRs (Fe salt) or Ca-WTRs ($CaCO_3$). Iron- and Al-based WTRs are the most commonly produced. There are over 1000 drinking water treatment plants in USA that use Al salt [$Al_2(SO_4)_3 \cdot 14H_2O$] as a coagulant for contaminant and color removal. More than 2 million tonnes of WTRs are generated each year (Prakash and Sengupta, 2003). The WTRs are enriched in Al and Fe hydroxides with total Al + Fe concentrations, ranging between 20 and 370 g kg^{-1} Metal hydroxides in WTRs are usually amorphous and they should be characterized by small particle size and greater specific surface area, than the corresponding crystalline phases (Makris et al., 2006). Oxides’ small size, coupled with their high surface area, makes them reactive and efficient sorbents for oxyanions (O’ Melia, 1989).

The WTRs can be obtained at minimal cost from the drinking-water treatment facilities, showing a cost-related advantage of WTRs relative to other currently available As sorbents. Arsenic removal by Al- and Fe-WTRs is typically a combination of external surface adsorption (ligand exchange) and intra-particle diffusion mechanisms (Makris et al., 2004). A relevant reaction between As and the Al-hydroxide component of the Al-WTR may be:

$$SOH^0 + H_3AsO_3^0 \leftrightarrow SOAs(OH)_2^0 + H_2O + H^+$$

where S is represented by Al in case of the Al-WTR.

The As sorption capacity of the WTRs (15,000 mg kg^{-1}) (Makris et al., 2006) are comparable, if not superior to that of other common industrial sorbents, such as, porous ferric hydroxide (As sorption capacity of 17,000 mg kg^{-1}) (Driehaus et al., 1998), or granular ferric hydroxide (8,000 mg kg^{-1}) (Badruzzaman et al., 2004). Iron-containing GAC had a As sorption capacity of 6570 mg As kg^{-1} (Gu et al., 2005) and granular activated alumina particles exhibited As sorption maxima in the order of 12,000 mg kg^{-1} (Lin and Wu, 2001), similar to As sorption capacities of the WTRs, suggesting that WTRs are effective As sorbents.

Arsenic sorption by WTRs is influenced by specific physicochemical properties of WTRs, such as, specific surface area, total C content and porosity (Makris et al., 2005). The X-ray absorption spectroscopy studies by Makris et al. (2007; 2009) further corroborated the stability of sorbed As by WTRs, forming inner-sphere mononuclear bidentate complexes with WTRs surface hydroxyls.

Both Al- and Fe-WTRs had a high affinity for AsO_3 and AsO_4 species. Anyway, the Al-WTR are able to sorb greater amounts of soluble AsO_4 than the Fe-WTR, while the Fe-WTR are able to sorb greater amounts of AsO_3 than the Al-WTR (Makris et al., 2006). Greater external and internal specific surface area of the Al-WTR than that of the Fe-WTR could explain the greater affinity of the Al-WTR for AsO_4 (Makris et al., 2006).

In the case of AsO_3, an abiotic reductive dissolution mechanism, which applies to the redox-sensitive Fe-WTR but not to the Al-WTR increases the amount of sorption sites by creating new surfaces, thereby accounting for the greater AsO_3 sorption by the Fe-WTR.

Recent literature has also shown that WTRs are cost-effective amendments that reduce excess soluble PO_4 concentrations in systems high in P (Makris et al., 2004; Dayton and Basta, 2005a). In fact, PO_4 and AsO_4 ions show many similarities in the chemical nature (tetrahedral geometry, atomic radii, bonding radii, ionization potential and electronegativities), so the WTRs exhibit a high affinity for each of them. Drinking-WTRs can dramatically reduce soluble PO_4 in soils and runoff from areas amended with different P-sources, either in the short-term (Gallimore et al., 1999; Haustein et al., 2000), or in the long-term (up to 80 d) (Makris et al., 2005).

Nagar et al. (2010) have investigated the effect of solution pH (3.0-9.0) on AsO_4 sorption by Al- and Fe-based WTR samples as a function of solid:solution ratio (SSR) and initial AsO_4 concentration. They have also evaluated the effect of competing ligands (phosphate and sulfate). At 200 g L^{-1} of SSR, maximum AsO_4 sorption (~100%) exhibited by the Fe-WTR was limited at the pH range of 3.0-7.0, whereas, the Al-WTR demonstrated ~100% AsO_4 sorption in the entire pH range. The negative pH effect on AsO_4 sorption became more pronounced with increasing initial AsO_4 concentrations and decreasing SSR. Sorption of AsO_4 by surfaces of both WTR decreased in the presence of PO_4, exhibiting strong pH dependence. Only for the Fe-WTR, increased dissolved iron concentrations at $pH > 7$ supported a Fe-hydroxide reductive dissolution mechanism to account for the enhanced As sorption at alkaline pH. Addition of sulfate did not influence AsO_4 sorption by both WTR (Nagar et al., 2010).

1.4 Compost

Compost obtained from the organic fraction of municipal solid waste and from other selected waste biomasses can be used effectively as an organic fertilizer on agricultural soil. The high content of stabilized organic matter and the presence of nutrients of a good quality compost are a guarantee of agronomic advantages; at the same time, the use of compost makes the re-use of organic wastes possible and has numerous advantages (Paris and Robotti, 1981; Zucconi and De Bertoli, 1982). The phyto-nutritive capacity of compost has often been demonstrated to be analogous to that of manure; the same level of productivity, both quantitatively and qualitatively, can be maintained by replacing manure with compost (Del-Zan, 1989; Beyea et al., 1993; Roe et al., 1993; Baldoni et al., 1994).

Composting of manure and other organic wastes is a microbiologically mediated process with which the readily degradable organic matter in organic wastes is degraded and stabilized. During the process, part of organic C is released as CO_2, part incorporated into microbial cells and part humified. The organic nitrogen primarily as protein prior to composting is mineralized to inorganic N (NH_4-N and NO_3-N), which is then re-synthesized into other forms of organic N in microbial biomass and humic substances during the composting process. Degradation of organic C during composting is carried out by bacteria, fungi, and actinomycetes, depending on the stage of degradation, the characteristics of materials, and temperature (Epstein, 1996; USDA, 2000). These microorganisms assimilate C and N in a different way. Differing nutrients available during composting will preferentially favor diverse microbial populations. Bacteria can utilize materials with narrow C:N of 10-20:1, while fungi can use materials with wide C:N of 150-200:1 (Griffin, 1985).

Compost turning or aeration is critical for a rapid degradation and high quality compost particularly for the food waste composting. Although organic matter can also be degraded under anaerobic condition, the degradation is slow and less efficient, and produces less heat and more undesirable products, including CH_4 and N_2O, which are greenhouse gases contributing to global warming (Hao et al., 2001). Considering that the end use of compost is primarily for nutrient recycling and promoting plant growth, aerobic stabilization process is the preferred method of composting to produce a stabilized or mature organic amendment.

Heat is generated from the decomposition of organic matter. Temperature rises when sufficient heat is trapped within the compost pile. Composting can generally be divided into three stages based on the temperature in the composting pile. As the temperature of composting pile rises, the degradation quickly moves from ambient temperature into mesophilic phase, which is followed by thermophlic phase of degradation, before returning gradually back to the ambient temperature when the degradation is mostly complete or compost is mature. Other major degradation products are CO_2, H_2O and NH_3 that can be further transformed into NO_2 and then NO_3 by nitrification.

Water is a critical factor in composting system. Microbial cells have a physiological need for water. In addition, water can function as a solvent of substrates and salts, a major heat storage medium due to its high specific heat capacity, and as temperature adjusting substances through evaporation. Theoretically, the water content of the compost could reach 100% without causing harmful effects itself. However, as water content increases, the rate of O_2 diffusion decreases. As O_2 becomes insufficient to meet the metabolic demand, the composting process slows down and become anaerobic. The upper limit of water content is between 60 and 80 %, depending on the composting materials (Golueke, 1991). A moisture level of 40 to 60 % by weight should be maintained throughout the composting period (US Composting Council, 1997). A moisture level below 40 %, while promoting aeration, restricts microbial activity. The microbial activity is severely restricted at 15 % moisture level.

A reduction of carbohydrate, hemicellulose, and cellulose during the composting process is accompanied by increased humification. The humification is an index of compost maturity. It is a critical component of composting as humic substances from composting are beneficial to soil physical and chemical properties and plant productivity. Accompanying with increase in humification is increases of alkyl C, aromatic C, carboxyl (-COOH), phenolic (-OH) and carbonyl (-CO) groups. The aromatic and phenolic C containing groups increased by 23 and 16 %, respectively, following composting of municipal solid waste (Chefetz et al., 1998). The other major changes in the characteristics of compost are the marked increase in the content of humic acids and consequently the cation exchange capacity of compost (Inbar et al., 1989). Because of increased aromatic nature of composting product, composting process influenced not the elemental composition of finished compost but the functional groups. The humic substances formed is dissimilar to soil humic substances as they have comparatively lower concentrations of total acidity, and carboxyl and phenolic functional groups than soil humic acids (Inbar et al., 1989).

The loss of C ranged from 46 to 62 % as compared to 19 to 42 % N loss during composting, depending on type of composting system, waste stream (e.g., lignin content) and composting conditions (e.g., temperature, moisture) (Eghball et al., 1997). The majority of C loss is from carbohydrates, hemicellulose, and cellulose as they constitute the majority of plant C and are comparatively more easily degradable than lignin. With a much greater loss of C than N during composting especially during the active decomposition by thermophilic microorganisms, the C:N ratio of organic materials in the compost mix declines also in a first-order faction (Inbar et al., 1989) and reached a steady state after 100 days of composting of cattle manure (Inbar et al., 1989; Chefetz et al., 1996). The ratio of C: N ratio of the finished compost [$(C:N)_{final}$] to the C: N ratio of composting mix initially [$(C:N)_{initial}$] is about 0.6 to 0.75 (Jimenez and Garcia, 1989). This indicates that the C:N ratio of the initial composting mix will be reduced by 25 to 40% under normal composting conditions. The C:N ratio of compost should be about 20 to prevent N immobilization and to facilitate the release of mineral N for crop use once the compost is added to soil (Allison, 1973). This suggests that a C:N ratio of about 30:1 (20 to 40) (USDA, 2000; B.C. Agriculture and Food, 1996) before composting is commenced is desirable. Initial C:N ratio over 40:1 is not conducive to the degradation of organic matter due to N immobilization at least initially (Allison, 1973). In contrast, low C:N ratios of feedstock, or overabundance of N, tend to cause the accumulation of NH_4-N as $(NH_4)_2CO_3$, which at high pH levels dissociates into NH_3 and CO_2. Rise in pH (> 8.5), coupled with elevated temperature in the composting pile during the thermophilic phase of degradation, promote the volatilization of odorous NH_3.

As the primary purposes of composting are to stabilize the organic wastes to facilitate recycling of nutrients in the organic wastes, and to reduce the volume of wastes going to the landfills, many types of organic wastes have been used as feedstock for composting. The wastes include sewage sludge, animal manures, yard waste, crop residues, municipal solid waste, fish scraps and mortality, and food waste and food process wastes. The materials vary widely in C:N ratios. Since the C:N ratio of the composting mixture initially should be about 30:1 (B.C. Agriculture and Food, 1996), co-composting is feasible for some of the materials, if they are available in or near the composting facility to reduce the distance and cost of transportation. Straw from grain crop, peat moss, sawdust, wood chips and shredded and ground papers, municipal solid waste typically have high C:N ratio and they can be blended with animal manures or biosolids for co-composting.

The presence of organic and inorganic contaminants in compost may, however, constitute a danger to the environment. It is the heavy metal content which is the main factor leading to restricted agricultural use of compost. Literature on the effect of compost use on heavy metal levels in the environment shows it to vary according to soil type, plant species and compost quality (Paris and Lucianer, 1986). Increased Zn, Cu and Pb levels have often been observed, both in the soil and plants, while other heavy metals, such Cd, Ni and Cr, increase less consistently (Bevacqua and Mellano, 1993; Baldoni et al., 1994; Barbera et al., 1989; Zamborlini et al., 1989; Businelli and Gigliotti, 1994). In the long term, the use of sewage sludge can also cause a significant accumulation of Zn, Cu, Pb, Ni and Cd in soil and plants (William et al., 1980; Mulchi et al., 1991). Based on the cumulative research in Europe into the agronomic use of compost, heavy metals tend to accumulate in soil and plants in the following order: Zn > Cu > Pb = Cd > Ni > Cr. The problem of heavy metals can, however, be overcome by composting only organic raw materials with a low level of potential contaminants. It has been shown that the use of products with a low level of heavy metals does not affect soil or plant metal content (Vigna-Guidi et al., 1990; Petruzzelli et al., 1991).

In many Countries, before 1980’s, the soil fertility was maintained mainly by the use of organic fertilizers such as farmyard, manure, straw and organic wastes (Yang and

Hansen, 1997). At the present, low soil organic matter content on arable lands has made them become less fertile (Yang and Hansen, 1997). The over use of inorganic fertilizers and intensive fieldcrop production can cause the quality of agricultural soils to decline. Reduced soil physical quality is, in turn, linked to declined crop performance and/or profitability, as well as negative environmental impacts related to the off-field movement of soil (wind/water erosion) and agrochemicals (pesticide/nutrient leaching into surface and ground waters) (Reynolds et al., 2002).

Application of organic by-products as compost to soil increases soil fertility by improving the physical and chemical properties and augmenting microbial activity (and is a common way to dispose of waste). Organic fertility inputs improve soil physical properties by lowering bulk density, increasing water-holding capacity and improving infiltration rates (Peterson et al., 1999).The addition of compost results in increased mineralization of nitrogen and also micronutrients (Dick and McCoy, 1993a). In horticulture compost can be also used as an alternative to peat as a growing medium and as a cover material to conserve moisture and suppress plant disease (Liu, 2000).

There is a lack of agreement over the influence of organic matter (OM) on As mobility. Cao and Ma (2004) used compost to remediate CCA-contaminated soils and recorded an effect of As adsorption, as found by others after compost application (Xu et al., 1991; Perez-de-Mora et al., 2007). Both Mench et al. (2003) and Hartley et al. (2009) observed large increases in leachable As from soils amended with compost probably due to dissolved organic carbon (DOC) competing with As for sorption sites such as those on Fe-oxide surfaces, causing increased As mobility (Redman et al., 2002). DOC can also facilitate the transport of metal contaminants through the formation of soluble metal-DOC complexes (Antoniadis and Alloway, 2002; Pohlman and McColl, 1988).

Although metal-DOC complexes are more mobile in soils, leading to groundwater contamination, these complexes have been shown to be less readily available for plant uptake, thereby alleviating phytotoxicity resulting from excessive metal accumulation in soils (Han et al., 2001).

The variety of agro-ecosystems and the diversity of organic inputs furnished by the several composts available on the market present a challenge for research and extension activities in soil fertility management (Palm et al., 2001).

CHAPTER 2 -

AIMS OF THE WORK

2.1 Aims of the present work

Contamination of terrestrial and aquatic ecosystems by As is a very sensitive environmental issue due to its adverse impact on human health. With greater public awareness of As poisoning in animal and human nutrition, there has been a growing interest in developing regulatory guidelines and remediation technologies for mitigating As-contaminated ecosystems.

There are several treatment technologies available to reduce As concentrations in contaminated water (MacPhee et al., 2001). The most effective As treatment processes include adsorption, ion exchange, reverse osmosis, and nanofiltration (MacPhee et al., 2001). The majority of As removal technologies from contaminated water treat AsO_4 much more effectively than AsO_3, so a pre-oxidation step is recommended for source waters containing AsO_3 at significant concentrations (Frankenberger, 2002). These As treatment technologies have been successfully applied to remove trace As concentrations from contaminated water, but most of them are cost-prohibitive for small communities or developing Countries, which are likely to face expensive and technically imposing challenges to meet the maximum contaminant level of 10 µg As L^{-1}. Several models show a wide range of costs for the different technologies, which can hinder their implementation to As-contaminated sources (Kapadia, 2000). For these reason, it is extremely important to investigate and promote new As remediation technologies able to remove As from contaminated areas in a cheap and safe way.

In the present work, the competition between AsO_4 with organic and inorganic ligands for the sorption sites on two LDHs, obtained by coprecipitating Mg with Al (Al-Mg-LDH) or Fe (Fe-Mg-LDH), was studied. LDHs are relatively simple and economical to synthesize by coprecipitation methods under laboratory conditions (Miyata, 1975;

Cavani, 1991), thus they can be produced in large quantities. LDHs also form in soil environments (e.g., green rusts) and present peculiar sorption capacities (Violante et al., 2008). Specifically, it was investigated: i) AsO_4 sorption on Al-Mg-LDH and Fe-Mg-LDH as affected by pH and varying concentrations of inorganic [nitrate (NO_3), nitrite (NO_2), phosphate (PO_4), selenite (SeO_3), sulphate (SO_4)] and organic [oxalate (OX), tartrate (TAR)] ligands, ii) the effect of residence time on the desorption of AsO_4 by these ligands and iii) the kinetics of AsO_4 desorption by PO_4. It was studied with special attention the sorption/desorption of AsO_4 in the presence of PO_4, because PO_4 is an analogous of AsO_4 and shows a good capacity to compete with AsO_4 on both LDHs and Al and Fe-oxides (Violante and Pigna, 2002). Furthermore, competition in sorption of these anions on LDHs have received scant attention.

Waste recycling and re-utilization are two energy-efficient processes that have gained popularity due to their environmental friendliness and cost-reductive advantages. An example of such processes is the utilization of a waste by-product, the drinking-water treatment residuals (WTRs), generated from the drinking-water treatment process as a cost-effective As sorbent. In fact, they can easily be obtained, at minimal cost, from the drinking-water treatment plants, because they are the waste material resulting from the treatment of water with Al and Fe salts. In the present work, it was evaluated the AsO_4 sorption by Fe- and Al-based WTR samples as a function of WTRs particle size at different initial As concentrations and solid:solution ratios (SSRs). Specifically, it was studied the AsO_4 sorption capacity of four different sub-samples of Fe- and Al-based WTR, each characterized by a its own particles size: 1000-590 µm, 590-250 µm, 250-125 µm and < 125 µm.

To evaluate the possible health risk to humans consuming crops irrigated with As contaminated water, information is needed regarding the soil-to-plant transportation of As and to minimize the accumulation of As in plants consumed directly by humans, farm animals or wildlife (Meharg and Hartley-Whitaker 2002). Apart from the health risk, the presence of As in irrigation water or in soil at an elevated level could hamper normal growth of plants with toxicity symptoms such as biomass reduction (Carbonell-Barrachina et al. 1997) and yield losses (Jiang and Singh 1994). The application of immobilizing agents to contaminated soils is a remediation technique that reduces both mobility and bioavailability of trace elements (Vangronsveld and Cunningham, 1998). Incorporation of low-cost, widely available materials as compost into soil for As immobilization offers various potential advantages over other methods such as cost, simple methodology and low environmental impact. In the present work it was carried out an experiment on an edible plant, the bean *(Phaseolus vulgaris* L.), irrigated with different solutions containing AsO_3 and grown in a As-uncontaminated soil amended with increasing amounts of stabilized compost. The aims of this experiment were to: i) study the influence of the compost application on the mobility and phyto-availability of As in soil; ii) study the influence of the compost on the growth of the bean plants and their uptake of As from contaminated systems. Bean was selected as the test plant of this study, because this crop is grown in several As contaminated areas and suffers from As toxicity.

CHAPTER 3 - MATERIALS AND METHODS

3.1 Study on the LDHs

3.1.1 Synthesis of the Al-Mg-LDH and Fe-Mg-LDH

The LDHs of Mg-Al (Al-Mg-LDH) and Mg-Fe (Fe-Mg-LDH) were prepared by the coprecipitation method (Costantino and Pinnavaia, 1995), whereby solutions containing $MgCl_2 \cdot 6H_2O$ and $AlCl_3 \cdot 6H_2O$ or $FeCl_3 \cdot 6H_2O$ (initial Mg/Al or Mg/Fe molar ratio equal to 2) were slowly added with stirring at 20 °C to NaOH solutions at pH 10.0 (Caporale et al., 2011). The suspension's pH was maintained for 24 h by adding 2 mol L^{-1} NaOH using an automatic titrator (Potentiograph E536 Metrom Herisau) in conjunction with an automatic syringe (burette 655 Dosimat), at 20 °C, after which they were centrifuged at 10,000 x g for 30 min, rinsed five times with deionized water and then dialyzed for 21 d, freeze dried and lightly ground to pass through a 0.315 mm sieve. The Al-Mg-LDH and Fe-Mg-LDH precipitates obtained were used for the sorption/desorption studies (Figure 8). Note, no effort was made to minimize contact with the atmospheric air during the preparation of the LDHs, in order to simplify the preparation method. Sub-samples of the Fe-Mg-LDH and Al-Mg-LDH were aged for 30 d at 50 °C, in order to study the influence of aging on the degree of crystallinity of these materials.

3.1.2 Characterization of the LDHs

The Al-Mg-LDH and Fe-Mg-LDH precipitates were characterized by X-ray diffraction (XRD) and Fourier Transform Infrared (FT-IR) spectroscopy (Caporale et al., 2011). The X-ray diffraction patterns of randomly oriented samples were obtained using a Rigaku diffractometer (Rigaku Co, Tokyo) equipped with Cu Kα radiation generated at

40 kV and 30 mA and a scan speed of 2° 2θ min^{-1}. The XRD traces were the results of eight summed signals. The FT-IR spectra of the LDH precipitates were obtained using diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. Sample preparation for the DRIFT determinations was as follows: 0.2 mg of the LDHs were mixed with 200 mg of over-dried KBr. The DRIFT spectra were obtained using a Perkin-Elmer Spectrum One FT-IR Spectrophotometer (Perkin Elmer USA), with a spectral resolution of 1 cm^{-1}.

The surface area of the precipitates was determined by H_2O sorption at 20 % relative humidity (Quirk, 1955).

3.1.3 Arsenate and PO_4 sorption isotherms

Suitable volumes of 0.1 mol L^{-1} solutions containing Na_2HAsO_4 or KH_2PO_4 were added to 100 mg of the LDHs, in order to have initial AsO_4 or PO_4 concentrations in the range of $4 \cdot 10^{-4}$ to $1 \cdot 10^{-2}$ mol L^{-1} for the Al-Mg-LDH and in the range of $6 \cdot 10^{-4}$ to $1.6 \cdot 10^{-2}$ mol L^{-1} for the Fe-Mg-LDH (Caporale et al., 2011). The final volume was adjusted to 20 mL with 0.01 mol L^{-1} KCl and the initial LDH/solution ratio was 5 g L^{-1}. The pH of each suspension was kept constant at 6.0 for 24 h at 20 °C by adding 0.1 or 0.01 mol L^{-1} HCl or KOH with the automatic titrator/syringe.

The sorption of AsO_4 onto the LDHs was carried out as a function of pH (4.0 to 10.0) by adding a suitable amount of AsO_4 (2100 and 3600 mmol kg^{-1} for Al-Mg-LDH and Fe-Mg-LDH, respectively, a quantity 40 % higher than that necessary to reach a maximum sorption at pH 6.0, as determined from the sorption isotherms) to 100 mg of the LDHs. The pH of the systems was kept constant for 24 h at 20 °C by adding 0.1 or 0.01 mol L^{-1} HCl or KOH using the automatic titrator/syringe.

In a separate experiment, 20, 50, 100 or 200 mg of Al-Mg-LDH or Fe-Mg-LDH were added to 20 mL of a solution containing $1.33 \cdot 10^{-3}$ mol AsO_4 L^{-1} (100 mg As L^{-1}). The initial LDH/solution ratio ranged from 1 to 10 g L^{-1}. The pH of each suspension was kept constant at 6.0 for 24 h at 20 °C by adding 0.1 or 0.01 mol L^{-1} HCl or KOH with the automatic titrator/syringe.

The suspensions were centrifuged at 10,000 x g for 20 min and then filtered through a 0.22-µm membrane filter. The filtrates were stored at 2 °C until analysis. The experiments were conducted in triplicate.

3.1.4 Sorption of AsO_4 in the presence of inorganic and organic ligands

To 100 mg of the Fe-Mg-LDH or Al-Mg-LDH at pH 6.0 was added suitable amounts of a 0.1 mol L^{-1} Na_2HAsO_4 solution so that the AsO_4 surface coverage of the Fe-Mg-LDH (2000 mmol kg^{-1}) and Al-Mg-LDH (600 mmol kg^{-1}) was about 70 %, based on the sorption isotherms and inorganic (NO_3 as $NaNO_3$, NO_2 as $NaNO_2$, PO_4 as KH_2PO_4, SeO_3 as $Na_2SeO_3 \cdot 5H_2O$, SO_4 as $MgSO_4 \cdot 7H_2O$) and organic (OX as $Na_2C_2O_4$, TAR as $C_4H_4Na_2O_6 \cdot 2H_2O$) ligands at initial ligand/AsO_4 molar ratio (R) of 1, 3 and 5 (Caporale et al., 2011). In the absence of competing ligands, all the AsO_4 added was completely sorbed after 24 h. The pH of each suspension was kept constant for 24 h at 20 °C by adding 0.1 or 0.01 mol L^{-1} HCl or KOH using the automatic titrator. The suspensions were then centrifuged at 10,000 x g for 20 min and then filtered through a

0.22-µm membrane filter. The filtrates were stored at 2 °C until analysis. The experiment was conducted in triplicate.

3.1.5 Effect of residence time on the desorption of AsO_4 by inorganic and organic ligands

To 100 mg of the Fe-Mg-LDH or Al-Mg-LDH at pH 6.0 was added suitable amounts of a 0.1 mol L^{-1} Na_2HAsO_4 solution so that surface coverage of the Fe-Mg-LDH (2000 mmol kg^{-1}) and Al-Mg-LDH (600 mmol kg^{-1}) was about 70 %, based on the sorption isotherms (Caporale et al., 2011). The systems were maintained at pH 6.0 for 24, 48 or 168 h at 20 °C by adding 0.1 or 0.01 mol L^{-1} HCl or KOH using the automatic titrator. All the AsO_4 added was completely sorbed in the 24, 48 and 168 h systems. Inorganic (NO_3, NO_2, PO_4, SeO_3, SO_4) and organic (OX, TAR) ligands (initial ligand/AsO_4 molar ratio = 3) were then added to the 24, 48 or 168 h AsO_4 sorbed LDH systems. The final volume was 20 mL and the final LDH/solution ratio was 5 g L^{-1}. After maintaining the systems at pH 6.0 with 0.1 or 0.01 mol L^{-1} HCl or KOH for 24 h at 20 °C with the automatic titrator, the suspensions were then centrifuged at 10,000 x g for 20 min and then filtered through a 0.22-µm membrane filter. The filtrates were stored at 2 °C until analysis. The experiment was conducted in triplicate.

3.1.6 Kinetics of desorption of AsO_4 by PO_4

The kinetic study was carried out using the 24 h AsO_4 sorbed Fe-Mg-LDH (2000 mmol kg^{-1}) and Al-Mg-LDH (600 mmol kg^{-1}) systems as described above and with an initial PO_4/AsO_4 molar ratio = 3 (Caporale et al., 2011). The amount of AsO_4 desorbed from the systems, maintained at pH 6.0 with 0.1 or 0.01 mol L^{-1} HCl or KOH (over the entire reaction period using the automatic titrator), by PO_4 was determined from 0.08 to 50 h at 20 °C. The suspensions from each sampling period were centrifuged at 10,000 x g for 20 min and then filtered through a 0.22-µm membrane filter. The filtrates were stored at 2 °C until analysis. The experiment was conducted in triplicate.

3.1.7 Arsenate and PO_4 determination

Arsenate and PO_4 in the filtrates were determined by ion chromatography (Liu et al., 2001; Pigna et al. 2006), using a Dionex DX-300 Ion Chromatograph (Dionex Co, Sunnyvale, CA), an Ion Pac AS11 column (4.0 mm), an eluent of 0.02 mol L^{-1} NaOH at a flow rate of 1 mL min^{-1} and a CD 20 conductivity detector combined with autosuppression. The average AsO_4 and PO_4 retention times were 2.8 and 2.0 min, respectively. The standard AsO_4 and PO_4 concentrations used were $5 \cdot 10^{-5}$ to $2 \cdot 10^{-3}$ mol L^{-1} and $1 \cdot 10^{-4}$ to $2 \cdot 10^{-3}$ mol L^{-1}, respectively (Caporale et al., 2011).

In the experiment where a $1.33 \cdot 10^{-3}$ mol AsO_4 L^{-1} solution was kept to react in presence of varying amounts of LDHs, AsO_4 concentration in the final solution was determined by an Hydride Generation Atomic Absorption Spectrophotometer (HG-AAS, AAnalyst 700, Perkin Elmer Instruments). The AsO_4 detection limit of this method was $2.7 \cdot 10^{-8}$ mol L^{-1}.

The amount of AsO_4 or PO_4 sorbed was determined by the difference between the amount initially added and that determined in the filtrates. The data are the mean of three determinations. The ± values in the Tables 2 and 3 indicate the standard deviation. The intraday repeatability study was carried out by the injection of the same standard solution five consecutive times (n = 5) in the same day under the same conditions. The interday precision was carried out for three successive days using the same conditions. The relative standard deviation of these measurements ranged from 1.8 to 3.2 %.

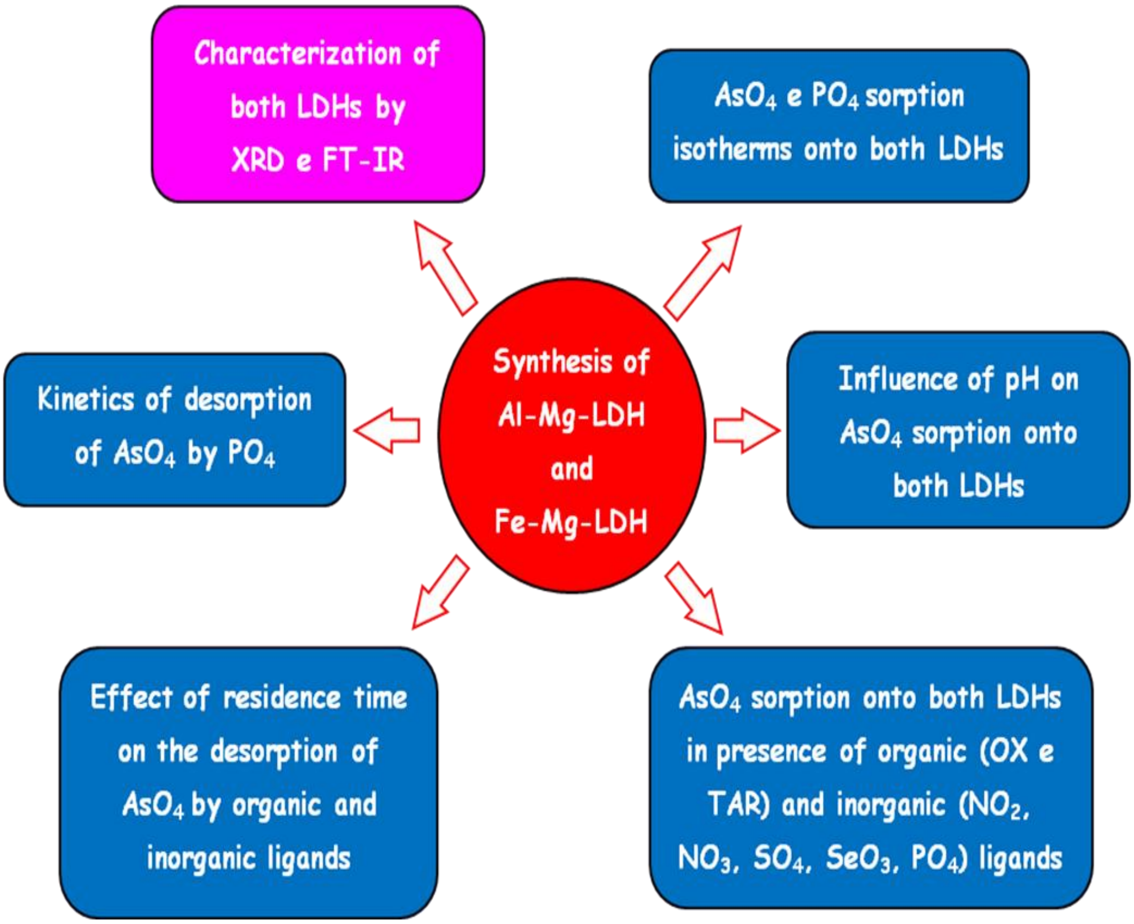


Figure 8 Schematic representation of the experiments realized on Al-Mg-LDH and Fe-Mg-LDH.

3.2 Study on the WTRs

3.2.1 WTRs collection and characterization

The study on the Al- and Fe-based WTR samples was conducted in the Earth and Environmental Studies Department of the Montclair State University (Montclair, NJ, USA), in collaboration with Dr. Dybiendu Sarkar and his group of research.

The Al-based WTR sample was obtained from the drinking-water treatment plant in Bradenton, FL, USA. The Al-WTR is produced upon addition of $Al_2(SO_4)_3$ and a small amount of a copolymer of sodium acrylate and acrylamide that leads to coagulation and flocculation of the raw water. Instead, the Fe-based WTR sample was obtained from the Hillsboro River water treatment plant in Tampa, FL, USA, where $Fe_2(SO_4)_3$ is used as the coagulant. Both WTR samples were originally collected from stockpiles that were formed within one year of production and then they were allowed to air-dry and finally passed through a 2-mm sieve before analyses.

Al- and Fe-based WTR samples were characterized for several physicochemical properties as reported in previous works (Makris et al., 2006; Nagar et al., 2009). Soluble reactive As concentrations of the WTRs and their pHs were measured in a 0.01 M KCl solution at a 1:10 solid:solution ratio, after 10 d of reaction. Total C and N were determined by combustion at 1010° C using a Carlo Erba NA-1500 CNS analyzer. Total P, Fe, Al, and As were determined by inductively-coupled plasma mass spectrometry (ICP-MS) following digestion according to the EPA Method 3050B (USEPA, 2000). Oxalate-extractable Fe and Al were determined by ICP-MS after extraction at a 1:60 solid:solution ratio, following the procedures of McKeague et al. (1971). Oxalate-extractable Fe and Al concentrations were determined using Tamm's reagent (Loeppert and Inskeep, 1996). Adequate blanks, duplicates and matrix spikes were used to meet quality assurance and quality control requirements.

The Al- and Fe-based WTR samples were also characterized by X-ray diffraction (XRD) and Scanning Electron Microscope (SEM). The X-ray diffraction patterns of randomly oriented samples were obtained using a Rigaku diffractometer (Rigaku Co, Tokyo) equipped with Cu Kα radiation generated at 40 kV and 30 mA and a scan speed of 2° 2θ min^{-1}. The XRD traces were the results of eight summed signals. Surface morphology and microstructure were examined using scanning electron microscopy (SEM, Philips XL 30).

Specific surface area of both 2-mm sieved WTRs were measured by Makris et al., (2004), using N_2 and CO_2 as the adsorbates in a volumetric apparatus (Quantachrome Autosorb-1, Quantachrome Corp.). WTRs were outgassed in an He flow at 70 °C for 4 h. Nitrogen and CO_2 gas sorption experiments were performed in liquid N_2 (-196 °C), and ethylene glycol baths (0 °C), respectively, using a thermostat (Fisher Isotemp 3017).

3.2.2 Arsenate sorption experiment on Fe- and Al-based WTR samples

2-mm sieved Fe- and Al-based WTR samples were milled in a china mortar and then sieved through four different sieves (having 1000, 590, 250 and 125 µm of pore diameter, respectively), in order to have four different sub-samples, each characterized by a its own particles size: 1000-590 µm, 590-250 µm, 250-125 µm and < 125 µm.

Each sub-sample of Fe- and Al-based WTRs was kept to react with three different solutions containing AsO_4 (1.33, 2.67 or 5.33 mmol L^{-1}), at three Solid Solution Ratios (SSRs) (50, 100 or 200 g WTR L^{-1}), as reported in Figure 9. Moreover, on Al-based WTR samples were carried out further investigations with two solutions containing higher concentration of AsO_4 (16.67 or 33.33 mmol L^{-1}), at the three SSRs above mentioned. Solutions containing AsO_4 were prepared in 0.01 M KCl and in 0.01 M of MES sodium salt buffer (Sigma-Aldrich, USA) using sodium hydrogenarsenate heptahydrate ($Na_2AsO_4 \cdot 7H_2O$ - Sigma-Aldrich, USA). The batch experiments were performed keeping to react 0.5, 1 and 2 g of each sub-sample of Fe- and Al-based WTRs with 10 mL of each solutions containing AsO_4, at pH 7.0 for 24 h, on a reciprocal shaker at 200 rpm. Following shaking, the suspensions were centrifuged at 5000 rpm and the supernatants were filtered through a 0.22-µm membrane filters. The filtrates were stored at 2 °C until analysis. The experiment was conducted in triplicate.

All the filtrates were analyzed for As by an Inductively Coupled Plasma Mass Spectrometer (ICP-MS), Perkin Elmer. The AsO_4 detection limit of this method was $8 \cdot 10^{-9}$ mol L^{-1}. The amount of AsO_4 sorbed by the Al- and Fe-based WTR samples was determined by the difference between the amount initially load and that determined in the filtrates. The data are the mean of three determinations.

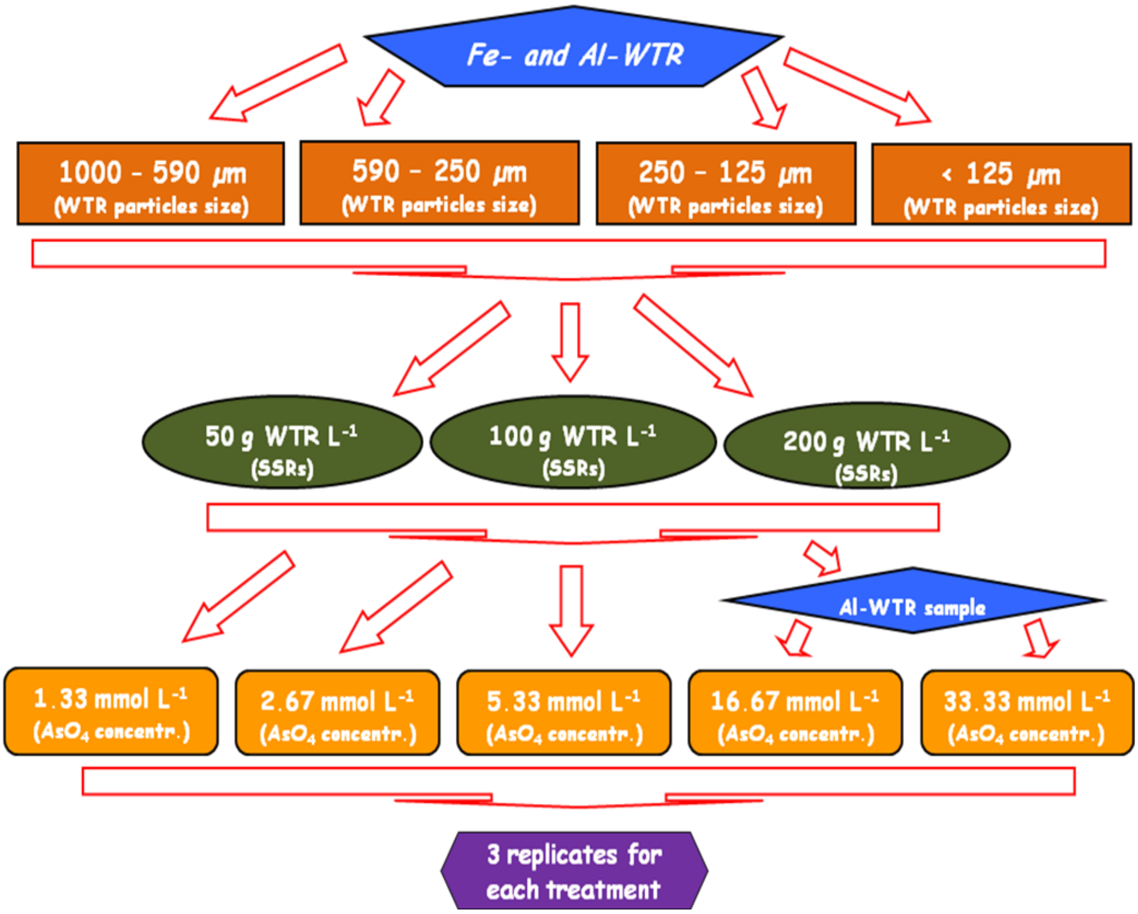


Figure 9 Schematic representation of the experiments carried out on Al- and Fe-WTR samples.

3.3 Study on the bean plants (*Phaseolus vulgaris* L.)

3.3.1 Compost characterization

The compost used in this experiment was characterized by ^{13}C Cross Polarization Magic Angle Spinning (CPMAS), Nuclear Magnetic Resonance (NMR) spectroscopy that allow a detailed characterization of the chemical composition of complex organic matter (Boehm et al., 1997; Kögel-Knabner, 2002; Pane et al., 2011). ^{13}C CPMAS-NMR analysis was realized by Prof. Piccolo's group of research, in CERMANU's laboratories of Faculty of Agriculture, Portici, NA, Italy.

^{13}C NMR spectrum was obtained in the solid state (CPMAS). An analysis was carried out with a Bruker AVANCE™ 300, equipped with a 4 mm Wide Bore MAS probe, operating at a ^{13}C resonating frequency of 75.475 MHz. The sample (100-150 mg) was packed in 4 mm zirconia rotors with Kel-F caps and spun at 13 ± 1 kHz. To account for possible inhomogeneity of the Hartmann-Hahn condition at high rotor spin rates, a ^{1}H ramp sequence was applied in CP experiments during a contact time (CT) of 1 ms. The ^{13}C-CPMAS experiments were conducted collecting 6000 scans with 2266 data points over an acquisition time of 25 ms, and a recycle delay of 2.0 s. The Bruker Topspin 1.3 software was used to collect and elaborate the spectrum.

The compost was been also characterized by an NCS Elemental Analyzer (NA 1500 Series 2).

3.3.2 Soil preparation and characterization

The uncontaminated soil used in the experiment was collected from the sub-surface layer (10-30 cm) of a grassland in Portici, Naples, Italy. After air-drying, the soil samples for bean cultivation and chemical analysis were passed through 5 and 2 mm sieves, respectively.

Soil fractions (sand, silt and clay) were separated by pipette and sieving method following pretreatment with H_2O_2 to oxidize organic matter, and dispersion aided by sodium hexametaphosphate (Indorante et al., 1990). Soil pH was measured by potentiometry in distilled water (1:2.5 soil/water ratio). Organic C content of soil was determined by wet digestion with a modified Walkley-Black procedure. For determination of CEC the soil was extracted with 1 M NH_4OAc at pH 7.0. Total soil N was determined using a NCS Elemental Analyzer (NA 1500 Series 2). Available P concentration was determined by colorimetric method using 0.5 M $NaHCO_3$ as the extractant (Olsen method). Arsenic soil background was extracted with concentrated HNO_3 and HF at 5:1. The concentrations of the total As were determined as discussed below in the section 3.3.7.

3.3.3 Experimental design

Bean plants *(Phaseolus vulgaris* L.) cultivar Borlotto Nano were cultivated in an unheated greenhouse, illuminated with natural light, during the months of late April, May and June 2011.

The treatments consisted of factorial combinations of As application at 4 rates in irrigation water [0 (As 0), 1 (As 1), 2 (As 2) and 3 (As 3) mg As L^{-1}] and three levels of compost application [0 (C 0), 300 (C 300), 600 (C 600) q ha^{-1}]. Treatments were replicated 5 times and the experimental design was completely randomized and rearranged every 3 days (Figure 10).

Beans were seeded in a polystyrene alveolar seedbed consisting of 90 holes (2.5 cm diameter, 4 cm depth), filled with soil mixed with commercial potting soil (70% soil in the final mixture). Two weeks after germination, seedlings were transplanted into the pots containing 8 kg of uncontaminated soil (one seedling/pot, 5 pots per treatment). At transplanting, 60 and 120 g of commercial Compost (aged 120 days) were supplied to the C 300 and C 600 pots, respectively, and mixed homogeneously with soil. During the first 5 days after transplanting, bean plants were irrigated with water and then irrigated with water containing sodium arsenite ($NaAsO_2$) at four different concentrations: 0 (As 0), 1(As 1), 2 (As 2) and 3 (As 3) mg As L^{-1}, until the beans were ripe. The developmental stage of the bean plants at the harvest time was maturity of the first fruit set (plants were 74 days old after germination and 60 days old after transplanting). Bean plants started their fruiting period after 22 days from first As application (plants were 41 days old after germination and 27 days old after transplanting).

The range of As concentrations was chosen to encompass the concentrations occurring in underground waters of the As affected areas of world. Contaminated water was added as required to maintain the soil moisture at 70 % of the field capacity. Arsenic irrigation was stopped 4 days before harvest.

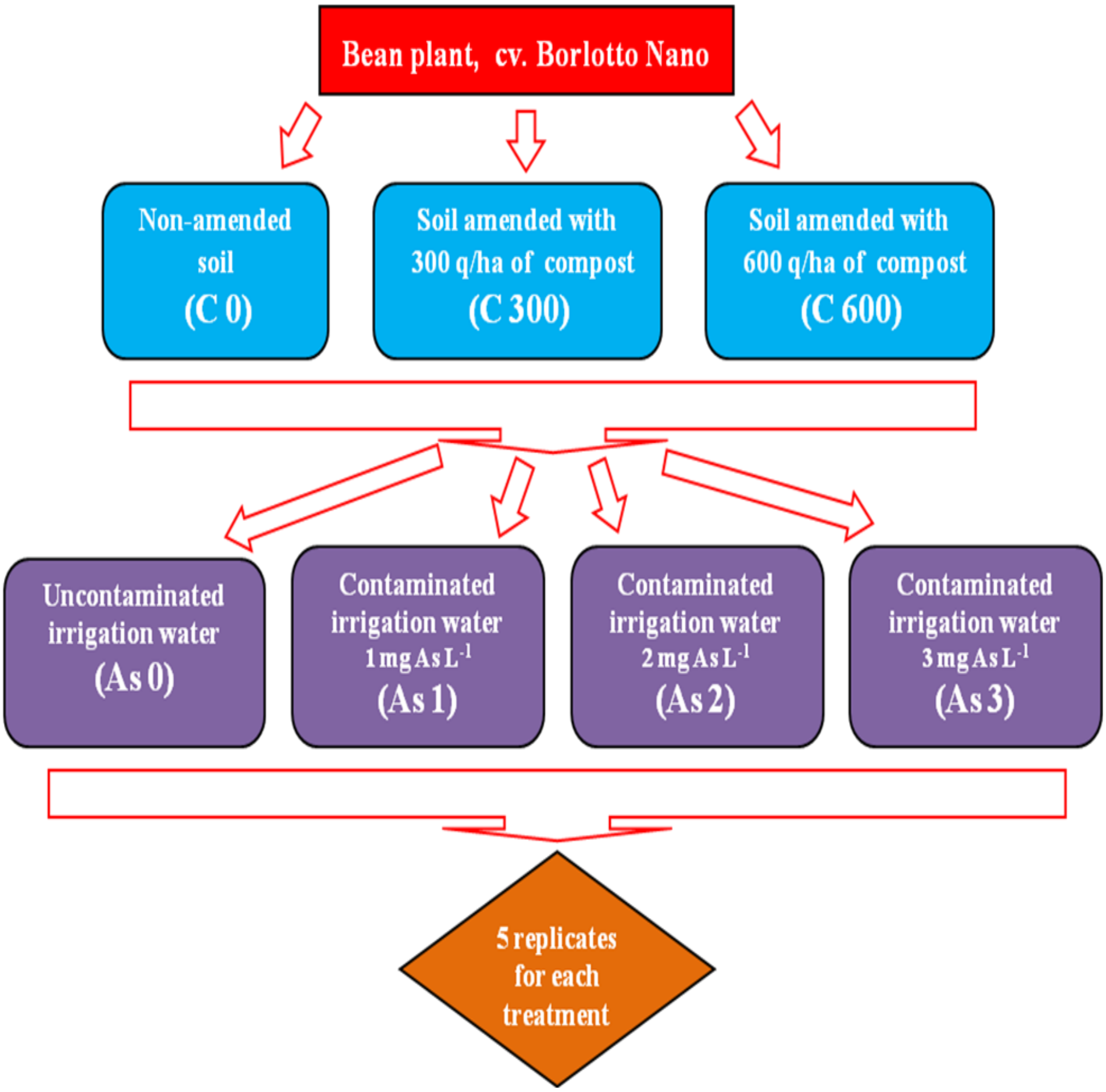


Figure 10 Schematic representation of the experiment on the growth of bean plants, irrigated with As contaminated solutions.

3.3.4 Chlorophyll A and B concentrations in bean leaves

Three leaves per bean plant were sampled and removed 40 days after transplanting in order to determine the chlorophyll A and B contents. Extraction of chlorophylls from bean leaves was carried out using 80 % acetone in deionized water (v/v). One gram of fresh leaves was homogenized with 5 mL of acetone and shaken for 1 h on a reciprocal shaker at 200 rpm. The homogenate was filtered through 0.22 µm filter, and the residue was similarly extracted once again and filtered. The two filtrates were combined and the final volume was made up to 10 mL. All extracts were assayed using Bio-Rad Benchmark Microplate reader. Chlorophyll A and B contents (mg g^{-1} dry weight) were calculated by absorbance values at 663 nm (D 663) and 645 nm (D 645) using the formula of Arnon (1949).

3.3.5 Harvest and samples collection

At the harvest, aboveground biomass and roots were sampled separately. Aboveground biomass were removed by cutting the base of the plant 1 cm above the soil surface with a sharp blade and separated in shoots (stems plus leaves biomass) and beans sub-samples. The fresh tissues of bean plants were weighted, washed with tap water, rinsed twice with deionized water in order to remove soil residues and then dried in oven for two days at 70 °C, to reach a constant weight. The dried samples of bean plants were weighed and then ground using a PM 200 ball mill (Retsch).

3.3.6 Determination of non- and specifically sorbed As in soil samples

Arsenic fractions in each soil sample were extracted through the first two-step sequential extraction procedure (SEP) (Wenzel et al., 2001). 1 g of each soil sample was kept to reach with 25 mL of a 0.05 M $(NH_4)_2SO_4$ for 4 h at 20 °C, on a reciprocal shaker at 150 rpm. Following shaking, the suspensions were centrifuged for 15 min at 3500 x g and the supernatants were filtered through a 0.45-µm membrane filters (Step 1). Subsequently, each soil sample was kept to reach with 25 mL of a 0.05 M $(NH_4)H_2PO_4$ for 16 h at 20 °C, on a reciprocal shaker at 150 rpm. Following shaking, the suspensions were centrifuged for 15 min at 3500 x g and the supernatants were filtered through a 0.45-µm membrane filters (Step 2). The As fractions extracted by this 2 sequential step were assumed to correspond to non-specifically sorbed As (Step 1) and specifically sorbed As (Step 2). The concentrations of the As fractions were determined as discussed below in the section 3.3.7.

3.3.7 Arsenic and P determination

Sub-samples of dried tissues and soils were digested in a microwave (Milestone, Digestor/Dring Ethos 900); 0.5 g of dried tissues were weighed into PTFE vessels and digested in 5 mL of HNO_3 (65 %), 0.5 mL of HF (50 %) and 2 mL of H_2O_2, while 0.5 g of soil samples were weighed into PTFE vessels and digested in 15 mL of HNO_3 (65 %) and 3 mL of HF (50 %). All solutions obtained were filtered and diluted to 50 ml.

The As concentrations in bean plants tissues and soil samples were determined by flow-injection hydride generation atomic absorption spectrometer, using a Perkin-Elmer AAnalist 700 interfaced with the FIAS 100 hydride generator. The reagents used for HG-AAS were 10% (v/v) HCl, 0.2% $NaBH_4$ in 0.05% NaOH. The samples were reduced prior to analysis with 5% (w/v) KI and 5% (w/v) ascorbic acid to improve sensitivity. The As detection limit provided by this method was $2 \cdot 10^{-3}$ mg L^{-1}.

Phosphorus concentrations in bean plants tissues were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Varian, Liberty 150). The P detection limit of this method was $1.2 \cdot 10^{-2}$ mg L^{-1}.

All analysis was carried out in triplicate. In each analytical batch at least one reagent blank and one internationally certified reference material (CRM), oriental tobacco leaves CTA-OTL-1, were included to assess precision and accuracy of the chemical analysis.

Data analyses were performed with Kaleidagraph 3.6. Differences were considered as statistically significant at $p < 0.05$ (Tukey's test).

CHAPTER 4 - RESULTS AND DISCUSSION

4.1 Study on the LDHs

4.1.1 Nature of the LDHs

The X-ray diffraction patterns of the Al-Mg-LDH and Fe-Mg-LDH are shown in Figure 11. Both LDHs showed peaks at about 0.760 (d_{003}), 0.380, 0.260, 0.153 and 0.150 nm and some asymmetric peaks at high angles (> 30° 2θ), characteristic of hydrotalcite (Miyata, 1975; Cavani et al., 1991; Ulibarri et al., 1991; Costantino and Pinnavaia, 1995; Rives, 2002). The peaks were sharp for the Al-Mg-LDH, whereas the peaks were broader for the Fe-Mg-LDH, which indicated that the Fe-Mg-LDH were less crystalline than the Al-Mg-LDH and/or the particles were of smaller size (Caporale et al., 2011). However, prolonging the aging for 30 d at 50 °C a higher degree of crystallinity and/or larger particles size of Fe-Mg-LDH was obtained (Figure 11), whereas Al-Mg-LDH remained practically unchanged (not shown). Probably, Fe-Mg-LDH sample aged 24 h at 20 °C was a mixture of materials of different crystallinity, size and nature (LDH and short-range ordered Fe and/or Mg oxides, (Violante and Huang, 1993). The peaks from the Fe-Mg-LDH were also shifted 0.02 nm (0.2 Å) higher compared to the Al-Mg-LDH. Similarly, slight differences in the basal spacing were observed in a series of (Al,Fe)-Mg-LDH, with CO_3 as the interlayer anion, which may have been due to structural differences, however, it was also possible that these small differences were due to small variations in the hydration degree of the interlayer (Fernández et al., 1998). Also, basal spacing is a function of the size and charge of the anion. Generally, basal spacing expands with increasing anion size and contracts for divalent anions versus monovalent anions as the divalent anions bond more strongly to the basal layers and interlayer water (Miyata and Okada, 1977; Miyata, 1983). Both Cl and CO_3 ions (atmospheric impurity) were expected to be in the basal interlayer of the LDHs, however, the proportion of these anions in the two LDHs could not be discerned, thus, whether this accounted for the difference in the basal spacing observed between the two LDHs is not known.

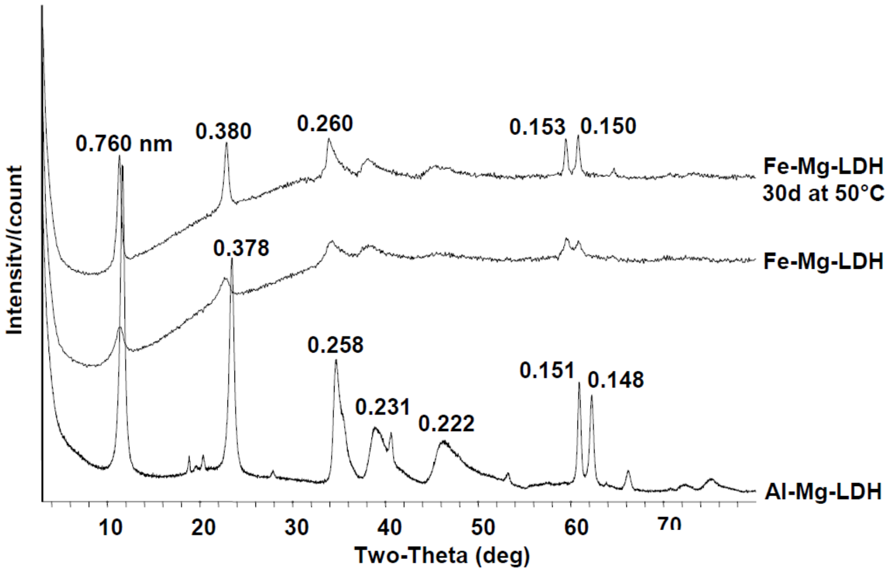
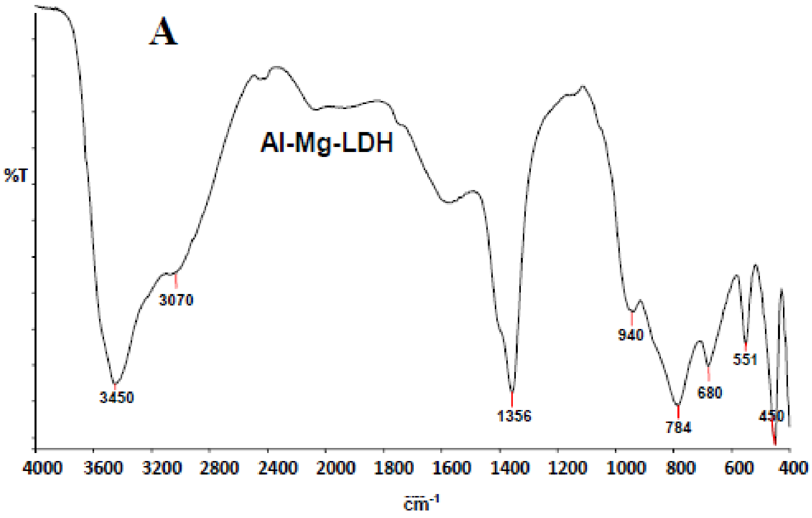


Figure 11 Powder X-ray diffraction patterns of Al-Mg-LDH and Fe-Mg-LDH aged at 20 °C and Fe-Mg-LDH aged for 30 d at 50 °C.

The FT-IR spectra of the Al-Mg-LDH and Fe-Mg-LDH are shown in Figure 12. The Al-Mg-LDH spectrum showed a peak in the hydroxyl stretching region centered at about 3450 cm^{-1}, attributed to the stretching vibrations of the hydroxyls attached to Al and Mg sheets and to water molecules in the basal interlayer (Violante et al., 2009; Caporale et al., 2011). The shoulder at about 3070 cm^{-1} was due to the interaction between the OH groups and the interlayer carbonate ions and the presence of the carbonate peak at 680 cm^{-1} also indicated that considerable amounts of carbonate were in the interlayer (Rives, 2002; Lv et al., 2006; Violante et al., 2009). The peaks at about 940, 780, 550, 450 cm^{-1} were ascribed to the Al-O stretching modes (Figure 12 A). The strong peak at 1356 cm^{-1} is due to carbonate mainly present in the basal interlayer. In a Zn-Al-Cl-LDH prepared in boil and N_2 purged water, a very weak carbonate peak (1354 cm^{-1}) was observed in the IR spectrum (Islam and Patel, 2010). The ratio of the hydroxyl/carbonate peak was 6, compared to 1 in this study, indicating that the carbonate concentration in the basal interlayers in this study was significant. The spectrum of Fe-Mg-LDH also had a strong carbonate peak at 1358 cm^{-1} indicating that significant amounts of carbonate were in the basal interlayer (Figure 12 B). The hydroxyl stretching region and the metal bands below 1000 cm^{-1} in the Fe-Mg-LDH aged 24 h at 20 °C appeared particularly broad indicating a lower crystallinity and/or smaller size of the particles (Violante et al., 2009), which is in agreement with the XRD results.



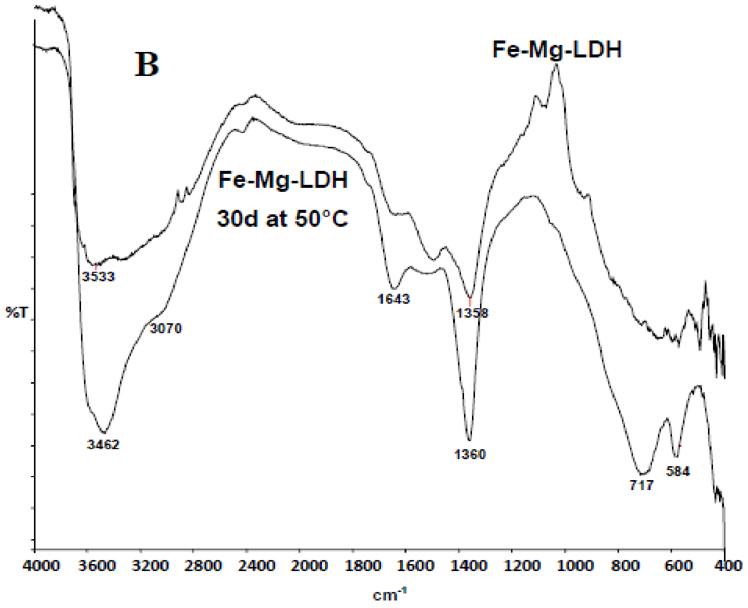


Figura 12 FR-IR spectra of Al-Mg-LDH (A) and Fe-Mg-LDH aged at 20 °C (B) and Fe-Mg-LDH aged for 30 d at 50 °C (B).

4.1.2 Sorption of AsO_4 onto LDHs

The sorption isotherms of AsO_4 onto the Al-Mg-LDH and Fe-Mg-LDH at pH 6.0, after 24 h of reaction period are shown in Figure 13. The sorption data of AsO_4 sorbed onto the LDH conformed to the Langmuir equation in the following form:

$$S = S_m K c / (1 + K c)$$

where S is the amount of AsO_4 sorbed per unit mass of adsorbent (mmol kg^{-1}), S_m is the maximum amount of AsO_4 that may be bound to the adsorbent (sorption capacity), c is the equilibrium solution concentration (mmol L^{-1}), and K is a constant related to the binding energy (Giles et al., 1974).

The sorption isotherms of AsO_4 to the two LDHs were typical L shaped curves (Giles et al., 1974), indicating that AsO_4 had a high affinity for the sorption sites on the LDHs, exchanging with the Cl and CO_3 ions in the interlayer. The Fe-Mg-LDH sorbed nearly twice the amount (mmol kg^{-1}) of AsO_4 compared to the Al-Mg-LDH (Figure 13), due, in part, to its greater surface area (273 and 219 m^2 g^{-1}, respectively) and lower degree of crystallinity (Caporale et al., 2011). The sorption isotherms of PO_4, which is an analogous of AsO_4 and showed a strong capacity to compete with AsO_4 (as discussed below) was also studied. The Fe-Mg-LDH sorbed more AsO_4 (Sm = 2595 mmol kg^{-1}) than PO_4 (Sm = 2470 mmol kg^{-1}), in contrast to the Al-Mg-LDH, which adsorbed more PO_4 (Sm = 1675 mmol kg^{-1}) than AsO_4 (Sm = 1490 mmol kg^{-1}) (Table 1). These findings may be attributed to the greater affinity of AsO_4 than PO_4 for Fe sites and, vice versa, to the greater affinity of PO_4 than AsO_4 for Al sites (Violante et al., 2002). Violante et al., 2002, also observed the same trend for AsO_4 and PO_4 sorbed on Fe-rich and Al-rich minerals.

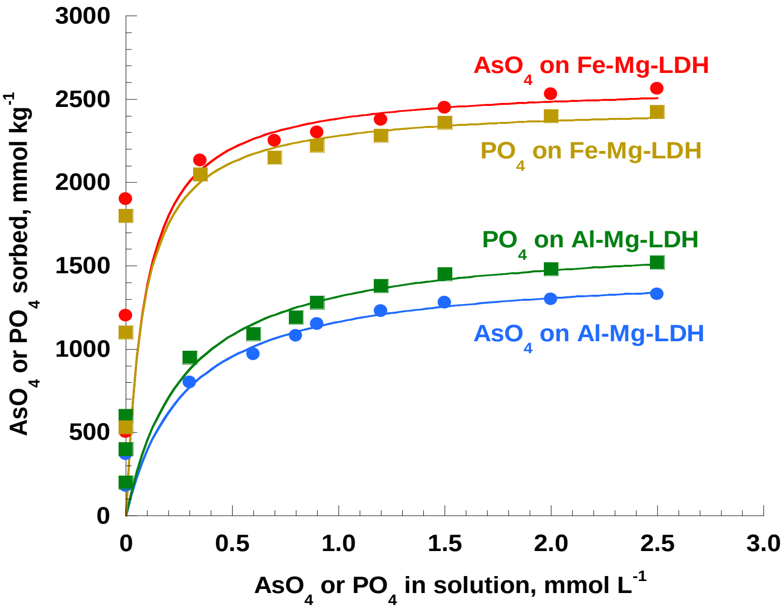


Figure 13 Sorption isotherms of AsO_4 and PO_4 onto Al-Mg-LDH and Fe-Mg-LDH at 20 °C and pH 6.0, after a reaction period of 24 h.

Thus, it is apparent that differences between the anions and/or differences between Fe and Al sorption sites also account for the higher amounts of anions sorbed by the Fe-Mg-LDH versus the Al-Mg-LDH. Studies have shown that the orientation of anions changes with increasing anion concentration, that the packing of anions is affected by layer charge and that hydrogen bonding between the anions with the surface hydroxyls/water in the interlayer can determine an anion's affinity for the sorption sites (Miyata, 1983; Khan and O'Hare, 2002; Liu et al., 2009), which may account for the reversal of affinities observed for AsO_4 and PO_4 for the Fe and Al sorption sites.

The Langmuir constant K was around an order of magnitude larger for the Fe-Mg-LDH compared to the Al-Mg-LDH for both AsO_4 and PO_4 (Table 1), indicating a higher affinity of the Fe-Mg-LDH for the anions, probably due to the presence of short-range Fe and/or Mg precipitates in this sample on which both AsO_4 and PO_4 may form strong inner-sphere complexes (Wang et al., 2010).

Table 1 Langmuir sorption capacity (*Sm*) and the constant K for AsO_4 and PO_4 as obtained from the sorption isotherms of the LDH.

Sample	**Surface area**	**AsO_4**			**PO_4**		
	$m^2 g^{-1}$	***Sm*** **(mmol kg^{-1})**	**K**	**R^2**	***Sm*** **(mmol kg^{-1})**	**K**	**R^2**
Al-Mg-LDH	219	1490 (6.8)*	3.3	0.98	1675 (7.6)*	3.9	0.95
Fe-Mg-LDH	273	2595 (9.5)*	31.0	0.94	2470 (9.0)*	20.6	0.96

* Numbers in parenthesis indicate the amount sorbed as mmol m^{-2} x 10^{-3}.

In the experiment carried out adding increasing amounts of the LDHs (1, 2.5, 5 or 10 g) to 1 L of solution containing $1.33 \cdot 10^{-3}$ mol AsO_4 L^{-1} (100 mg As L^{-1}), we found that 1 g of the Al-Mg-LDH or Fe-Mg-LDH dropped the concentration of AsO_4 to $1.28 \cdot 10^{-6}$ mol L^{-1} (0.096 mg As L^{-1}) and $1.24 \cdot 10^{-6}$ mol L^{-1} (0.093 mg As L^{-1}), respectively, whereas the addition of 10 g of the Al-Mg-LDH or Fe-Mg-LDH dropped the concentration of the above mentioned solution to $3.06 \cdot 10^{-7}$ mol L^{-1} (0.023 mg As L^{-1}) and $2.26 \cdot 10^{-7}$ mol L^{-1} (0.017 mg As L^{-1}), respectively (data not shown). By interpolation of these data with an exponential curve, we found that the addition of 15.3 and 13.0 g L^{-1} of Al-Mg-LDH and Fe-Mg-LDH, respectively, would be enough to drop the concentration of the $1.33 \cdot 10^{-3}$ mol AsO_4 L^{-1} (100 mg As L^{-1}) solution to the world health organization limit, equal to $1.33 \cdot 10^{-7}$ mol AsO_4 L^{-1} (0.01 mg As L^{-1}) (Caporale et al., 2011).

The effect of pH (from 4.0 to 10.0) on the sorption of AsO_4 onto Al-Mg-LDH and Fe-Mg-LDH samples, after 24 h of reaction, is shown in Figure 14. AsO_4 sorption onto the samples decreased by increasing pH (Caporale et al., 2011). The rate of decline in the amount of AsO_4 sorbed was, however, relatively constant, decreasing the fastest for the Fe-Mg-LDH (270 mmol AsO_4/pH unit) compared to the Al-Mg-LDH (210 mmol AsO_4/pH unit). This behavior may be attributed to the high affinity of OH ions for LDHs (Cavani et al., 1991; Pigna et al., 2006) and/or to the value of zero point charge (pzc) of two sorbents. At pH < pzc, the positively charged surfaces of the sorbents facilitated the sorption of the negatively charged AsO_4 (Fernández et al., 1998; Miyata and Okada, 1977). The pzc for LDHs was reported to be in the range 7.0 - 9.0 (Violante et al., 2009), so in alkaline systems the sorption of AsO_4 anions onto the LDH surfaces should be inhibited. At pH > pzc, OH ions dominate the system, resulting in a charge reversal on the surfaces of the sorbents which led to electrostatic repulsion of AsO_4 ions (Miyata, 1983).

Deprotonation of the surface hydroxyl groups and/or the change to more negative species of AsO_4 (e.g., H_3AsO_4, $H_2AsO_4^-$) (pKa = 2.1, 6.9, 11.5) occurs with the addition of hydroxyl ions, both of which could account for the decline in the sorbed AsO_4 with increasing pH. Based on Ksp and pH_{PZNC} of metal hydroxides, the affinity of Al^{3+} for the hydroxyl was less than that for Fe^{3+} (Hou and Song, 2004). Thus, it appears that the deprotonation of the surface hydroxyl groups on the Fe-Mg-LDH may be more important for controlling AsO_4 sorption than on the Al-Mg-LDH. Interestingly, (You et al., 2001b) observed that SeO_3 (pKa = 2.46, 7.3) sorption in the absence of competing anions on Al-Mg-LDH was relatively constant between pH 4.0 to 10.0. Also it was shown that the Al-Mg-LDH had a high pH buffering capacity (i.e., constant) between pH 4.0 to 10.0. Thus, it appears that AsO_4 sorption was more influenced by the protonation of the surface hydroxyl groups than SeO_3. Hence, the properties of anion also play an important role in the sorption process.

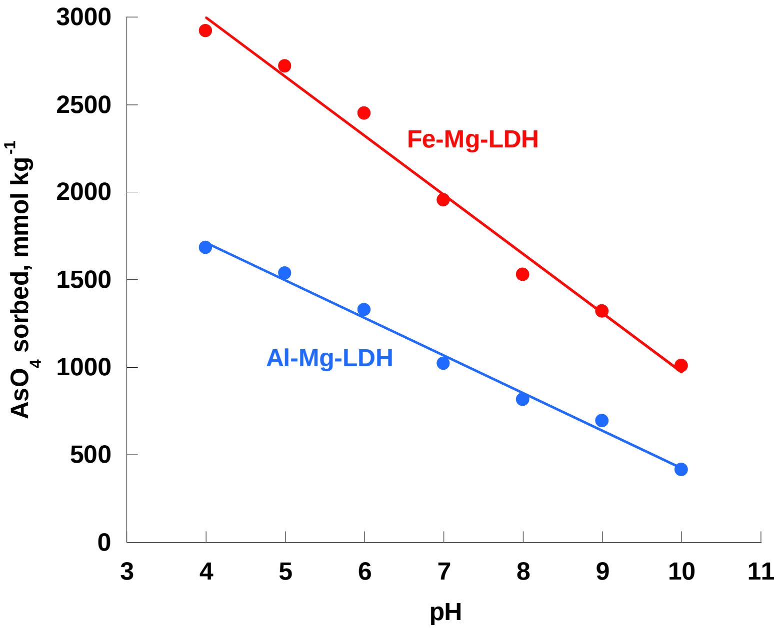


Figure 14 Effect of pH on the sorption of AsO_4 at 20 °C onto Al-Mg-LDH and Fe-Mg-LDH after a reaction period of 24 h.

4.1.3 Sorption of AsO_4 in the presence of inorganic and organic ligands

The sorption of AsO_4 in the presence of increasing concentrations of inorganic (NO_3, NO_2, PO_4, SeO_3, SO_4) and organic (OX, TAR) ligands on Al-Mg-LDH and Fe-Mg-LDH, at pH 6.0, and after a 24 h reaction period are shown in Figure 15. The initial ligand/AsO_4 molar ratio (R) were 1, 3 and 5, but only the data at R = 1 and 5 are shown for sake of clarity. The efficiency (%) of the ligands in preventing AsO_4 sorption is calculated by subtracting the amount sorbed from that initially added, divided by the amount initially added (e.g., [(600-560)/600 x 100] = 6.6 %). The efficiency of the anions to compete with AsO_4 for the sorption sites on the Al-Mg-LDH was in the order $NO_3 < NO_2 < SO_4 < SeO_3 < TAR < OX << PO_4$ at all molar ratios examined (Figure 15 A), while on the Fe-Mg-LDH the order was $NO_3 < SO_4 \approx NO_2 < TAR < OX < SeO_3 << PO_4$ (Figure 15 B) (Caporale et al., 2011) .

The inhibition of AsO_4 sorption increased by increasing the initial ligand concentration and was greater on Al-Mg-LDH than on Fe-Mg-LDH, evidently because AsO_4 anions have a stronger affinity for Fe than Al (Violante et al., 2002) and for the presence in Fe-Mg-LDH of short-range-ordered materials on which AsO_4 forms very strong inner-sphere complexes not easily desorbable by competing ligands (Goldberg et al., 2001; Yang et al., 2006; Pigna et al., 2006).

Many factors affect the sorption of organic and inorganic anions onto LDHs as the valency, the size and the capacity of each single ligand to form outer- or inner-sphere complexes on the surfaces of the minerals. The negligible effect of NO_3 and NO_2 on AsO_4 sorption could be ascribed to the fact that these ions are monovalent and are nonspecific anions in solid-liquid interfacial reactions (Davis and Burgoa, 1995). Furthermore, they have a lower ionic potential than AsO_4, resulting in their weaker competition ability with AsO_4 for binding sites on LDHs (Goh and Lim, 2010).

SO_4 is expected to form outer-sphere complexes on clay surfaces (Frankenberger, 2002; Smedley and Kinniburgh, 2002; Pigna et al., 2006; Violante et al., 2008) at pH ≥ 6, while SeO_3, OX, TAR and PO_4 are all expected to form inner-sphere complexes, which probably accounts for the low competitiveness of SO_4 compared to the other anions with AsO_4 for the sorption sites on the LDH surfaces.

The only difference in the order between the two LDHs being that the organic acids were less effective than SeO_3 in competing with AsO_4 on the Fe-Mg-LDH versus the

Al-Mg-LDH. The efficiency of SeO_3 to inhibit AsO_4 sorption was lightly greater on Fe-Mg-LDH than Al-Mg-LDH; in fact, SeO_3 replaced more AsO_4 from Fe-Mg-LDH than Al-Mg-LDH (as discussed below).

The 10-20 % decrease in efficiency of the organics for the Fe-Mg-LDH compared to the Al-Mg-LDH systems indicated that the affinity of the organic acids for the sorption sites on the two LDH was different, attributed to the difference in their bonding with the Al and Fe in the LDHs. The results are contrary to that expected based on the stability constants (log k) for tartrate-Fe (6.5), oxalate-Fe (7.6), tartrate-Al (5.84) and oxalate-Al (6.28) (Martell and Smith, 1997).

Divalent forms of OX and TAR are expected to exist in solution at pH 6.0 (pKa values for OX = 1.2, 4.2; TAR = 2.98, 4.34; SeO_3 = 2.46, 7.3), which could account for them competing more effectively with AsO_4 than SeO_3 on the Al-Mg-LDH but does not explain why SeO_3 competed more effectively with AsO_4 than the organic acids for the sorption sites on the Fe-Mg-LDH. A possible explanation of this behavior is that SeO_3 seems to form a mixture of outer-sphere and inner-sphere complexes on minerals containing Al, whereas forms inner-sphere complexes on goethite and ferrihydrite (Peak, 2006). Furthermore, anion size and anion orientation were observed to influence sorption of anions in the interlayer of LDHs (Meyn et al., 1990). Thus, differences in the steric and electronic factors of the sorption sites in the interlayer of the Al-Mg-LDH and Fe-Mg-LDH and/or of the anions likely influenced the affinity of the organic acids for the sorption sites.

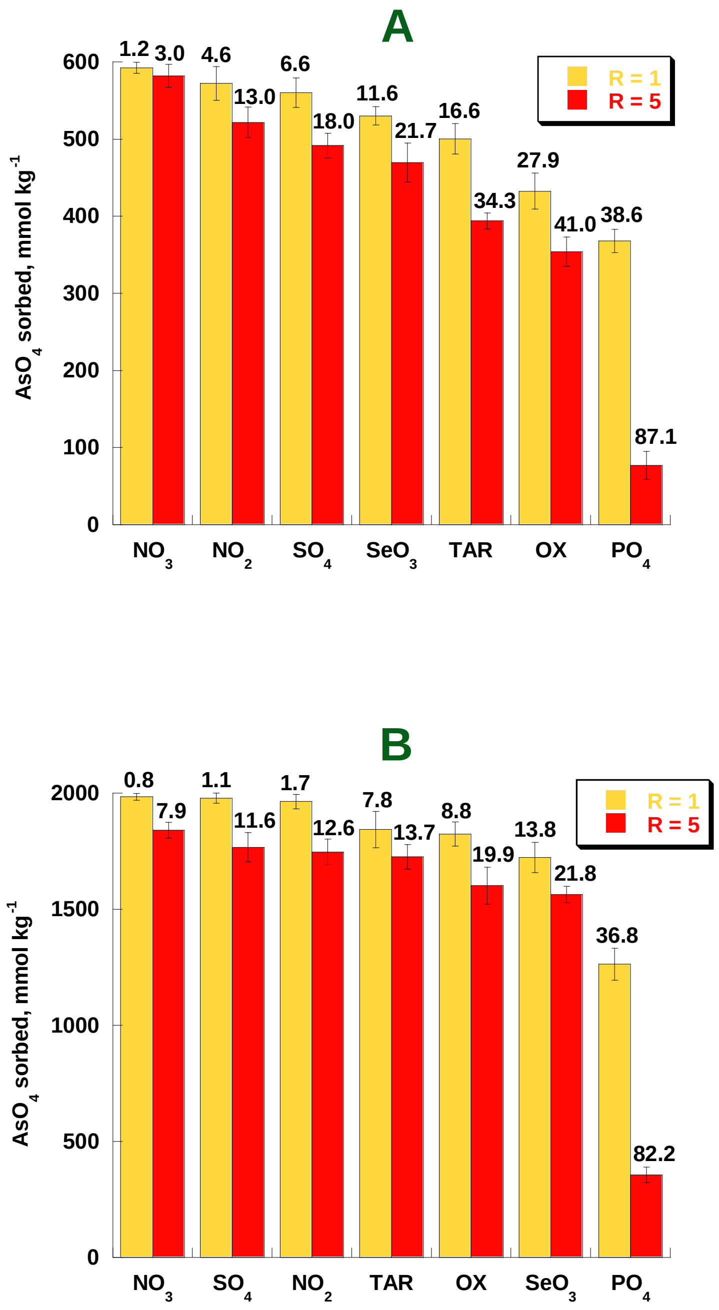


Figure 15 The amount of AsO_4 sorbed onto the Al-Mg-LDH (A) and Fe-Mg-LDH (B) in the presence of increasing concentrations of inorganic and organic ligands after a reaction time of 24 h; initial ligand/AsO_4 molar ratio = 1 (yellow) and 5 (red). The numbers indicate the efficiency (%) of the ligands in preventing AsO_4 sorption. The initial AsO_4 concentration for the Al-Mg-LDH and Fe-Mg-LDH was 600 and 2000 mmol kg^{-1}, respectively.

4.1.4 Effect of residence time on the desorption of AsO_4

Initially AsO_4 was sorbed by the Al-Mg-LDH (600 mmol kg^{-1}) and Fe-Mg-LDH (2000 mmol kg^{-1}) at pH 6.0 for either a reaction period of 24, 48 or 168 h (i.e., residence time). The desorption of AsO_4 from the Al-Mg-LDH and Fe-Mg-LDH by the inorganic and organic ligands, for an initial ligand/AsO_4 molar ratio (R) of 3, as affected by the residence time of AsO_4 are shown in Tables 2 and 3, respectively. The amounts of AsO_4 desorbed from the LDHs decreased with an increase in the AsO_4 residence time (Caporale et al., 2011). Precisely, the quantities of AsO_4 removed by PO_4 decreased from 72.8 to 62.6 % from Al-Mg-LDH (Table 2) and from 62.5 to 54.5 % from Fe-Mg-LDH (Table 3) by increasing the residence time of AsO_4 from 24 to 168 h.

After a residence time of 168 h the amounts of AsO_4 replaced by OX, TAR, SeO_3, SO_4, NO_2 and NO_3 from Al-Mg-LDH ranged from 20.7 % by OX to 0.9 % by NO_3. The capacity of these ligands in removing AsO_4 from Fe-Mg-LDH was still lower ranging from 7.0 % for TAR to 0.7 % for NO_3, evidencing that AsO_4 is more strongly sorbed on minerals containing Fe than Al. Negligible amounts of AsO_4 (< 5%) were replaced by NO_2 and NO_3.

Other studies on Fe and Al oxides (Arai and Sparks, 2002; Pigna et al., 2006) have also shown that an increase in residence time of AsO_4 resulted in a decrease in its desorption by competing anions. Clearly, increased diffusion into the LDH and the formation of a stronger bond between the AsO_4 and the surface sorption sites of the sorbents may account for reduce efficiency with an increase in the AsO_4 residence time.

The ability of the anions to desorb AsO_4 from the sorption sites on the Al-Mg-LDH was in the order $NO_3 < NO_2 < SeO_3 \approx SO_4 < TAR < OX << PO_4$ at all residence times examined (Table 2), while on the Fe-Mg-LDH the order was $NO_3 < SO_4 \approx NO_2 <$ TAR $\leq$ OX $< SeO_3 \ll PO_4$ (Table 3).

The effect of increasing residence time on desorbing AsO_4 was similar for all the ligands, for both LDHs, varying from 2 to 10 %. However, for the Al-Mg-LDH systems with PO_4, TAR and OX, 10 to 20 % more AsO_4 was desorbed compared to the Fe-Mg-LDH systems for the same residence time, due to the fact that AsO_4 was more strongly sorbed by the Fe-Mg-LDH than the Al-Mg-LDH (Wang et al., 2010).

Comparison of these trends to that observed for the systems where both ligand and AsO_4 were added simultaneously (Figure 15) showed that they were the same, but under the same conditions lower amounts of AsO_4 were replaced by all the ligands when AsO_4 was sorbed before ligands.

Table 2 Effect of residence time on AsO_4 desorption (%) from the Al-Mg-LDH by inorganic and organic ligands after a reaction time of 24 h.

Ligand	**Residence time**	**AsO_4 sorbed[1]**	**AsO_4 desorbed**
	hours	**mmol kg^{-1}**	**%**
NO_3	24	588.6 ± 11.0	1.9 ± 0.2
	48	590.1 ± 8.6	1.6 ± 0.1
	168	594.8 ± 4.7	0.9 ± 0.1
NO_2	24	557.3 ± 28.1	7.1 ± 0.5
	48	563.4 ± 37.2	6.1 ± 0.6
	168	581.2 ± 17.6	3.1 ± 0.3
SeO_3	24	539.6 ± 44.3	10.1 ± 0.5
	48	545.2 ± 37.6	9.1 ± 0.6
	168	568.3 ± 28.7	5.3 ± 0.7
SO_4	24	524.8 ± 30.8	12.5 ± 1.0
	48	533.4 ± 33.5	11.1 ± 0.7
	168	562.4 ± 28.9	6.3 ± 0.5
TAR	24	486.4 ± 42.1	18.9 ± 1.8
	48	493.4 ± 37.5	17.8 ± 1.5
	168	503.5 ± 28.6	16.1 ± 1.1
OX	24	414.0 ± 22.3	31.0 ± 1.7
	48	432.7 ± 36.7	27.9 ± 1.8
	168	475.9 ± 30.5	20.7 ± 1.6
PO_4	24	163.2 ± 15.4	72.8 ± 5.5
	48	184.6 ± 16.5	69.2 ± 3.8
	168	224.1 ± 18.1	62.6 ± 2.9

[1] AsO_4 added initially was 600 mmol kg^{-1}, initial ligand/AsO_4 molar ratio = 3.

Table 3 Effect of residence time on AsO_4 desorption (%) from the Fe-Mg-LDH by inorganic and organic ligands after a reaction time of 24 h.

Ligand	**Residence time**	**AsO_4 sorbed**[1]	**AsO_4 desorbed**
	hours	**mmol kg^{-1}**	**%**
NO_3	24	1929.4 ± 58.0	3.5 ± 0.2
	48	1952.2 ± 40.6	2.4 ± 0.2
	168	1990.1 ± 8.8	0.5 ± 0.1
SO_4	24	1920.4 ± 66.1	4.0 ± 0.3
	48	1939.7 ± 52.8	3.0 ± 0.2
	168	1986.5 ± 12.2	0.7 ± 0.1
NO_2	24	1911.3 ± 71.8	4.4 ± 0.3
	48	1942.1 ± 49.1	2.9 ± 0.2
	168	1980.2 ± 15.4	1.0 ± 0.1
TAR	24	1804.9 ± 112.2	9.8 ± 0.5
	48	1826.9 ± 77.5	8.7 ± 0.6
	168	1860.1 ± 88.4	7.0 ± 0.6
OX	24	1791.1 ± 100.6	10.4 ± 0.5
	48	1856.6 ± 89.7	7.2 ± 0.4
	168	1969.7 ± 24.8	1.5 ± 0.1
SeO_3	24	1703.7 ± 90.2	14.8 ± 1.2
	48	1784.3 ± 82.3	10.8 ± 0.6
	168	1891.8 ± 78.8	5.4 ± 0.4
PO_4	24	749.5 ± 42.6	62.5 ± 4.9
	48	810.5 ± 60.2	59.5 ± 4.7
	168	910.8 ± 57.8	54.5 ± 5.1

[1] AsO_4 added initially was 2000 mmol kg^{-1}, initial ligand/AsO_4 molar ratio = 3.

4.1.5 Kinetics of AsO_4 desorption by PO_4

The amount of AsO_4 initially sorbed by the Al-Mg-LDH and Fe-Mg-LDH was 600 and 2000 mmol kg^{-1}. The AsO_4 desorbed from the LDHs by PO_4 (initial PO_4/AsO_4 molar ratio of 3), as a function of time was shown in Figure 16. The amounts of AsO_4 desorbed from the LDHs increased with time, being characterized by an initially very fast desorption reaction followed by a much slower desorption reaction until a plateau was reached (Figure 16 A) (Caporale et al., 2011). The amount of AsO_4 desorbed at 5 mins for the Al-Mg-LDH and Fe-Mg-LDH was 53 and 42%, respectively, indicating that some AsO_4 was slightly more strongly bound to the Fe-Mg-LDH versus the Al-Mg-LDH. After a reaction period of 24 h the Al-Mg-LDH and Fe-Mg-LDH released 70 and 63% of the bound AsO_4, respectively, suggesting that the main difference between the two LDHs was in the amount of more easily desorbable AsO_4, that is, less strongly bound AsO_4. In contrast, for Al and Fe (oxy)hydroxides about 25 and 15% of the AsO_4 was desorbed by PO_4 (initial PO_4/AsO_4 R = 4) after a reaction period of 24 h (Pigna et al., 2006). Hence, AsO_4 was more strongly sorbed by the Al and Fe (oxy)hydroxides versus the LDHs.

The kinetics of AsO_4 desorption were well described by the Elovich equation (Figure 16 B). The linear form of this equation (Yurtsever and Sengil, 2009) is given by

$$q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln t$$

where q_t is the amount of AsO_4 desorbed for a given time (t), and α and β are the Elovich coefficients, representing the initial desorption rate (mmol kg^{-1} min^{-1}) and the desorption coefficient (mmol kg^{-1}), respectively.

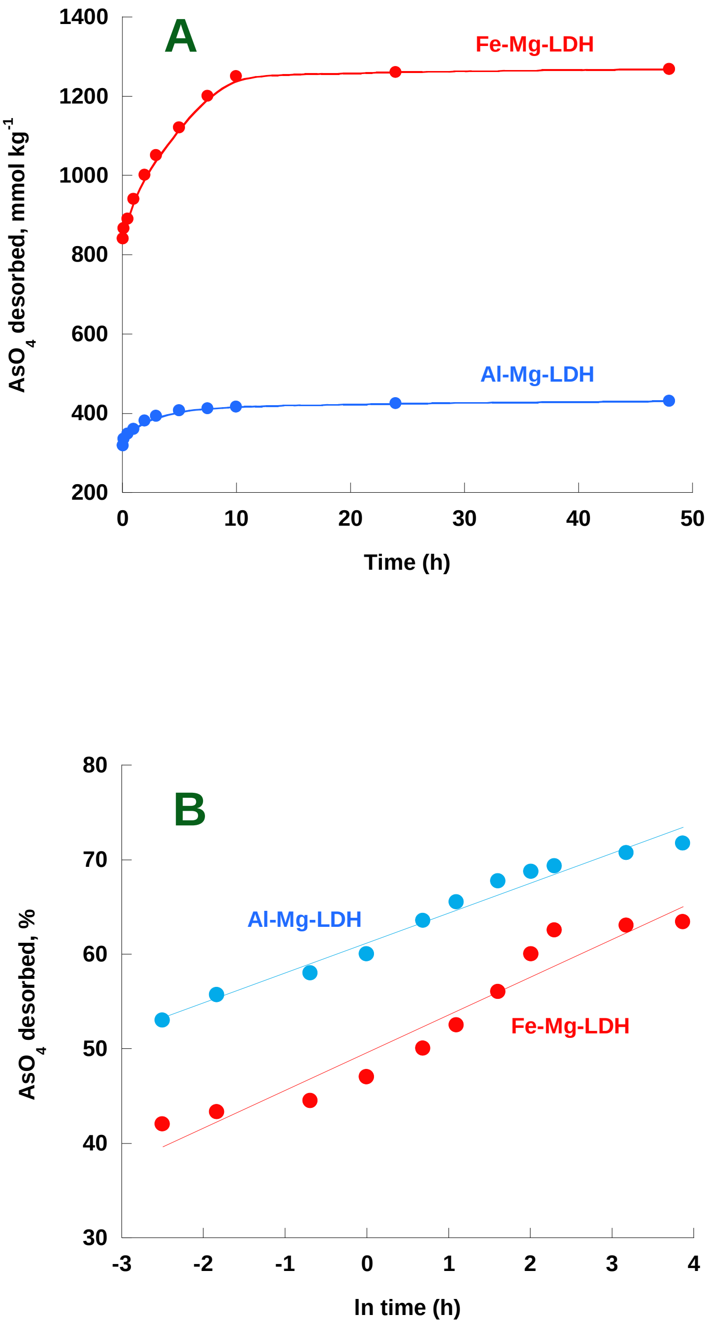


Figure 16 Kinetics of desorption of AsO_4 by PO_4 from the Al-Mg-LDH and Fe-Mg-LDH (A), also described by the Elovich equation (B). The initial AsO_4 concentration for the Al-Mg-LDH and Fe-Mg-LDH was 600 and 2000 mmol kg^{-1}, respectively. The initial PO_4/AsO_4 molar ratio was 3.

The initial AsO_4 desorption rate coefficient (α) and desorption coefficient (β) were larger for the Al-Mg-LDH than the Fe-Mg-LDH (Table 4), which also supports the contention that the difference between the two LDHs was in the amount of easily desorbable AsO_4. Further examination of the Elovich equation (Figure 16 B) showed there were subtle changes around 1 and 10 h in the rate of AsO_4 desorption, for both LDHs (more apparent for Fe-Mg-LDH than the Al-Mg-LDH). This may indicate that there was a change in the desorption process, which may include a change in pzc, the types of desorption site and/or the anions themselves, which was applicable for both LDH. For pure Al and Fe (oxy)hydroxides (goethite, ferrihydrite, gibbsite, $Al(OH)_3$), subtle changes were only observed in AsO_4 desorption by PO_4 for goethite (Pigna et al., 2006), which was also attributed to a change in the desorption process.

Table 4 Kinetic paramaters by simply regression analysis of AsO_4 desorption by PO_4 for the reaction period 5 mins to 48 h for the LDH using the Elovich kinetic equation.

Sample	**Elovich Kinetic Equation**	R^2	**P**	**F**	α^b	β^b
			$\cdot 10^{-8}$		**$\cdot 10^{5}$**	
Al-Mg-LDH	$q_t^a = 288.9 + 19.03 \ln(t)$	0.971	1.81	342	745	0.0525
Fe-Mg-LDH	$q_t = 662.6 + 80.1 \ln(t)$	0.921	175	119	3.13	0.0124

[a] q_t is the amount of AsO_4 desorbed (mmol kg^{-1}) in time t (min)

[b] α and β are Elovich coefficient obtained from the Elovich kinetic model

$q_t = (1/\beta)\ln(\alpha\beta) + (1/\beta)\ln(t)$

4.1.6 Conclusions on the work on the LDHs

Differences in the steric and electronic factors of the sorption sites in the interlayer of the Al-Mg-LDH and Fe-Mg-LDH and/or of the anions influenced sorption/desorption of AsO_4. The sorption isotherms showed that the incorporation of Fe into Mg-LDH versus Al resulted in the sorption of more AsO_4. AsO_4 sorption on the LDHs varied with different competing anions, and the efficiency of the organic ligands in competing with AsO_4 differed between the two LDHs. The desorption of AsO_4 by the anions decreased with increasing AsO_4 residence time. The AsO_4/PO_4 desorption kinetics experiment indicated that there were greater amounts of more easily desorbable AsO_4 on the Al-Mg-LDH compared to the Fe-Mg-LDH.

The synthesis of LDH of different chemical composition and their ability to effectively sorb anions in the presence of competing anions deserves further attention.

4.2 Study on the WTRs

4.2.1 Al- and Fe-based WTR samples characterization

General physicochemical properties of the WTR are reported in Table 5 and have also been discussed in previous works (Makris et al., 2006; Nagar et al., 2009).

Both WTRs were acidic. Total As concentrations of the WTRs were within the range of published values for other WTRs (1.9-9.7 and 8.5-17 mg kg^{-1} for Fe- and Al-WTRs, respectively) (Jain et al., 2005). The KCl-extractable As concentrations were < 0.03 mg kg^{-1}, suggesting minimum risk for As dissolution from the untreated (no As added) WTRs. The KCl-extractable As represented a negligible fraction of total (< 0.01 %) (Makris et al., 2006). Total P content was also within the typical range for the WTRs (0.3-4.0 g P kg^{-1}) (Dayton and Basta, 2005b). Total P, as well as As concentrations measured in the WTRs comes from the raw water treated in drinking-water treatment plants and becomes a part of the WTR structure.

Table 5 General physicochemical properties of the Al- and Fe-based WTR samples.

Sample	pH	Total						KCl-extr.	OX-extractable	
		C	N	P	Al	Fe	As	As	Al	Fe
		g kg^{-1}					mg kg^{-1}		g kg^{-1}	
Al-WTR	5.52	243 ± 1.9	5.8 ± 0.4	3.2 ± 0.4	87.1 ± 6.3	4.6 ± 0.4	15 ± 0.2	< 0.03	82.3 ± 5.3	4.1 ± 0.3
Fe-WTR	6.08	155.4 ± 1.2	8.8 ± 0.7	2.7 ± 0.3	1.34 ± 0.2	169 ± 15.1	13 ± 0.1	< 0.03	0.36 ± 0.04	78.6 ± 7.2

The X-ray diffraction patterns and the SEM images of the Al- and Fe-based WTR samples are shown in Figure 17 and 18, respectively.

The XRD of the Al-WTR is reported in Figure 17 A and have not revealed any sharp diffraction characteristic peak over a broad range of d-spacings (5-75°, 2θ). This indicates poorly ordered particles within the Al-WTR sample. In fact, OX-extractable Al concentrations, usually associated with the non-crystalline phase of metal hydroxides, were close to total (94 % of total Al), consistent with an amorphous nature of the Al-WTR (Table 5). This observation is also in agreement with other authors (Dayton and Basta, 2001; Makris and O'Connor, 2007; Babatunde et al, 2009). Similarly, the FT-IR spectrum of the Al-WTR ranging from 500 to 4000 cm^{-1} have not provided clear information regarding peaks (Babatunde et al., 2009).

The XRD of the Fe-WTR is reported in Figure 17 B and revealed sharp diffraction characteristic peaks at about 0.442 (d_{003}), 0.331 and 0.137 nm and some broad peaks at about 0.212 and 0.181 nm. This spectrum indicated that the Fe-based WTR particles showed a higher degree of crystallinity than those of Al-WTR sample and/or the their particles were of bigger size. The Fe-WTRs had also showed a lower oxalate-extractable Fe values as a percentage of total Fe (46 %) when compared with the Al-WTR, confirming that Fe-WTR particles are characterized by a greater degree of crystallinity (Table 5).

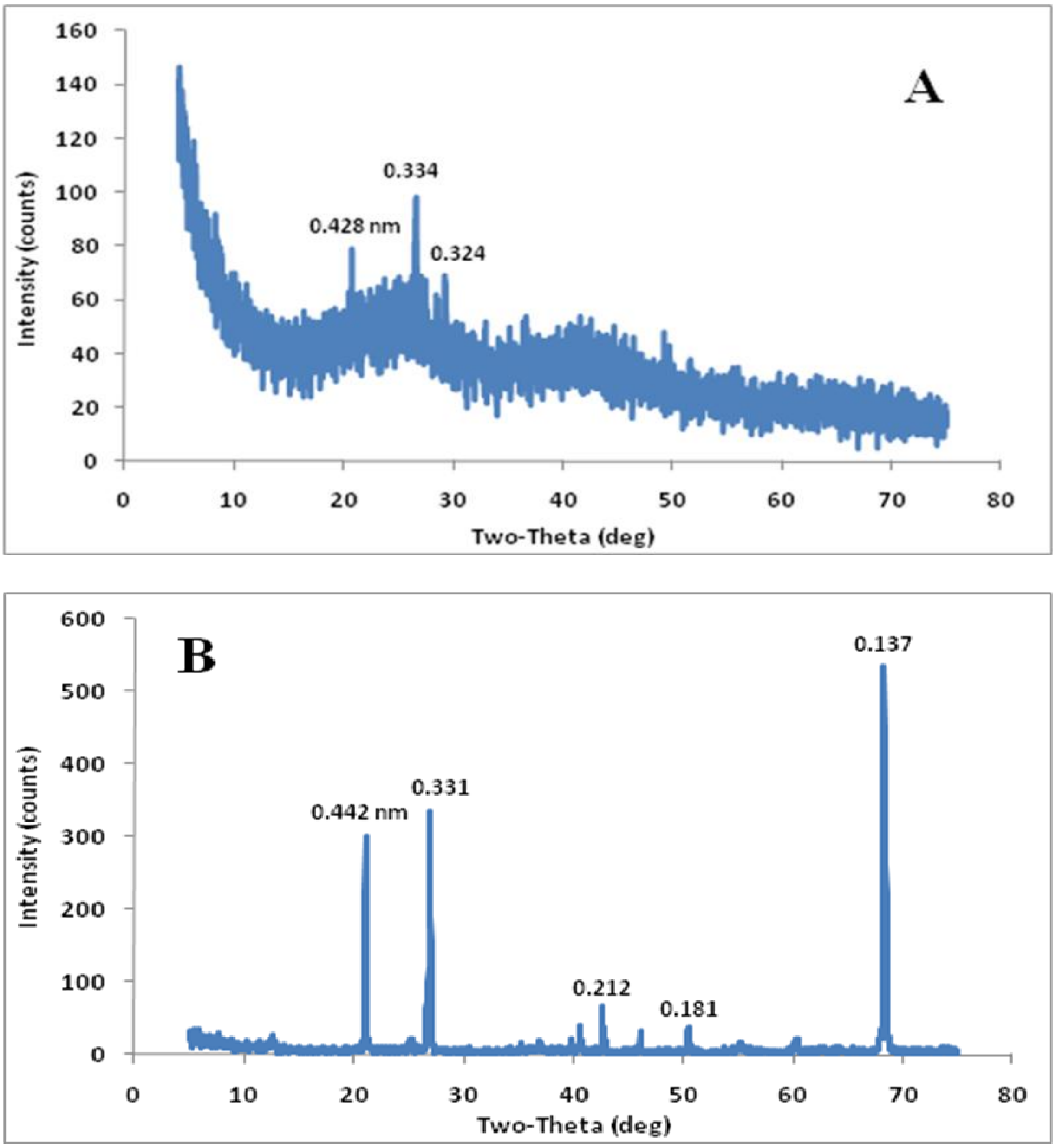


Figure 17 Powder X-ray diffraction patterns of Al- (A) and Fe-based (B) WTR samples.

Scanning electron images showed similar particle morphology for both WTR samples (Figure 18). Particle surfaces ranged from rough to fairly smooth. Images showed the irregular shape and a more variable size of Fe-WTR particles (Figure 18 B) with respect to that of Al-WTRs (Figure 18 A). The higher presence of big particles for unit of sample mass usually corresponds to a lower surface area of the sorbent. In fact, Makris et al. (2004) found that Al-WTR's specific surface area, measured by N_2 and CO_2 BET-SSA analysis, was 104.9 m^2 g^{-1}, almost 4-fold higher than that of Fe-WTR sample, equal to 27.5 m^2 g^{-1}.

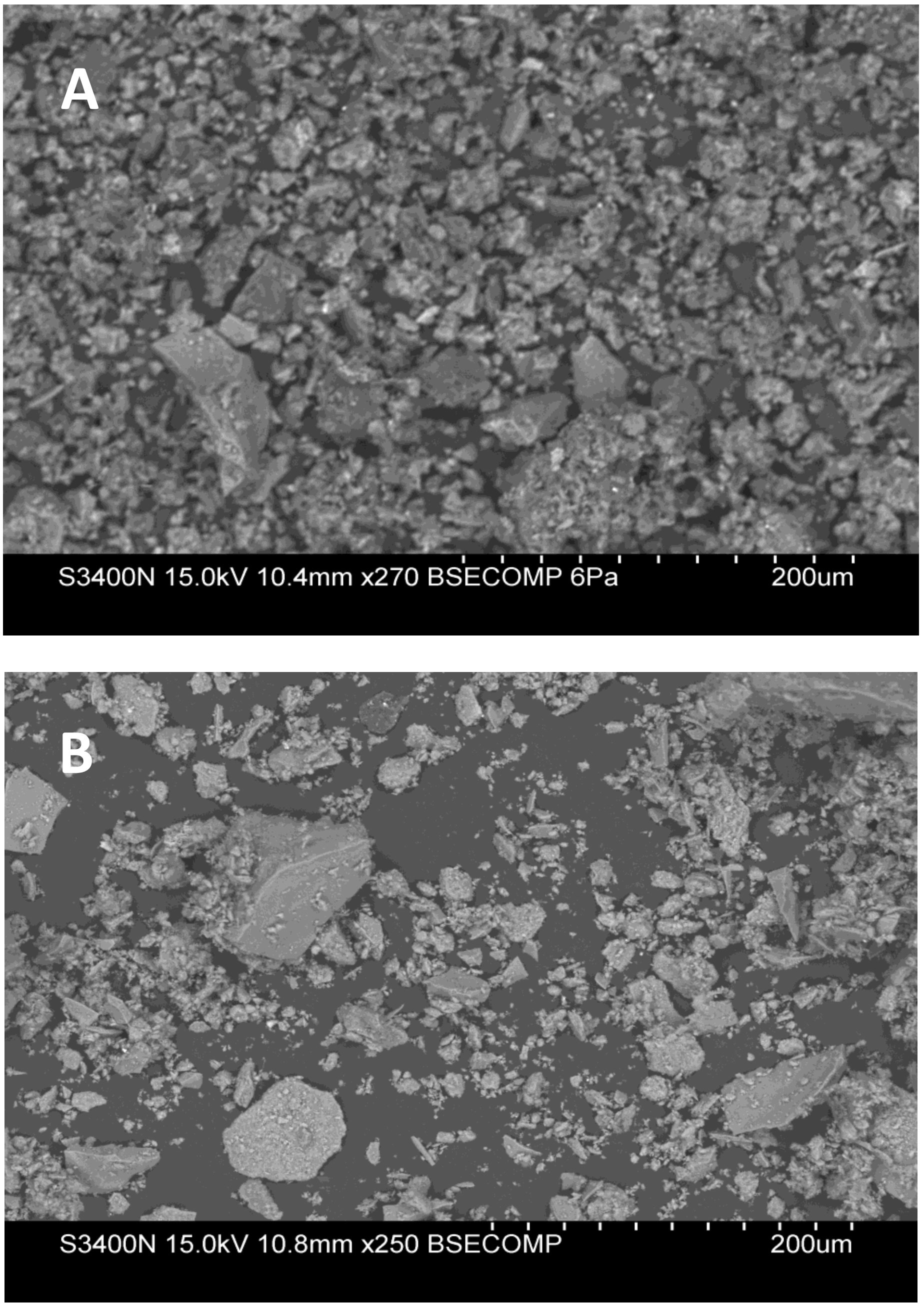


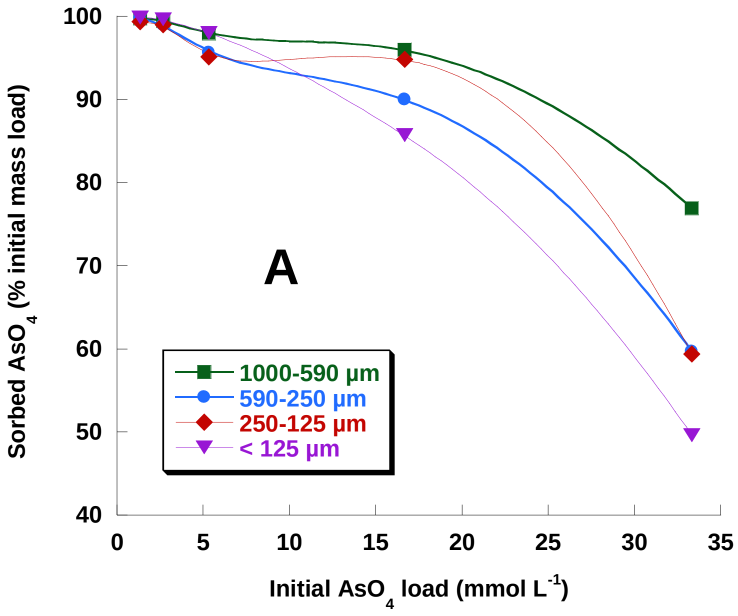
Figure 18 Scanning electron images of Al- (A) and Fe-based (B) WTR samples. Scale bar equal to 200 µm.

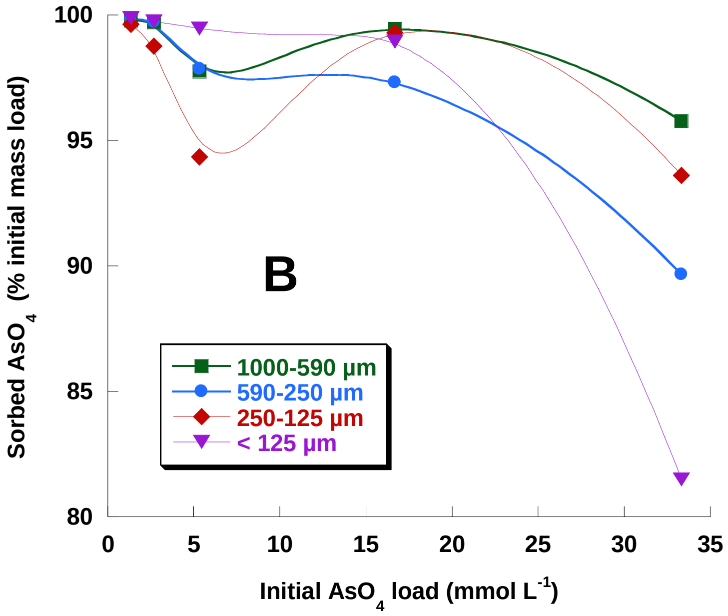
4.2.2 Arsenate sorption on Al- and Fe-based WTR samples

The capacity of the Al- and Fe-based WTR samples to retain AsO_4 were studied in batch experiments, with different solutions containing AsO_4 (1.33, 2.67 and 5.33 mmol L^{-1} for both WTR samples and also 16.67 and 33.33 mmol L^{-1} for Al-WTR), at three different SSRs (50, 100, and 200 g WTR L^{-1}).

Both WTR samples show a high affinity for AsO_4. Anyway, the Al-WTR samples were able to sorb much greater amounts of AsO_4 than the Fe-WTR. Al-WTR samples sorbed around 100 % of AsO_4 loaded with solutions containing the lower concentrations of AsO_4 (1.33, 2.67 and 5.33 mmol L^{-1}), at all SSRs, with no significant difference among different Al-WTR particles sizes (Figure 19). With higher concentrations of AsO_4 in solution (16.67 and 33.33 mmol L^{-1}), AsO_4 sorption capacity of Al-WTR was affected by SSRs and WTRs particles sizes. At the lowest SSR (50 g L^{-1}), Al-WTR samples sorbed from 85 to 95% and from 50 to 77% of AsO_4 loaded with solutions containing 16.67 and 33.33 mmol L^{-1}, respectively (Figure 19 A). The greater the SSR, the higher the amounts of AsO_4 sorbed on Al-based WTR samples. In fact, at the intermediate SSR (100 g L^{-1}) these samples sorbed most of the AsO_4 loaded up to solution containing 16.67 mmol L^{-1} (Figure 19 B), while at the highest SSR (200 g L^{-1}) they were able to sorb most of the AsO_4 loaded with all solutions used in the experiments (Figure 19 C). This considerable AsO_4 sorption capacity of the Al-WTR can be explained by the high external and internal specific surface area (Makris et al., 2006).

The influence of particles size on the AsO_4 sorption capacity of the Al-WTR appeared evident with solutions containing higher AsO_4 concentrations (16.67 and 33.33 mmol L^{-1}). Surprisingly, the biggest the Al-WTR particles (1000-590 µm) the highest was the AsO_4 sorption capacity, whereas the smallest the Al-WTR particles (< 125 µm) the lowest the AsO_4 sorption capacity. In fact, the biggest Al-WTR particles, kept to react with solution containing 33.33 mmol AsO_4 L^{-1}, sorbed an amount of AsO_4 26, 14 and 1 % higher than that sorbed by the smallest Al-WTR particles, at 50, 100 and 200 of SSRs, respectively. A possible explanation of this trend could be that the smallest Al-WTR particles, characterized by a low degree of crystallinity, have formed aggregates during the reaction at pH 7.0 for 24 h; in other words, the aggregation of the particles caused a partial reduction of their surface area and consequently there was a decrease of their capability to sorb AsO_4 from the different solutions used in the experiments. This trend occurred at all the SSRs of the experiments (Figure 19 A, B and C).





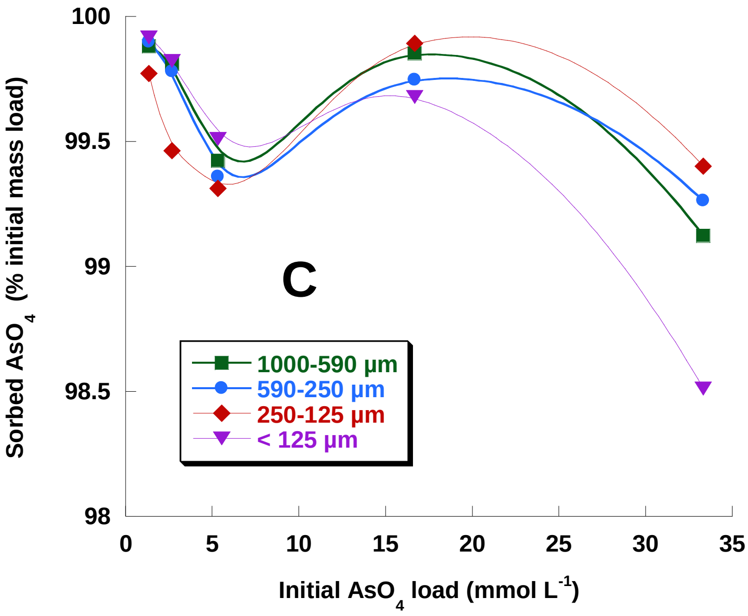
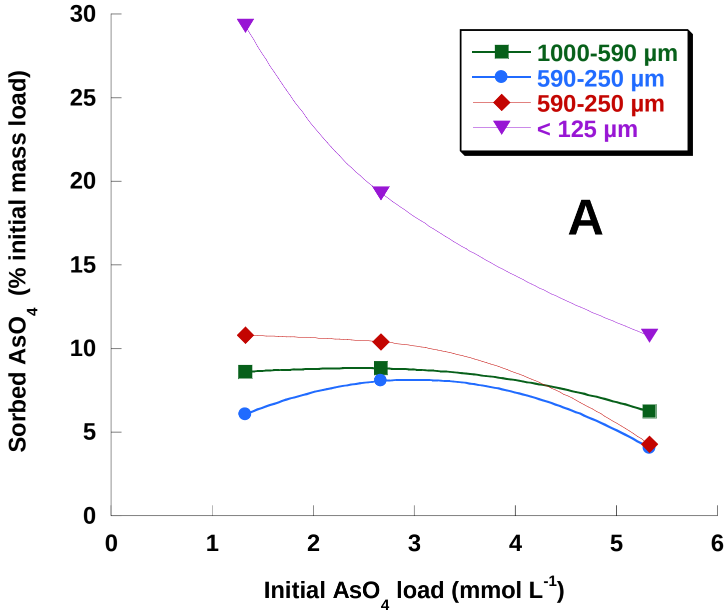


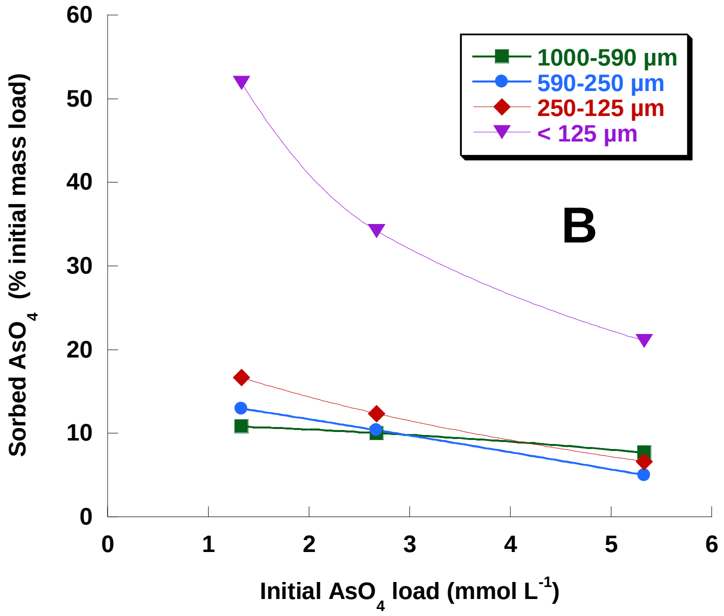
Figure 19 Amount of AsO_4 sorbed by Al-based WTR sample at (A) 50 g L^{-1}, (B) 100 g L^{-1} and (C) 200 g L^{-1} of SSRs, as a function of different Fe-WTR particles size (1000-590 µm, 590-250 µm, 250-125 µm and < 125 µm).

Fe-WTR sample showed a lower AsO_4 sorption capacity with respect to that of Al-WTR (Figure 20). Similar data were obtained by Makris et al. (2006), where Fe-WTR showed a lower/higher AsO_4/AsO_3 sorption capacity than that of Al-WTR.

However, the influence of Fe-WTR particles size on the AsO_4 sorption capacity was greatly pronounced when compared to that of the Al-WTRs (Figure 20 A, B and C). In fact, the smallest Fe-WTRs particles (< 125 µm) were able to sorb much more AsO_4 than the bigger ones. The lower the AsO_4 concentration in solutions, the higher the difference in AsO_4 sorption capacity occurred among the smallest Fe-WTR particles size and the bigger ones. For example, at the lowest SSR (50 g L^{-1}), the smallest Fe-WTR particles sorbed around 30, 19 and 11 % of AsO_4 loaded with solutions containing 1.33, 2.67 and 5.33 mmol L^{-1}, respectively, while the bigger Fe-WTR particles were able to sorb, on average, just 11, 8 and 5% of AsO_4 loaded by those solutions, respectively (Figure 20 A). Furthermore, at the highest SSR (200 g L^{-1}), the smaller the Fe-WTR particles size, the higher the AsO_4 removal from solutions by Fe-WTR samples (Figure 20 C). Indeed, 200 g L^{-1} of the smallest Fe-WTR particles (< 125 µm) were able to sorb around 80, 52 and 40 % of AsO_4 loaded with solutions containing 1.33, 2.67 and 5.33 mmol L^{-1}, respectively, more or less 4-fold the amounts of AsO_4 sorbed by the biggest Fe-WTR particles (1000-590 µm).

The influence of the SSR on the AsO_4 sorption capacity of different Fe-WTR particles also occurred and it was much more pronounced for the smallest Fe-WTR particles (< 125 µm), especially when they were kept to react with solution containing 1.33 mmol AsO_4 L^{-1} (Figure 20 A, B and C).


Sorbed AsO4 (% initial mass load)
Initial AsO4 load (mmol L-1)
0
5
10
15
20
25
30
0
1
2
3
4
5
6
1000-590 µm
590-250 µm
590-250 µm
< 125 µm
A


Sorbed AsO4 (% initial mass load)
Initial AsO4 load (mmol L-1)
0
10
20
30
40
50
60
0
1
2
3
4
5
6
1000-590 µm
590-250 µm
250-125 µm
< 125 µm
B

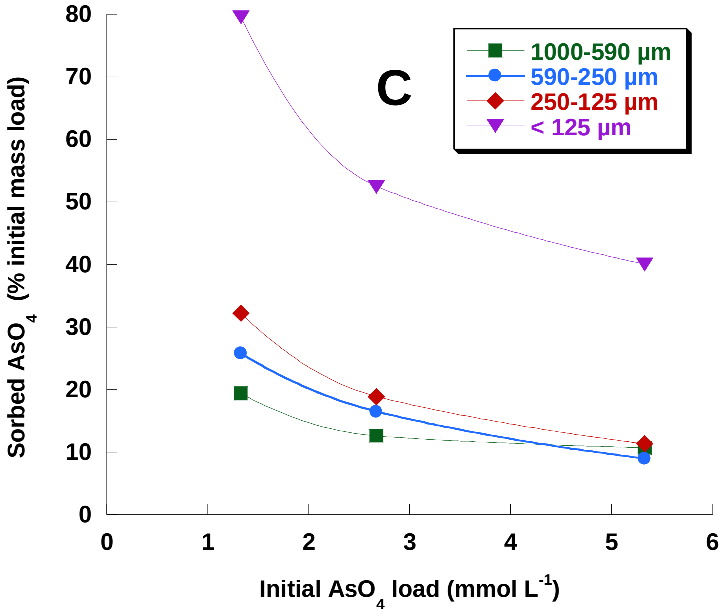


Figure 20 Amount of AsO_4 sorbed by Fe-based WTR sample at 50 g L^{-1} (A), 100 g L^{-1} (B) and 200 g L^{-1} of SSRs (C), as a function of different Fe-WTR particles size (1000-590 µm, 590-250 µm, 250-125 µm and < 125 µm).

In the present work, AsO_4 sorption capacity of Al- and Fe-WTR samples was studied at pH 7.0, in order to evaluate the potentiality of these samples in As removing from contaminated water at neutral pH. However, Nagar et al. (2010) have investigated the effect of pH, ranging from 3.0 to 9.0, on AsO_4 sorption by these samples. They found that the sorption of AsO_4 by Al-WTR was not particularly affected by solution pH, whereas they noted a large influence of the pH on the AsO_4 sorption capacity of the Fe-WTR. The AsO_4 sorption by Fe-WTR reached a maximum at pH 3.0, but it decreased by increasing pH. So, it is interesting to note that an increase of AsO_4 sorption capacity of the Fe-WTR could be easily realized through a decreasing of solution pH.

Makris et al. (2006), tested the ability of PO_4 on AsO_4 desorption from the Al- and Fe-based WTR samples. They found that AsO_4 desorption from both WTRs was minimal, suggesting irreversible sorption. They noted that the AsO_4 desorption has not exceeded the 0.5 % and the 4 % of previously sorbed AsO_4 by the Al- and Fe-WTR, respectively. This is a favorable behavior with respect to stability of As sorbed to the retentive surfaces of the WTRs. In fact, it is very important that an anion as PO_4, whose concentrations in water typically exceed those of AsO_4, shows insignificant effect on AsO_4 sorption by both WTR samples.

XANES and EXAFS measurements also provided solid evidence regarding the stability of sorbed As (Makris et at., 2007; Makris et al., 2009). Indeed, surface hydroxyls of both WTRs form inner-sphere mononuclear bidentate complexes with sorbed As (Figure 21; Makris et at., 2007; Makris et al., 2009).

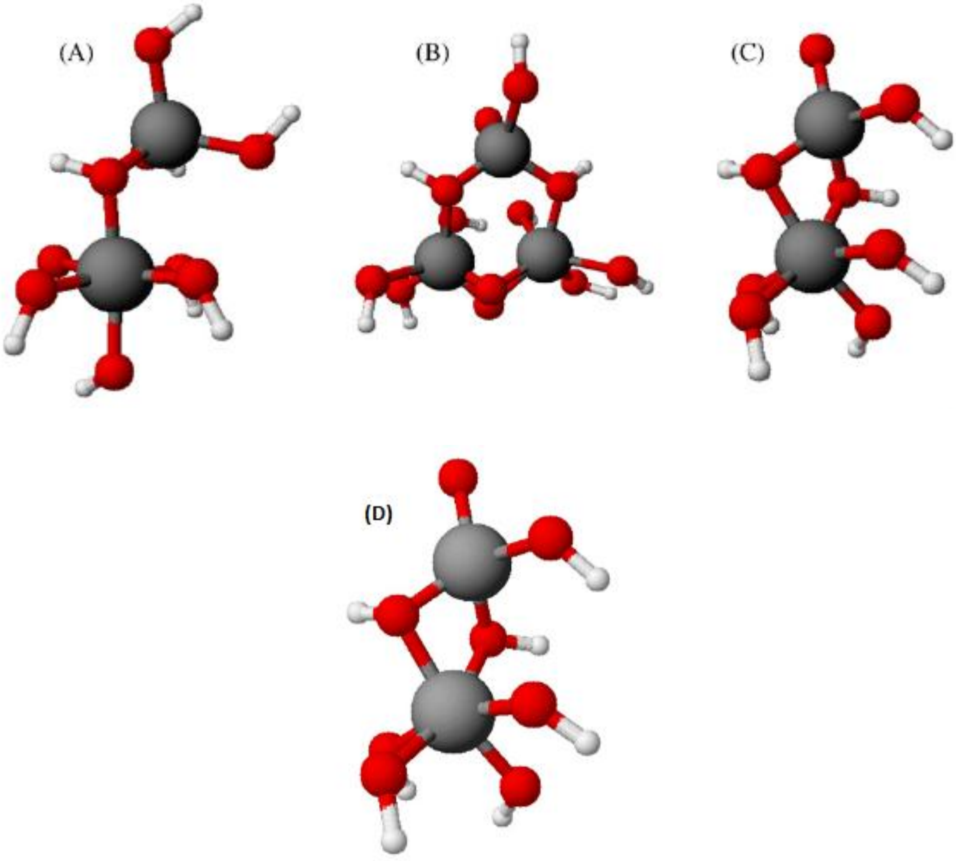


Figure 21 Models for the surface binding of AsO_4 to the Al- and Fe-WTR. AsO_4 in a monodentate coordination to the Al (A), AsO_4 bridging to Al centers with monodentate binding to each Al center (B), AsO_4 with bidentate binding to one Al center (C) and AsO_4 with bidentate binding to one Fe center (D).

4.2.3 Conclusions on the study on the WTRs

This study indicates that the Al- and Fe-based WTR samples could be considered as a viable and economic technology to remediate As-contaminated water by stable As immobilization on their surfaces. Al-based WTR sample showed a higher AsO_4 sorption capacity with respect to that of Fe-WTR, at neutral pH. The influence of particle size on the AsO_4 sorption capacity of the Al-WTR appeared evident only with higher AsO_4 concentrations in solution; precisely, the bigger the Al-WTR particles size, the greater the amounts of AsO_4 removed from contaminated solutions. Vice versa, the capacity of the Fe-based WTR samples to retain AsO_4 was much more affected by their particles size. The smallest Fe-WTRs particles (< 125 µm), in fact, were able to sorb much more AsO_4 than the bigger ones.

In other words, Al- and Fe-based WTR samples exhibited promising characteristics, such as low cost, high As affinity and little desorbability, as evidenced by desorption studies (Makris et al., 2006) and XAS measurements (Makris et at., 2007; Makris et al., 2009). So, they can be highly beneficial for small communities or developing Countries because they can provide a safe and efficient As removal from contaminated systems.

4.3 Study on the bean plants (*Phaseolus vulgaris* L.)

4.3.1 Compost and soil characterization

The ^{13}C-CPMAS-NMR analysis is been reported in Figure 22 and Table 6, and revealed an evident O-alkyl-C region (65-110 ppm, mainly associated with sugars and polysaccharides) and a large aliphatic alkyl-C region (0-45 ppm, characteristic of lipids). The regions associated with aromatic C (140-110 ppm), methoxyl C (65-45 ppm) and carboxyl C (190-165 ppm) were less developed, whereas the region associated with phenolic C (165-140 ppm) was not very significant (Figure 22 and Table 6).

Total N, C and H content in compost, C/N and H/C ratios are reported in Table 7, whereas the principal physical and chemical properties of the As-uncontaminated soil used in the experiment are reported in Table 8.

Table 6 Relative distribution (%) of the different regions determined during the ^{13}C-CPMAS-NMR analysis.

	190-165	**165-140**	**140-110**	**110-65**	**65-45**	**45-0**
	Carboxyl-C	**Phenolic-C**	**Aromatic-C**	**O-Alkyl-C**	**CH_3O-C/C-N**	**Alkyl-C**
				%		
Compost	6.7	3.3	9.7	52.0	8.0	20.3

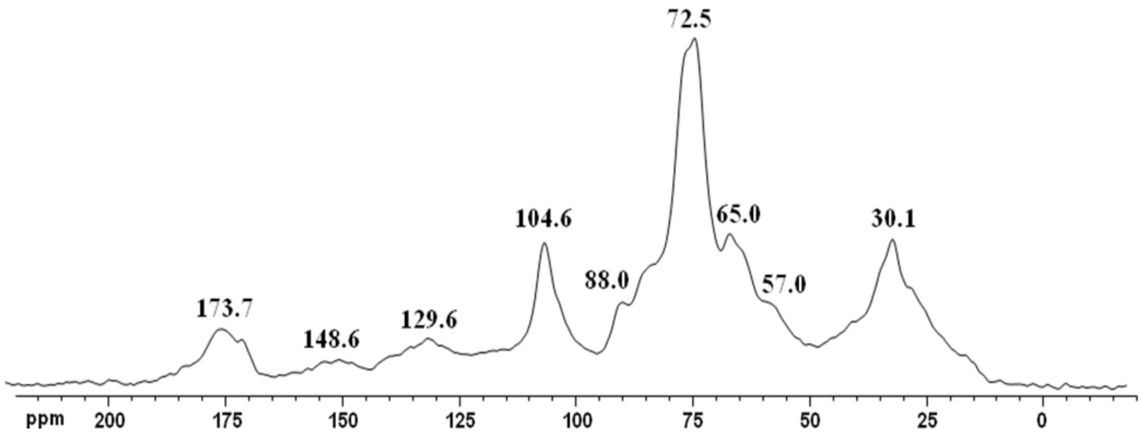


Figure 22 The ^{13}C-CPMAS-NMR analysis of the compost used in the experiment.

Table 7 Elemental Analysis of the compost used in the experiment.

	N	**C**	**H**	**C/N**	**H/C**
		%			
Compost	2.43	32.19	4.62	15.45	1.72

Table 8 General physical and chemical properties of the As-uncontaminated soil used in the experiment.

Soil properties	**Results**
Sand (g kg^{-1})	518
Silt (g kg^{-1})	316
Clay (g kg^{-1})	166
Soil pH (in H_20)	6.78
Organic Carbon (g kg^{-1})	19.1
CEC (mequiv 100 g^{-1})	14.83
Total N (g kg^{-1})	1.1
Available P (mg P_2O_5 kg^{-1})	12.7
Total As (mg kg^{-1})	7.6

4.3.2 Plants growth and As toxicity

Bean plants growth (roots, shoots and beans dry matter production) was significantly affected by As and compost treatments (Table 9). Increasing As concentration in the irrigation water decreased markedly the dry biomass of bean plants, indicating the phytotoxic effect of As. For plants grown without compost application (C 0) there was a decrease in total biomass of 12.2 % (As 1), 37 % (As 2) and 50.8 % (As 3) with respect to control treatment (As 0). This reduction was less severe in the C 300 and C 600 treatments, where plants grew 11 % and 13.2 % (As 1), 27.3 % and 24.1 % (As 2), 43 % and 35.8 % (As 3), respectively, less than their own control treatments (As 0).

Increasing compost application increased significantly beans biomass (Table 9). It is interesting to note that the higher the concentration of As in irrigation water, the greater the increase of beans biomass realized by the application of compost to the soil, indicating the ameliorative influence of compost in alleviating the phytotoxicity of As. In fact, at the lowest As treatment (As 1), plants amended with compost, (C 300) and (C 600), grew 8.7 % and 17.6 %, respectively, more than those grown without compost supply (C 0), whereas at the highest As treatment (As 3) they grew 26.0 % (C 300) and 53.5 % (C 600) more than those of control treatment (C 0). The major effect of compost application was realized on the bean yield, where at the highest As treatment (As 3) there was an increase of production of 40.7 % and 78.3 %, respectively, in (C 300) and (C 600), with respect to control treatment (C 0). Furthermore, the higher the amounts of compost application, the lower the decrease of bean yield occurred by increasing As concentration in irrigation solutions. For example, at the highest As treatment (As 3), there was a decrease in bean yield of 59.4 % (C 0), 49.7 % (C 300) and 41.7 % (C 600) than to beans production of their own As control treatment (As 0).

The addition of organic matter to soil, especially in the form of compost, results in increased mineralization of macro (nitrogen and phosphorus, in particular) and also micronutrients (Dick and McCoy, 1993b). Application of compost to soil increases soil fertility by improving the physical and chemical properties and augmenting microbial activity. The phytonutritive capacity of compost has often been demonstrated to be analogous to that of manure (Roe et al., 1993; Baldoni et al., 1994). Compost mineralization during the experiment surely increased the P concentration in the soil, so higher concentration of P was available for uptake by bean plants. P concentration in soil and its phyto-availability play a prominent role in As toxicity to plants, due to the physicochemical similarities of two elements (Adriano, 2001).

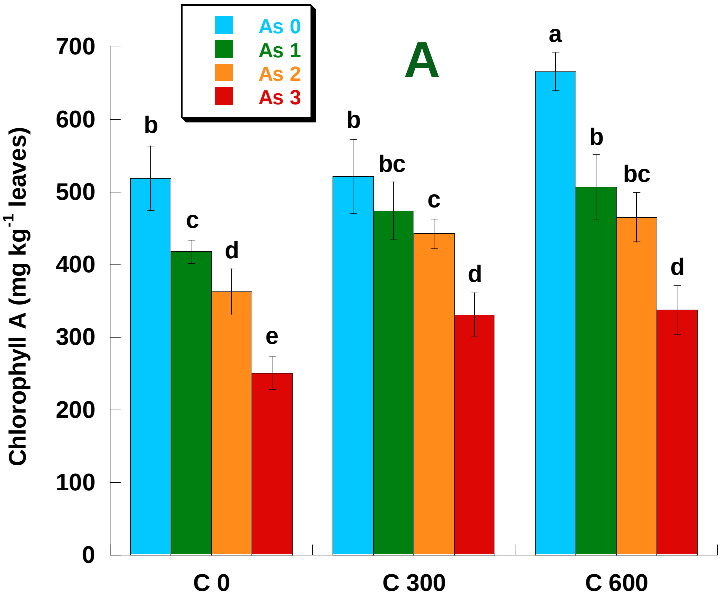
Studies on As toxicity have shown that plant species not resistant to As suffer considerable stress upon exposure, with symptoms ranging from inhibition of roots growth through to death (Meharg and Macnair 1991; Paliouris and Hutchinson 1991; Carbonell-Barrachina et al. 1995). In our experiment, As toxicity symptoms started to appear 18-20 d after first As addition in the plants irrigated with the highest As concentration (As 3) in solution, being the most impacted, whereas in the lower As concentration treatments, (As 1) and (As 2), they appeared some days later than As 3. Initial symptoms were red-brown necrotic spots on older leaves, followed by the senescence of the leaves. At any rate, no bean plant died during our experiment.

Table 9 Roots, shoots, bean yield and total biomass (g) in bean plants.

As conc.	**Roots**	**Shoots**	**Beans**	**Total biomass**	**Roots/shoots**
mg L^{-1}	**g**				
Control C 0	2.96 ± 0.23 ab	6.74 ± 0.29 ab	6.23 ± 0.32 b	15.93	0.439
1	2.56 ± 0.20 b	5.84 ± 0.24 b	5.59 ± 0.26 c	13.99	0.438
2	1.96 ± 0.14 c	4.88 ± 0.20 cd	3.2 ± 0.17 g	10.04	0.402
3	1.27 ± 0.09 d	4.03 ± 0.15 e	2.53 ± 0.11 h	7.83	0.315
Control C 300	3.22 ± 0.14 a	7.02 ± 0.17 a	7.08 ± 0.35 a	17.32	0.459
1	2.85 ± 0.22 b	6.45 ± 0.26 ab	6.11 ± 0.27 b	15.41	0.442
2	2.35 ± 0.18 bc	5.33 ± 0.12 c	4.91 ± 0.09 d	12.59	0.441
3	1.75 ± 0.10 cd	4.56 ± 0.19 d	3.56 ± 0.07 f	9.87	0.384
Control C 600	3.45 ± 0.16 a	7.55 ± 0.48 a	7.74 ± 0.34 a	18.74	0.457
1	3.02 ± 0.22 ab	7.01 ± 0.53 a	6.24 ± 0.30 b	16.27	0.431
2	2.63 ± 0.08 b	6.21 ± 0.44 b	5.38 ± 0.23 c	14.22	0.424
3	2.14 ± 0.11 c	5.37 ± 0.37 c	4.51 ± 0.25 e	12.02	0.399

4.3.3 Chlorophyll A and B concentrations in bean leaves

As a result of many negative effects on plants, arsenic causes a reduction of the photosynthesis rate (Miteva and Merakchiyska, 2002). Arsenic damages the chloroplasts membranes and disorganized the membranes structure. The damages of chloroplasts structure during the treatments with high As level imply functional changes of the integral photosynthetic process. By increasing As concentration in irrigation water, in fact, bean leaves showed a decrease in both chlorophyll A and B concentration (Figure 23). In plants non-amended with compost (C 0), chlorophyll A concentration was 519.0, 417.8, 363.1 and 250.8 mg kg^{-1}, respectively, in As 0, As 1, As 2 and As 3 treatments (Figure 23 A), whereas chlorophyll B concentration was 213.2, 163.7, 144.0 and 120.2 mg kg^{-1}, respectively (Figure 23 B). The influence of compost application on both chlorophyll A and B concentration, was also significant. In C 300 and C 600 treatments occurred, on average, an increase of 17 % and 28 %, respectively, of chlorophyll A concentration in bean leaves with respect to that of the compost control plants (C 0), whereas there was an increase of 8 % (C 300) and 30 % (C 600) of chlorophyll B concentration compared to that of C 0 plants.



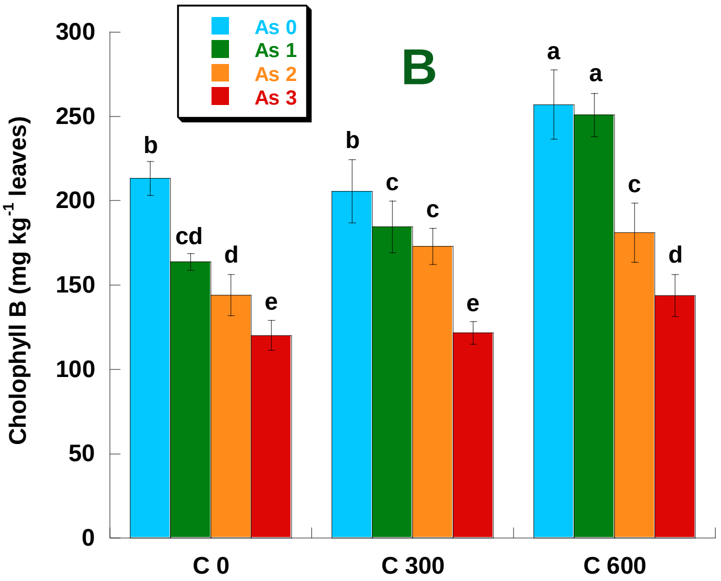


Figure 23 Chlorophyll A (A) and B (B) concentrations (mg kg^{-1}) in bean leaves.

4.3.4 Concentration and content of As in plants

Arsenic concentration in roots was, on average, 1.5-1.8 fold and 3.5-4.1 fold higher than As concentrations in shoots and bean yield, respectively, in all experimental treatments (Table 10). A possible explanation of this findings may be that bean plants showed a typical behavior of the plants sensitive to As toxicity, which usually tend to limit the As translocation from roots to shoots and yield. However, a low As allocation in bean yield is definitely desirable, because a high content of As in edible part of the plant could cause contamination of the human food-chain, being beans a low-cost proteins source and a staple food in many Countries around the world. Abedin et al. (2002) also observed that a very large amount of As retained in roots compared to its content in straw and grain. Carbonell-Barrachina et al. (1997), in a similar experiment, found that in tomato plants, 83.2 % of all the adsorbed As remained in the roots system, 16.8 % in the stems and only 7.3 % reached the leaves. Other literature studies (Duxbury et al., 2002; Rahman et al., 2007) reported similar results.

Arsenic concentration in roots, shoots and bean yield increased significantly with increasing As in irrigation water, particularly in the roots (Table 10). In fact, by increasing As level in irrigation water from As 1 to As 3, As roots concentrations ranged from 1.16 to 4.79 mg kg^{-1}, from 1.11 to 4.36 mg kg^{-1} and from 1.4 to 3.2 mg kg^{-1}, respectively, in C 0, C 300 and C 600 treatments. Similar results on wheat watered with increasing concentration of As in solutions are been found by Pigna et al. (2009).

We also found that the compost application reduced the As concentration in all tissues of the amended plants than those non-amended (Table 10). For example, at the highest As concentration in irrigation water (As 3), the As concentrations in roots, shoots and bean yield were 4.79, 2.68 and 1.08 mg kg^{-1}, respectively, in C 0 treatment, 4.36, 2.13 and 0.86 mg kg^{-1}, respectively, in C 300 treatment and 3.87, 1.71 and 0.63 mg kg^{-1}, respectively, in C 600 treatment. Plants amended with compost showed a lower As uptake because As mobility was reduced through the adsorption on the organic matter of the compost. It has been reported that oxyanion adsorption was enhanced in the presence of organic matter as pH decreases (Sposito, 1984). Xu et al. (1991) reported that acidification and organic matter addition reduced As mobility with As adsorption reaching a maximum at around pH 5.0.

Bliek et al. (2008) reported that in plants grown under luxurious PO_4 supply, increased AsO_4 tolerance is achieved through a reduction of AsO_4 to AsO_3 and subsequent vacuolar sequestration as AsO_3-phytochelatin complex.

Table 10 As concentration (mg kg^{-1}) in roots, shoots and bean yield.

As conc. in sol. (mg L^{-1})	As concentration in plant tissues (mg kg^{-1}) Roots	Shoots	Beans
Control C 0	0.24 ± 0.02 g	0.18 ± 0.01 h	0.08 ± 0.01 f
1	1.16 ± 0.09 e	0.98 ± 0.05 f	0.64 ± 0.03 c
2	2.93 ± 0.23 c	1.76 ± 0.14 c	0.87 ± 0.04 b
3	4.79 ± 0.31 a	2.68 ± 0.17 a	1.08 ± 0.09 a
Control C 300	0.20 ± 0.01 h	0.13 ± 0.01 i	0.06 ± 0.01 f
1	1.11 ± 0.10 e	0.93 ± 0.04 f	0.58 ± 0.04 cd
2	2.55 ± 0.18 cd	1.42 ± 0.11 d	0.67 ± 0.02 c
3	4.36 ± 0.34 ab	2.13 ± 0.16 b	0.86 ± 0.06 b
Control C 600	0.18 ± 0.02 h	0.10 ± 0.01 j	0.05 ± 0.01 g
1	0.94 ± 0.06 f	0.72 ± 0.05 g	0.39 ± 0.03 e
2	2.27 ± 0.21 d	1.18 ± 0.09 e	0.51 ± 0.04 d
3	3.87 ± 0.27 b	1.71 ± 0.12 c	0.63 ± 0.02 c

The total As amount taken by bean plants was studied through the As content in the different plant tissues (Table 11). It was significantly affected by As concentration in irrigation water. The higher the As concentration in irrigation solution the higher the As content in most bean tissues. In C 0 treatment, for example, As roots content increased from 3.0 (As 1) to 6.1 µg plant^{-1} (As 3), As shoots content increased from 5.7 (As 1) to 10.8 µg plant^{-1} (As 3), whereas As bean yield content decreased from 3.6 (As 1) to 2.7 µg plant^{-1} (As 3) due to low bean yield realized in plants watered with the highest As concentration in solution (As 3).

Despite plants amended with compost produced higher biomass, in most of experimental treatments they showed a lower As content in their own tissues than that in non-amended plants, so compost application has limited the As uptake by plants (Table 11).

Table 11 As content (µg plant^{-1}) in roots, shoots and bean yield.

As conc. in sol. (mg L^{-1})	As content in plant tissues Roots	 Shoots	 Beans
	(µg plant^{-1})		
Control C 0	0.71 ± 0.06 d	1.21 ± 0.10 e	0.50 ± 0.04 d
1	2.97 ± 0.23 c	5.72 ± 0.43 cd	3.58 ± 0.20 a
2	5.74 ± 0.47 b	8.59 ± 0.72 b	2.78 ± 0.16 b
3	6.08 ± 0.52 b	10.80 ± 0.91 a	2.73 ± 0.12 b
Control C 300	0.64 ± 0.05 d	0.91 ± 0.08 f	0.42 ± 0.03 e
1	3.16 ± 0.22 c	6.00 ± 0.54 c	3.54 ± 0.27 a
2	5.99 ± 0.47 b	7.57 ± 0.68 b	3.29 ± 0.21 a
3	7.63 ± 0.56 a	9.71 ± 0.84 ab	3.06 ± 0.15 ab
Control C 600	0.62 ± 0.05 d	0.75 ± 0.06 g	0.39 ± 0.03 e
1	2.84 ± 0.18 c	5.05 ± 0.33 d	2.43 ± 0.18 c
2	5.97 ± 0.48 b	7.33 ± 0.56 b	2.74 ± 0.24 b
3	8.28 ± 0.71 a	9.18 ± 0.89 a	2.84 ± 0.19 b

Arsenic shoots/roots ratio (between concentration values) decreased by increasing compost addition, in all As experimental treatments (Figure 24). These results demonstrate that the better nutritional state of the plants amended with compost has allowed to limit the translocation of As from roots to shoots.

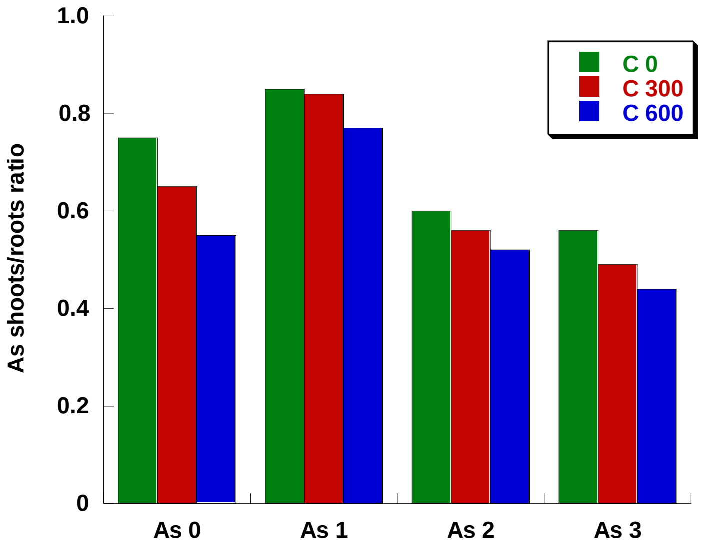


Figure 24 As shoots/roots ratio (between concentration values) in bean plants.

4.3.5 Concentration and content of P in plants

Phosphorus concentration in roots, shoots and bean yield have been significantly affected by compost application, particularly in the shoots and bean yield (Table 12). By increasing compost application from C 0 to C 600, P shoots concentrations ranged from 3.29 to 4.68 mg kg^{-1}, from 2.78 to 4.13 mg kg^{-1}, from 2.33 to 3.42 mg kg^{-1} and from 1.87 to 3.1 mg kg^{-1}, respectively, in As 0, As 1, As 2 and As 3 treatments. We also found a markedly influence of the As concentration in irrigation water on the P concentration in plant tissues, particularly in the shoots and bean yield (Table 12). In fact, there was a significantly decrease of the P concentration in bean yield of 31.4 % (C 0), 36.7 % (C 300) and 39.3 % (C 600) in As 3 treatment, with respect to control treatment (As 0). Non-resistant plants can be made more resistant to As by raising their

P status, as the P is taken more effectively compared to As (Meharg and Macnair, 1992; Lee et al., 2003). Also, in As-resistant plants with high P status a reduced As sensitivity has been observed, which is not due to a difference in As influx, but is presumably a result of higher cytoplasmatic P status, decreasing As toxicity within the cell (Meharg, 1994). The effects due to P nutrition on As metabolism could be the following: i) high plant P status leads to a downregulation of the As/P plasma-lemma transporters; ii) high cellular P levels will result in greater competition with As for biochemical processes where As substitutes for P (Meharg, 2005).

Table 12 P concentration (mg kg^{-1}) in roots, shoots and bean yield.

As conc. in sol.	P concentration in plant tissues		
	Roots	Shoots	Beans
(mg L^{-1})	(mg kg^{-1})		
Control C 0	2.30 ± 0.19 b	3.29 ± 0.22 c	2.61 ± 0.24 b
1	2.41 ± 0.22 ab	2.78 ± 0.13 d	2.73 ± 0.19 b
2	2.18 ± 0.12 bc	2.33 ± 0.21 e	2.12 ± 0.13 c
3	1.96 ± 0.15 c	1.87 ± 0.16 f	1.79 ± 0.08 d
Control C 300	2.64 ± 0.20 a	3.91 ± 0.32 b	3.24 ± 0.25 a
1	2.56 ± 0.09 ab	3.55 ± 0.17 b	2.90 ± 0.17 ab
2	2.60 ± 0.14 ab	2.73 ± 0.08 d	2.56 ± 0.18 b
3	2.38 ± 0.18 b	2.66 ± 0.20 d	2.05 ± 0.08 c
Control C 600	3.01 ± 0.25 a	4.68 ± 0.39 a	3.64 ± 0.24 a
1	2.93 ± 0.18 a	4.13 ± 0.24 a	2.88 ± 0.20 ab
2	2.72 ± 0.12 a	3.42 ± 0.25 bc	3.02 ± 0.23 ab
3	2.55 ± 0.06 ab	3.10 ± 0.33 cd	2.21 ± 0.17 c

Influence of both compost application and As concentration in irrigation water has significantly occurred in P content in all plant tissues (Table 13). The higher the compost application the higher the P contents occurred in plant tissues, whereas the higher the As concentration in irrigation water the lower was the P contents in roots, shoots and bean yield. The major influence of compost application on the P content has been determined in the plants watered with the highest As concentration (As 3), where P contents in bean yield ranged from 2.5 to 5.4 mg plant^{-1} in C 0, from 7.5 to 16.6 mg plant^{-1} in C 300 and from 4.5 to 10.0 mg plant^{-1} in C 600 treatment.

Table 13 P content (mg plant^{-1}) in roots, shoots and bean yield.

	P content in plant tissues		
As conc. in sol.	**Roots**	**Shoots**	**Beans**
(mg L^{-1})	**(mg plant^{-1})**		
Control C 0	6.81 ± 0.42 c	22.17 ± 1.87 c	16.26 ± 0.99 c
1	6.17 ± 0.51 cd	16.23 ± 1.22 de	15.26 ± 1.13 d
2	4.27 ± 0.35 e	11.37 ± 0.93 f	6.78 ± 0.57 g
3	2.49 ± 0.16 f	7.54 ± 0.55 h	4.53 ± 0.30 h
Control C 300	8.50 ± 0.74 b	27.45 ± 2.02 b	22.94 ± 0.28 b
1	7.30 ± 0.58 c	22.90 ± 1.31 c	17.72 ± 0.84 c
2	6.11 ± 0.48 cd	14.55 ± 0.67 e	12.57 ± 1.08 e
3	4.16 ± 0.32 e	12.13 ± 1.05 f	7.30 ± 0.66 g
Control C 600	10.38 ± 0.95 a	35.33 ± 3.13 a	28.17 ± 1.85 a
1	8.85 ± 0.74 ab	28.95 ± 2.58 b	17.97 ± 0.97 c
2	7.15 ± 0.65 c	21.24 ± 1.37 c	16.25 ± 0.65 cd
3	5.46 ± 0.46 d	16.65 ± 0.75 d	9.97 ± 0.37 f

Phosphorus shoots/roots ratio (between concentration values) increased by increasing compost addition in all As experimental treatments, while decreased by increasing As concentration in irrigation water (Figure 25). These results demonstrate that the higher phyto-availability of P in soil has increased the uptake of P by roots and allowed a higher translocation of P from roots to aboveground plant tissues. Cox and Bell (1996), postulated that since As can substitute for P in the plant, but is unable to carry out P's role in energy transfer, the plant reacts as if there is a P deficiency. Thus, as plant As increases, the plant may react by increasing P uptake.

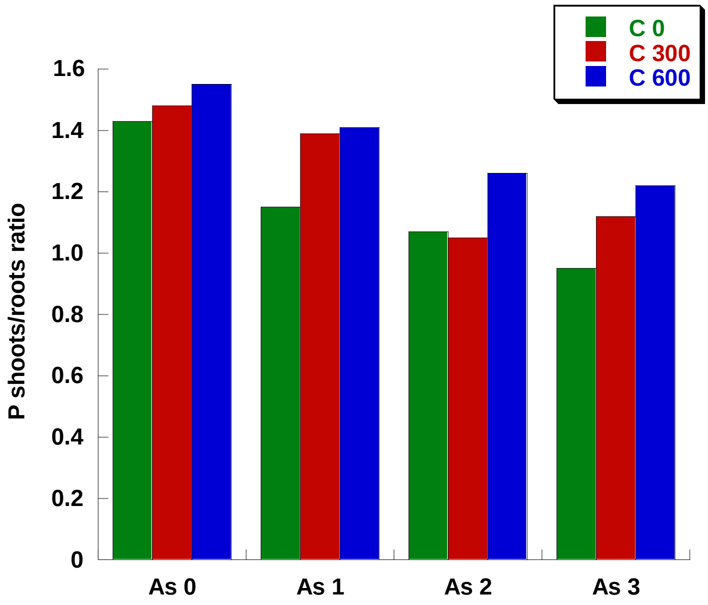
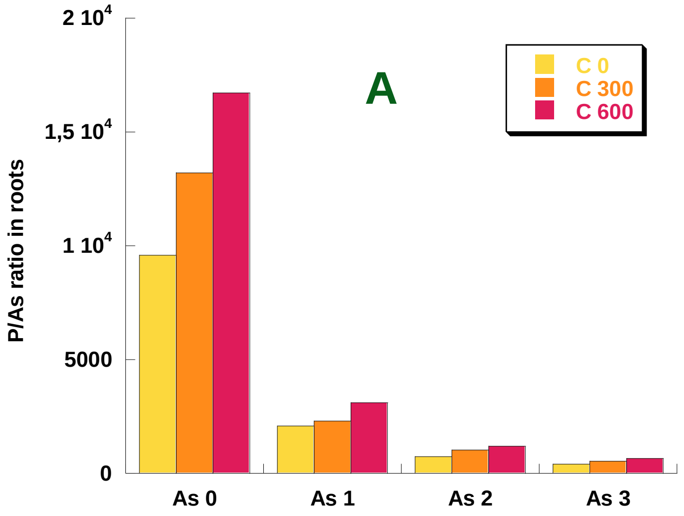
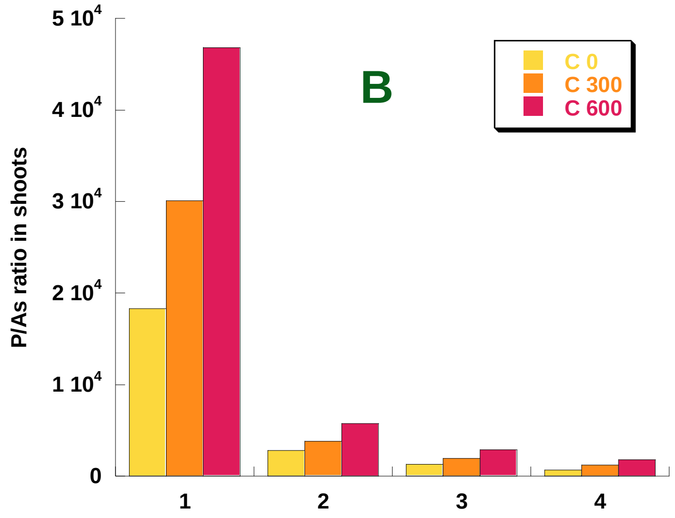


Figure 25 P shoots/roots ratio (between concentration values) in bean plants.

We also calculated the different P/As concentration ratios in roots, shoots and bean yield (Figure 26 A, B and C). We found that they decreased by increasing As concentration in irrigation water, whereas they increased with increasing compost application. Furthermore, the bean yield showed the highest P/As concentration ratio, in all experimental treatments (Figure 26 C), followed by shoots (Figure 26 B) and roots (Figure 26 A), because of the limited translocation of As from roots to aboveground plant tissues.





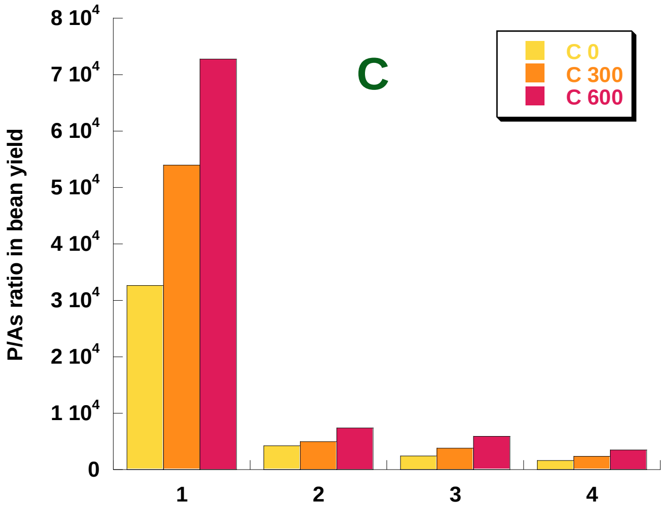


Figure 26 P/As concentration ratios in roots (A), shoots (B) and bean yield (C).

4.3.6 Non- and specifically sorbed As concentrations in soil samples

The concentration of the free-fraction of As in soil samples (non-specifically sorbed As) decreased significantly by increasing amount of compost application and increased markedly by increasing concentration of As in irrigation solutions (Figure 27). In soil samples amended with compost, there was a decrease of the concentration of non-specifically sorbed As, on average, of 20.2 % and 40.8 %, respectively, in C 300 and C 600 treatments, compared to compost control (C 0).

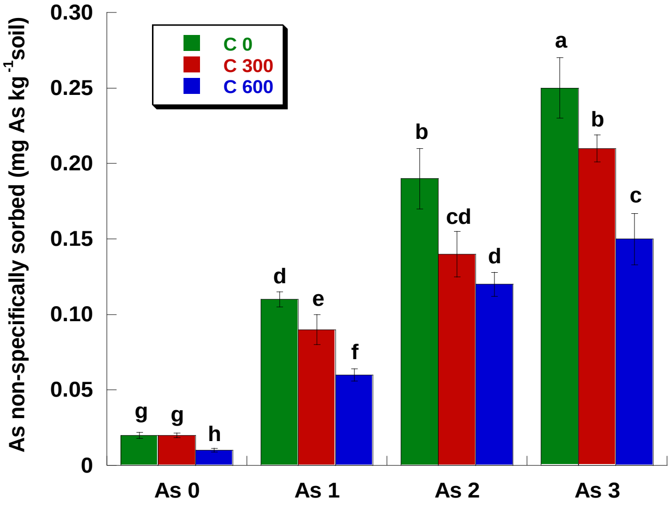


Figure 27 Non-specifically sorbed As concentration in soil samples.

The concentration of specifically sorbed As in soil samples was also greatly influenced by compost application and As treatments (Figure 28). The higher the compost application the higher was the concentration of specifically sorbed As. In fact, in C 300 treatment there was an increase of the specifically sorbed As concentration ranged from 5.0 % (As 1) to 12.3 % (As 3) with respect to that of the compost control treatment (C 0), whereas in C 600 soil samples this increase ranged from 27.5 % (As 1) to 46.7 % (As 2). This findings indicate that higher content of organic matter in the soils amended with compost has determined a higher sorption of As, derived by irrigation solutions. In fact, the mobilization of metals in soils can be minimized through chemical and biological immobilization using a range of soil amendments, such as lime, PO_4 compounds and stabilized compost (Adriano et al., 1982; Basta et al., 2001; Bolan et al., 2003b).

Moreover, the higher the As concentration in irrigation water, the higher was the concentrations of both As non- and specifically sorbed in soil samples.

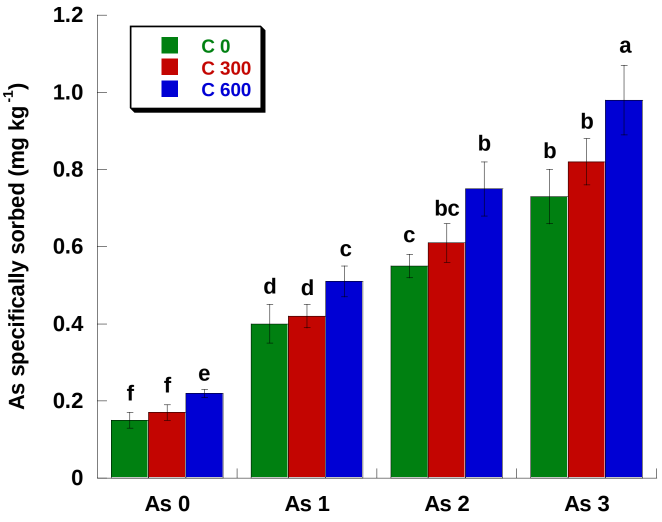


Figure 28 Specifically sorbed As concentrations in soil samples.

4.3.7 Conclusions on the study on the bean plants

The results of the present study suggest that the growth of bean plants and the As upkake by biomasses were substantially affected by the mobility of As in soils and the plant management. Higher mobility of As in soil resulted in higher As uptake by bean plants. Arsenic phytotoxic effect was evident, as the growth of roots, aboveground biomass and bean yield were attenuated by increasing concentration of As in irrigation water. Arsenic concentrations used in the irrigation water of this work could be found in many As-contaminated groundwaters and so pumped by farmers for agricultural purposes. The findings presented in this work also indicate that the compost, rich in organic matter but inherently low in As content, acted as a sink by sequestering As in soils, thereby reducing its phytotoxic effect on plants growth. Since one of the primary objectives of remediating contaminated sites is to reduce the bio-availability of metals, *in situ* immobilization using quality compost may offer a promising option. In the present work, the beneficial effect of compost application on the reduction of mobility and phyto-availability of As in soil was just evaluated for a short duration. In future, it could be extremely important to examine the long-term impact of compost addition on the mobility of As in soil. With compost, one of the main concerns about its long-term efficiency is the potential for As to mobilize if and when the organic matter undergoes significant oxidation. In fact, there is some uncertainty about metals becoming more mobile and phyto-available with time through natural decomposition of the added compost, which also requires careful examination.

CHAPTER 5 - GENERAL CONCLUSIONS

5.1 Overall conclusions

Nowadays, risk management of As-contaminated soil and aquatic ecosystems is an important issue and a great challenge. Its success is necessary to promote sustainable environmental health and also to minimize the adverse impact on humans.

Many technological developments occurred in the last years are leading to a gradual economic growth of many Countries, but, at the same time, they cause serious environmental risks and damages, including As contamination. Large concentrations of As appear frequently in drinking-water, posing an important environmental issue, particularly in densely populated areas where the demand for water is very high. In fact, 130 million people across the world are exposed to levels of As in their drinking-water that exceed the WHO recommended limit of 10 μg L^{-1} and 50 million of these are exposed to level of over 50 μg L^{-1}, five times this limit. The latest estimates suggest that 1 to 100 persons who routinely drink water containing 50 μg L^{-1} or more As will die for cancers alone. For each person who dies, many more will suffer from the painful and stigmatizing effects of chronic As poisoning (Ravenscroft et al., 2009). So, urgent action must be taken to reduce these impacts by providing access to safe water as a basic human right. Delaying mitigation will increase death and disease.

The immobilization of As on the surfaces of sorbents is considered by the scientific community, a effective and safe removal method of As from contaminated water. However, the high cost of production of most sorbents capable to remove AsO_3 and AsO_4 ions from contaminated solutions, strongly limits their spread and use, on a large scale. It is therefore necessary to research and study novel sorbents at low cost, easily synthesized, or even by-products coming from production processes, available for free or at very low price. Surveys conducted in the present work have followed exactly this line of thought, through the study of the removal capacity of AsO_4 from contaminated solutions by LDHs (easily reproducible anionic clays at low cost) and WTRs (by-products coming from drinking-water treatment plants). The implementation of decontamination systems of As-contaminated waters by providing for LDHs and/or WTRs use would be able to combine the lower costs of remediation and effective removal of the metalloid from them. In fact, the AsO_4 sorption capacity exhibited by LDHs and WTRs is absolutely comparable to that of the more expensive sorbents. In addition, data on the AsO_4 desorption, previously sorbed on the LDHs surfaces, by the most common anions of competition, as well as by desorption studies (Makris et al., 2006) and XAS measurements (Makris et at., 2007; Makris et al., 2009) on WTRs, let us assert that these sorbents are able to retain strongly the metalloid on their surfaces, ensuring thus a rapid and sure removal of As from contaminated waters.

Another well-known concern is As entering the food chain, affecting food safety. This poses a potential dietary risk to human health in addition to the risk from drinking contaminated water. Food chain contamination by As, in fact, has become a burning issue in recent years because of their potential bio-accumulation (Lokeshwari, 2006). Therefore monitoring programs for As contribute to improving food safety, warn of actual and potential food scares, and facilitate evaluation of possible health hazards by providing continuous information on levels of environmental pollution (Dogheim, 2004).

Less well-known but potentially more serious is the risk of As to crop production. Continuous build up of As in the soil from As-contaminated irrigation water reduces crop yields in the long term.

The presence of As in soils and/or groundwaters used for agricultural purposes, causes a strong abiotic stress to the cultivated plants, which manifests itself through the reduction of biomasses and, specially, yields, mostly non-tradable, both for the size that the high As concentration. It is therefore desirable to identify and develop production techniques capable of limiting the mobility and phyto-availability of As in soil, through the stabilization of the metalloid on the more recalcitrant soil fractions.

The use of a modern soil amendant as compost in the present work, in addition to improve bean plants growth and their nutritional status, has allowed to limit the As uptake by biomasses, through the immobilization of the metalloid, derived by irrigation water, on/in their humified organic macromolecules. Furthermore, the supply of nutrients through an organic fertilizer as compost falls within the context of organic farming, eco-friendly production system, which ensures the sustainability of the soil, improving its fertility.

CHAPTER 6 - REFERENCES

6.1 References

Abedin M.J., Cresser M.S., Meharg A.A., Feldmann J., Cotter-Howells J. (2002). Arsenic accumulation and metabolism in rice (*Oryza sativa* L.). Environ. Sci. Technol. 36: 962-968.

Adriano D.C., Page A.L., Elseewi A A., Chang A.C. (1982). Cadmium availability to Sudan-grass grown on soils amended with sewage sludge and fly ash. J. Environ. Qual. 11: 197-203.

Adriano D.C. (2001). Trace Elements in Terrestrial Environments: Biogeochemistry, Bioavailability and Risks of Metals, 2nd edition, Springer, New York.

Aggett J., Aspell A.C. (1980). Arsenic contamination in an apple orchard. Environ. Pollut. Ser. A. 22: 39-46.

Allison F.E. (1973). Soil organic matter and its role in crop production. Elsevier Scientific Publ. Company, Amsterdam.

Anderson L.C.D., Bruland K.W. (1991). Biogeochemistry of arsenic in natural waters; the importance of methylated species. Environ. Sci. Technol. 25: 420-427.

Andreae M.O. (1977). Determination of arsenic species in natural waters. Anal. Chem. 49: 820-825.

Andreae M.O., Klumpp D. (1979). Biosynthesis and release of organoarsenic compounds by marine algae. Environ. Sci. Technol. 13: 738-741.

Andreae M.O. (1980). Arsenic in rain and the atmospheric mass balance of arsenic. J. Geophys. Res. 85: 4512.

Antoniadis V., Alloway B.J. (2002). The role of DOC in the mobility of Cd, Ni and Zn in sewage sludge-amended soils. Environ. Pollut. 117(3): 515-521.

Arai Y., Sparks D.L. (2002). Residence time effects on arsenate surface speciation at the aluminum oxide-water interface. Soil Sci. 167: 303-314.

Armstrong C.W., Stroube R.B., Rubio T. (1984). Outbreak of fatal arsenic poisoning caused by contaminated drinking water. Arch. Environ. Health 39: 276-279.

Arnon D.I. (1949). Copper enzymes in isolated chloroplast polyphenoloxidase in B*eta vulgaris*. Plant Physiol. 24: 1-15.

Aten C.F., Bourke J.B., Martini J.H., Walton J.C. (1980). Arsenic and lead in an orchard environment. Bul. Environ. Contam. Toxicol. 24: 108-115.

Babatunde A.O., Zhao Y.Q., Burke A.M., Morris M.A., Hanrahan J.P. (2009). Characterization of aluminium-based water treatment residual for potential phosphorus removal in engineered wetlands. Environ. Pollut. 157: 2830-2836.

Badruzzaman M., Westerhoff P., Knappe D.R.U. (2004). Intraparticle diffusion and adsorption of arsenate onto granular ferric hydroxide (GFH). Water Res. 38: 4002-4012.

Baldoni G., Cortellini L., Maroncelli C., Toderi G. (1994). Utilizzazione di fanghi di depurazione e di compost su colture erbacee: risultati di un quadriennio di prove in area padana. In: Provincia di Forli-Cesena, editor. Compost: dai rifiuti una risorsa per l'agricoltura. Cesena, Italy: Stampa Lito Tuttastampa, pp. 117-127.

Barbera A., Canepa D., Facco S., Franzin F. (1989). Metalli pesanti da concimi minerali e compost: accumulo nel terreno. In: Istituto Agrario di San Michele, editor. Compost: Production and Use. Proc. Int. Symp. Compost: Production and Use, pp. 459-464, San Michele all'Adige, Trento, Italy, 20-23 June 1989.

Basta N.T., Gradwohl R., Snethen K.L., Schroder J.L. (2001). Chemical immobilization of lead, zinc and cadmium in smelter-contaminated soils using biosolids and rock phosphate. J. Environ. Qual. 30: 1222-1230.

Baum M.K., Miguez-Burbano M.J., Campa A., Shor-Posner G. (2000). Selenium and interleukins in persons infected with human immunodeficiency virus type 1. J. Infectious Diseases 182(1): 69-73.

B.C. Agriculture and Food (1996). Composting fact sheet. British Columbia Ministry of Agriculture and Food, Abbotsford, BC, Canada.

Beck M.A., Kolbeck P.C., Shi Q., Rohr L.H., Morris V.C., Levander O.A. (1994). Increased virulence of a human enterovirus (coxsackievirus B3) in selenium deficient mice. J. Infectious Diseases 170: 351-357.

Bender J., Lee R.F., Phillips P. (1995). Uptake and transformation of metals and metalloids by microbial mats and their use in bioremediation. J. Indust. Microbiol. 14: 113-118.

Beretka J., Nelson P. (1994). The current state of utilization of fly ash in Australia. In Ash: A Valuable Resource, vol. 1, pp. 51-63. South African Coal Ash Association.

Berg M., Tran H.C., Nguyen T.C., Pham H.V., Schertenleib R., Giger W. (2001). Arsenic contamination of groundwater and drinking water in Vietnam: A human health threat. Environ. Sci. Technol. 35: 2621-2626.

Bergholm J., Dryler K. (1989). Studies on the Fixation of Arsenic in Soil and on the Mobility of Arsenic, Copper and Chromium in CCA Contaminated Soil. Report 161, Swedish Wood Preservation Institute, Stockholm, Sweden.

Bergman Ö (1991). Urlakning från Tryckimpregnerat Virke: En Litteratur Studie. Report 163, Swedish Wood Preservation Institute, Stockholm, Sweden, pp.36 (in Swedish).

Bergquist E.R., Fischer R.J., Sugden K.D., Martin B.D. (2009). Inhibition by methylated organo-arsenicals of the respiratory 2-oxo-acid dehydrogenases. J. Organomet. Chem. 694: 973-980.

Bettley F.R., O'Shea J.A. (1975). The absorption of arsenic and its relation to carcinoma. Br. J. Dermatol. 92: 563-568.

Bevacqua R.F., Mellano V.J. (1993). Sewage sludge compost's cumulative effects on crop growth and soil properties. Compost Sci. Utilization 1(3): 34-37.

Beyea J., De Chant L., Conditt M., Jones B. (1993). Wet bag composting trial yields promising results. Biocycle 34(4): 72-75.

Bhattacharya P., Nordqvist S., Jacks G. (1995). Status of arsenic contamination in the soils around a former wood preservation facility at Konsterud, Kristinehamn Municipality, Värmland County, Western Sweden. In: 5th Seminar on Hydrogeology and Environmental Geochemistry, B. Bölviken Seminar-95, Norges Geologiske Undersökelse, Report 95, pp. 70-72.

Bhattacharya P., Nordqvist S., Jacks G. (1996). Heavy metals in soils: a case study for potential arsenic contamination in the environment around the site of former wood preservation facility in Central Sweden. In: P Aagaard, J Jahren, eds. The Rosenqvist Symposium on Clay Minerals in the Modern Society. Inst Geol, Univ Oslo, Norway, Report 69, pp. 9-10.

Bhattacharya P., Jacks G. (2000). Arsenic contamination in groundwater of the sedimentary aquifers in the Bengal Delta Plains: a review. In: Bhattacharya P., Welch A.H., eds. Arsenic in Groundwater of Sedimentary Aquifers. Pre-Congress Workshop, 31st Int Geol Cong, Rio de Janeiro, Brazil, pp. 18-21.

Bhattacharya P., Welch A.H. (2000). Arsenic in groundwater of sedimentary aquifers. In: V Subramanian, ed. Proc Brain Storming Session on "The Arsenic Problem". UNESCO-ENVIS Publication, Jawahar Lal Nehru University, New Delhi, India. 2000, pp. 29-41.

Bishop R.F., Chisholm D. (1962). Arsenic accumulation in Annapolis Valley orchard soils. Can. J. Soil Sci. 42: 77-80.

Bliek T., Bleeker P.M., Vooijs R., Arnetoli M., Schat H. (2008). The role of arsenate reductase in arsenate toxicity and tolerance in plants. Presented in 20th New Phytologist Symposium "Arsenic: Unravelling its metabolism and speciation in plants", Aberdeen, Scotland, UK.

Boehm M.J., Wu T., Stone A.G., Kraakman B., Iannotti D.A. (1997). Cross polarized magic-angle spinning ^{13}C nuclear magnetic resonance spectroscopic characterization of soil organic matter relative to culturable bacterial species composition and sustained biological control of *Pythium* root rot. Applied and Environmental Microbiology 63: 162-168.

Boisson J., Mench M., Vangronsveld J., Ruttens A., Kopponen P., DeKoe T. (1999). Immobilization of trace metals and arsenic by different soil additives: Evaluation by means of chemical extractions. Commun. Soil Sci. Plant Anal. 30: 365-387.

Bolan N.S., Thiyagarajan S. (2001). Retention and plant availability of chromium in soils as affected by lime and organic amendments. Aust. J. Soil Res. 39: 1091-1103.

Bolan N.S., Adriano D.C., Naidu R. (2003a). Role of phosphorus in (im)mobilization and bioavailability of heavy metals in the soil-plant system. Rev. Environ. Contam. Toxicol. 177: 1-44.

Bolan N.S., Adriano D.C., Mani P., Duraisamy A., Arulmozhiselvan S. (2003b). Immobilization and phytoavailability of cadmium in variable charge soils: I. Effect of phosphate addition. Plant Soil 250: 83-94.

Bolan N.S., Adriano D.C., Mahimairaja S. (2004). Distribution and bioavailability of trace elements in livestock and poultry manure by-products. CRC Crit. Rev. Environ. Sci. Tech. 34: 291-338.

Bothe J.V., Brown P.W. (1999). Arsenic immobilization by calcium arsenate formation. Environ. Sci. Tech. 33: 3806-3811.

Boyle R.W., Jonasson I.R. (1973). The geochemistry of arsenic and its use as an indicator element for geochemical prospecting. Journal of Geochemical Exploration 2: 252-296.

Braman R.S., Foreback C.C. (1973). Methylated forms of arsenic in the environment. Science 182: 1247-1249.

Bringezu S. (1990). Arsen im Holzschutz-mögliche Gesundheits-und Umweltgef ährdun-gen. Holz als Roh-und Werkstoff 48: 237-243.

Brooks R.R., Lee J., Reeves R.D., Jaffre T. (1977). Detection of nickeliferous rocks by herbarium species of indicator plants. J. Geochem. Explor. 7: 49-57.

Brooks R.R., Robinson B.H. (1998). Aquatic phytoremediation by accumulator plants. In: “Plants that Hyperacccumulate Heavy Metals: Their Role in Phytoremediation, Microbiology, Archaeology, Mineral Exploration and Phytomining” (Brooks R.R., Ed.), pp. 203-226. CAB International, Wallingford.

Broome C.S., McArdle F., Kyle J.A.M., Andrews F., Lowe N.M., Hart C.A., Arthur J.R., Jackson M.J. (2004). An increase in selenium intake improves immune function and poliovirus handling in adults with marginal selenium status: Am. J. Clin. Nutr. 80: 154-162.

Buchet J.P., Lauwerys R., Roels H. (1981). Comparison of the urinary excretion of arsenic metabolites after a single oral dose of sodium arsenite, monomethylarsonate or dimethylarsinate in man. Int. Arch. Occup Environ. Health 48: 71-79.

Burlo F., Guijarro I., Barrachina A.A.C., Vlaero D. (1999). Arsenic species: Effects on and accumulation by tomato plants. J. Agric. Food Chem. 47: 1247-1253.

Businelli M., Gigliotti G. (1994). Applicazione del compost da residui solidi urbani in agricoltura. In: Provincia di Forli-Cesena editor. Compost: dai rifiuti una risorsa per l'agricoltura. Cesena, Italy: Stampa Lito Tuttastampa, pp. 114-115.

Can B., Ulusu N.N., Kiline K., Leyla Acan N., Saran Y., Turan B. (2005). Selenium treatment protects diabetes-induced biochemical and ultrastructural alterations in liver tissue: Biol. Trace Elem. Res. 105(1-3): 135-150.

Cao X.D., Ma L.Q. (2004). Effects of compost and phosphate on plant arsenic accumulation from soils near pressure-treated wood. Environ. Pollut. 132: 435-442.

Caporale A.G., Pigna M., Dynes J.J., Cozzolino V., Zhu J., Violante A. (2011). Effect of inorganic and organic ligands on the sorption/desorption of arsenate on/from Al-Mg and Fe-Mg layered double hydroxides. J. Hazard. Mater. 198: 291-298.

Carnö B. (1983). Urlakning i samband med impregnering. Naturvårdsverket, Report SNV PM 1778, pp. 42 (in Swedish).

Carbonell-Barrachina A.A., Burlò F., Mataix J. (1995). Arsenic uptake, distribution, and accumulation in tomato plants - effect of arsenite on plant growth and yield. Journal of Plant Nutrition 18: 1237-1250.

Carbonell-Barrachina A.A., Burlo F., Burgos-Hernandez A., Lopez E., Mataix J. (1997). The influence of arsenite concentration on arsenic accumulation in tomato and bean plants. Scientia Horticulturae 71: 167-176.

Carja G., Nakamura R., Niiyama H. (2005). Tailoring the porous properties of iron containing mixed oxides for As(V) removal from aqueous solutions. Micropor. Mesopor. Mater. 83 (1-3), 94-100.

Cavani F., Trifirb F., Vaccari A. (1991). Hydrotalcite-type anionic clays: preparation, properties and applications, Catal. Today 11: 173-301.

Chakraborti D., Rahman M.M., Paul K., Chowdhury U.K., Sengupta M.K., Lodh D., Chanda C.R., Saha K.C., Mukherjee S.C. (2002). Arsenic calamity in the Indian subcontinent: What lessons have been learned? Talanta 58: 3-22.

Challenger F. (1945). Biological methylation. Chem. Rev. 36: 315-361.

Challenger F., Lisle D.B., Dransfield P.B. (1954). Studies on biological methylation. XIV. The formation of trimethylarsine and dimethylselenide in mould cultures from methyl sources containing ^{14}C. J. Chem. Soc. 2: 1760-1771.

Chatterjee A., Das D., Mandal B.K., Chowdhury T.R., Samanta G., Chakraborti D. (1995). Arsenic in ground-water in 6 districts of West-Bengal, India - the biggest arsenic calamity in the world. 1. Arsenic species in drinking-water and urine of the affected people. Analyst 120: 643-650.

Chatterjee A., Southwood M.H., Basilico D. (1999). Verbs, events and spatial representations. Neuropsychologia 37: 395-402.

Chefetz B., Hatcher P.G., Hadar Y., Chen Y. (1996). Chemical and biological characterization of organic matter during composting of municipal solid waste. J. Environ. Qual. 25(4): 776-785.

Chefetz B., Adani F., Genevini P., Tambone F., Hadar Y., Chen Y. (1998). Humic-acid transformation during composting of municipal solid waste. J. Environ. Qual. 27: 794-800.

Chen S.L., Wilson D.B. (1997). Genetic engineering of bacteria and their potential for Hg2þ bioremediation. Biodegradation 8: 97-103.

Chen W., Yang J., Chen J., Bruch J. (2006). Exposures to silica mixed dust and cohort mortality study in tin mines: exposure-response analysis and risk assessment of lung cancer. Am. J. Ind. Med. 49: 67-76.

Chisholm D. (1972). Lead, arsenic, and copper content of crops grown on lead arsenate treated and untreated soils. Can. J. Plant Sci. 52: 583-588.

Christen K. (2001). The arsenic threat worsens. Environ. Sci. Technol. 35: 286-291.

Civantos D.P., Rodriguez A.L., Aguado-Borruey J.M. (1995). Fuminant malignant arrythmia and multiorgan failure in acute arsenic poisoning. Chest 108: 1774-1775.

Clark L.C., Combs G.F. Jr., Turnbull B.W., Slate E.H., Alberts D. (1996). The nutritional prevention of cancer with selenium 1983-1993: a randomized clinical trial. JAMA 276: 1957-1963.

Clement W.H., Faust S.D. (1981). The release of arsenic from contaminated sediments and muds. J. Environ. Sci. Health 16(1): 87-91.

Cohen S.M., Arnold L.L., Eldan M., Lewis A.S., Beck B.D. (2006). Methylated arsenicals: the implications of metabolism and carcinogenicity studies in rodents to human risk assessment. Crit. Rev. Toxicol. 36: 99-133.

Costantino V.R.L., Pinnavaia T.J. (1995). Basic properties of $Mg^{2+}{}_{1-x}$ $Al^{3+}{}_{x}$ layered double hydroxides intercalated by carbonate, hydroxide chloride and sulphate anions. Inorg. Chem. 34: 883-892.

Corma A., Palomares A.E., Rey F., Márquez F. (1997). Simultaneous catalytic removal of SO_x and NO_x with hydrotalcitederived mixed oxides containing copper, and their possibilities to be used in FCC units. J. Catal. 170(1): 140-149.

Cox M.S., Bell P.E. (1996). Differential tolerance of canola to arsenic when grown hydroponically or in soil. Journal of Plant Nutrition 19: 1599-1610.

Crecelius E.A. (1975). The geochemical cycle of arsenic in Lake Washington and its relation to other elements. Limnol. Oceanogr. 20(3): 441-451.

Crecelius E.A. (1977). Changes in the chemical speciation of arsenic following ingestion by man. Environ. Health Perspect. 19: 147-150.

Cullen N.M., Wolf L.R., Stclair D. (1995). Pediatric arsenic ingestion. Am. J. Emergency Med. 13: 432-435.

Cunningham S.D., Lee C.R. (1995). Phytoremediation: Plant-based remediation of contaminated soils and sediments. In: “Bioremediation: Science and Applications” (Skipper H.D., Turco R.F., Eds.), pp. 145-156, SSSA Special Publication No 43. SSSA, ASA and CSSA, Madison, WI.

Cunningham S.D., Berti W.R., Huang, J.M. (1995). Phytoremediation of contaminated soils. TIBTECH 13: 393-397.

Das D., Samanta G., Mandal B.K., Chowdhury T.R., Chanda C.R. (1995). A simple household device to remove arsenic from groundwater and two years performance report of arsenic removal plant for treating groundwater with community participation. School of Environmental Studies. Jadavpur University, Calcutta, India.

Das J., Das D., Dash G.P., Das D.P., Parida K.M. (2004). Studies on Mg/Fe hydrotalcite-like-compound (HTlc) - II. Removal of chromium (VI) from aqueous medium. Int. J. Environ. Stud. 61(5): 605-616.

Das J., Patra B.S., Baliarsingh N., Parida K.M. (2006). Adsorption of phosphate by layered double hydroxides in aqueous solutions. Appl. Clay Sci. 32(3-4): 252-260.

Dat J., Vandenabeele S., Iranova E., Van Montagu M., Inze D., Van Breusegem F., (2000). Dual action of the active oxygen species during plant stress responses. Cell. Mol. Life Sci. 57: 779-795.

Davenport J.R., Peryea F.J. (1991). Phosphate fertilizers influence leaching of lead and arsenic in soil contaminated with lead arsenate. Wat. Air Soil Pollut. 57-58: 101-110.

Davis J.G., Burgoa B. (1995). Interactive mechanisms of anion adsorption with calcium leaching and exchange. Soil Sci. 160: 237-314.

Dayton E.A., Basta N.T. (2001). Characterization of drinking water treatment residuals for use as a soil substitute. Water Environment Research 73: 52-57.

Dayton E.A, Basta N.T. (2005a). Using drinking water treatment residuals as a Best Management Practice to reduce phosphorus Risk Index scores. J. Environ. Qual. 34: 2112-2117.

Dayton E.A., Basta N.T. (2005b). A method for determining the phosphorus sorption capacity and amorphous aluminum of aluminum-based drinking water treatment residuals. J. Environ. Qual. 34: 1112-1118.

Del Hoyo C. (2007). Layered double hydroxides and human health: An overview, Applied Clay Science 36: 103-121.

Del Razo L.M., Rellano M.A., Cebrian M.E. (1990). The oxidation states of arsenic in well-water from a chronic arsenicism area of northern Mexico. Environ. Pollut. 64: 143-153.

Del-Zan F. (1989). Prove agronomiche di compost diversi per origine e tecnologia produttiva: effetti indotti a breve termine sul terreno e su quattro colture erbacee. In: Istituto Agrario di San Michele, editor. Compost: Production and Use. Proc. Int. Symp. Compost: Production and Use, pp. 251-270. Istituto Agrario di San Michele all'Adige, Trento, Italy, 20-23 June 1989.

Deuel L.E., Swoboda A.R. (1972). Arsenic toxicity to cotton and soybeans. J. Environ. Qual. 1: 317-320.

Dick W.A., McCoy E.L. (1993a). Enhancing Soil Fertility by Addition of Compost. In: Science and Engineering of Composting. Hoitink H., Keener H.M. (Eds.), pp. 622-644, Renaissance Publications, Worthington, OH.

Dick W.A., McCoy E.L. (1993b). Science and engineering of composting: Design, environmental, microbiological and utilization aspects. Hoitink H.A., Keener H.M. (Eds.), Ohio Agricultural Research and Development Center. The Ohio State University, 622.

Dogheim S.M., Ashraf El M.M., Alla S.A.G., Khorshid M.A., Fahmy S.M. (2004). Pesticides and heavy metals levels in Egyptian leafy vegetables and some aromatic medicinal plants. Food Additives and Contaminants 21(4): 323-330.

Dove P.M., Rimstidt J.D. (1994). Silica-water interactions. In: SILICA: Physical Behavior, Geochemistry and Materials Applications, 29: 259-308. MSA Rev: Mineral.

Driehaus W., Jekel M., Hildebrandt U. (1998). Granular ferric hydroxide - a new adsorbent for the removal of arsenic from natural water. J. Water Service Res. Technol. AQUA 47: 30-35.

Duxbury J.M., Mayer A.B., Lauren J.B., Hassan N. (2002). Arsenic content of rice in Bangladesh and its impacts on rice productivity. Presented in 4th Annual Conference on Arsenic Contamination in Groundwater in Bangladesh: Cause, Effect and Remedy, Dhaka, Bangladesh.

Eghball B., Power J.F., Gilley J.E., Doran J.W. (1997). Nutrient, carbon, and mass loss during composting of beef caddle feedlot manure. J. Environ. Qual. 26: 189.

Eisler R. (2004). Arsenic hazards to humans, plants, and animals from gold mining. Rev. Environ. Contam. Toxicol. 180: 133-165.

Elliott H.A., Dempsey B.A. (1991). Agronomic effects of land application of water treatment sludges. J. AWWA 83: 126-131.

Epstein E. (1996). The Science of composting. Technomic Publishing Company Inc., Lancaster, PA.

ETCS, European Topic Centre Soil (1998). Topic report: Contaminated sites. European Environment Agency.

Evans D.G., Duan X. (2006). Preparation of layered double hydroxides and their applications as additives in polymers, as precursors to magnetic materials and in biology and medicine. Chem. Commun. 5: 485-496.

Fennell J.S., Stacy W.K. (1981). Electrocardiographic changes in acute arsenic poisoning. Irish J. Medical Sci. 150: 338-339.

Ferguson J.F., Gavis J. (1972). A review of the arsenic cycle in natural waters. Wat. Res. 6: 1259-1274.

Fernández J.M., Ulibarri M.A., Labajos F.M., Rives V. (1998). The effect of iron on the crystalline phases formed upon thermal decomposition of Mg-Al-Fe hydrotalcites, J. Mater. Chem. 8: 2507-2514.

Fitz W.J., Wenzel W.W. (2002). Arsenic transformations in the soil-rhizosphere-plant system: Fundamentals and potential application to phytoremediation. J. Biotechnol. 99: 259-278.

Flora S. (1999). Arsenic-induced oxidative stress and its reversibility following combined administration of N-acetylcysteine and meso 2,3-dimercaptosuccinic acid in rats. Clin. Exp. Pharm. Physiol. 26: 865-869.

Foster A.L., Brown G.E., Parks G.A., Tingle T.N., Voigt D.E., Brantley S.L. (1997). XAFS determination of As(V) associated with Fe(III) oxyhydroxides in weathered mine tailings and contaminated soil from California, USA. J. De Physique IV 7: 815-816.

Foster A.L., Brown G.E. Jr., Tingle T.N., Parks G.A. (1998). Quantitative arsenic speciation in mine tailings using X-ray absorption spectroscopy. Am. Mineral. 83: 553-568.

Francesconi K., Visoottiviseth P., Sridokchan W., Goessler W. (2002). Arsenic species in an arsenic hyperaccumulating fern, *Pityrogramma calomelanos*: A potential phytoremediator of arsenic-contaminated soils. Sci. Total Environ. 284: 27-35.

Frankenberger W.T., Losi M.E. (1995). Application of bioremediation in the clean up of heavy metals and metalloids. In: “Bioremediation: Science and Applications” (Skipper H.D., Turco R.F., Eds.), pp. 173-210, SSSA Special Publication No 43. SSSA, ASA and CSSA, Madison, WI.

Frankenberger W.T. Jr. (2002). Environmental chemistry of arsenic, Marcel Dekker, New York.

Gailer J., George G.N., Pickering I.J., Prince R.C., Ringwald S.C. (2000). A metabolic link between arsenite and selenite: the seleno-bis(S-glutathionyl) arsinium ion. J. Am. Chem. Soc. 122: 4637-4639.

Gallimore L.E., Basta N.T., Storm D.E., Payton M.E., Huhnke R.H., Smolen M.D. (1999). Water treatment residual to reduce nutrients in surface runoff from agricultural land. J. Environ. Qual. 28: 1474-1478.

Gao S., Burau R.G. (1997). Environmental factors affecting rates of arsine evolution from and mineralization of arsenicals in soil. J. Environ. Qual. 26: 753-763.

Giles C.H., Smith D., Huiston A. (1974). A general treatment and classification of the solute adsorption isotherm. I. Theoretical. J. Colloid Interface Sci. 47: 755-765.

Gilmore J.T., Wells B.R. (1980). Residual effects of MSMA on sterility in rice cultivars. Agron. J. 72: 1066-1067.

Goh K.H., Lim T.T., Dong Z. (2008). Application of layered double hydroxides for removal of oxyanions: A review. Water Research 42: 1343-1368.

Goh K.H., Lim T.T. (2010). Influences of co-existing species on the sorption of toxic oxyanions from aqueous solution by nanocrystalline Mg/Al layered double hydroxide. J. Hazard. Mater. 180: 401-408.

Goldberg S., Johnston C.T. (2001). Mechanisms of arsenic adsorption on amorphous oxides evaluated using macroscopic measurements, vibrational spectroscopy, and surface complexation modeling. J. Colloid Interface Sci. 234: 204-216.

Golueke C.G. (1991). Principles of composting. In: The staff of Biocycle Journal of Waste Recycling, The Art and Science of Composting, The JG Press, Pennsylvania, pp. 14-27.

Gonzaga M.I.S., Santos J.A.G., Ma L.Q. (2006). Arsenic phytoextraction and hyperaccumulation by fern species. Sci. Agric. 63: 90-101.

Goswamee R.L., Sengupta P., Bhattacharyya K.G., Dutta D.K. (1998). Adsorption of Cr(VI) in layered double hydroxides. Appl. Clay Sci. 13(1): 21-34.

Granchinho S.C.R., Polishchuk E., Cullen W.R., Reimer, K.J. (2001). Biomethylation and bioaccumulation of arsenic(V) by marine alga *Fucus gardneri*. Appl. Organometallic Chem. 15: 553-560.

Greenwood N.N., Earnshaw A. (1984). Chemistry of the Elements. Pergamon Press: Oxford, pp. 1392-1420.

Griffin D.M. (1985). Bacteria in nature, vol. 1, Plenum, London.

Gu Z., Fang J., Deng B. (2005). Preparation and evaluation of GAC based iron-containing adsorbents for arsenic removal. Environ. Sci. Technol. 39: 3833-3843.

Gulledge J.H., O’Connor J.T. (1973). Removal of arsenic (V) from water by adsorption on aluminium and ferric hydroxides. Am. Water Works Assoc. J. 65: 548-552.

Han D.K., Eng J., Zhou H., Aebersold R. (2001). Quantitative profiling of differentiation-induced microsomal proteins using isotope-coded affinity tags and mass spectrometry. Nat. Biotechnol. 19: 946-951.

Hao X.Y., Chang C., Larney F.J., Travis G.R. (2001). Greenhouse gas emissions during cattle feedlot manure composting. J. Environ. Qual. 30: 376-386.

Hartley W., Dickinson N.M., Clemente R., French C., Piearce T.G., Sparke S., Lepp N.W. (2009). Arsenic stability and mobilization in soil at an amenity grassland overlying chemical waste (St. Helens, UK). Environ. Pollut. 157: 847-856.

Hartley-Whitaker J., Ainsworth G., Meharg A.A. (2001). Copper- and arsenate-induced oxidative stress in *Holcus lanatus* L. clones with differential sensitivity. Plant Cell Environ. 24: 713-722.

Haustein G.K., Daniel T.C., Miller D.M., Moore P.A. Jr., Mcnew R.W. (2000). Aluminum-containing residuals influence high-phosphorus soils and runoff water quality. J. Environ. Qual. 29: 1954-1959.

Hindmarsh J.T., McCurdy R.F. (1986). Clinical and environmental aspects of arsenic toxicity. CRC Crit. Rev. Clin. Lab. Sci. 23: 315-347.

Hlavay J., Polyak K. (1997). Removal of arsenic ions from drinking-water by novel type adsorbents. In: “Arsenic: Exposure and Health Effects” (Abernathy C.O., Calderon R.L., Chappell W.R., Eds.), pp. 382-392. Chapman & Hall, New York.

Hopenhayn-Rich C., Biggs M.L., Smith A.H. (1998). Lung and kidney cancer mortality associated with arsenic in drinking water in Cordoba, Argentina. Int. J. Epidemiol. 27: 561-569.

Hou W.G., Song S.E. (2004). Intrinsic surface reaction equilibrium constants of structurally charged amphoteric hydrotalcite-like compounds. J. Colloid Interface Sci. 269: 381-387.

Hughes M.F. (2002). Arsenic toxicity and potential mechanisms of action. Toxicol. Lett. 133: 1-16.

Inbar Y., Chen Y., Hadar Y. (1989). Solid-state ^{13}C nuclear magnetic resonance and infrared spectroscopy of composted organic matter. Soil Sci. Soc. Am. J. 53: 1695-1701.

Indorante S.J., Follmer L.R., Hammer R.D., Koenig P.G. (1990). Particle-size analysis by a modified pipette procedure. Soil Science Society of America Journal 54: 560-563.

Islam M., Patel R. (2010). Synthesis and physicochemical characterization of Zn/Al chloride layered double hydroxide and evaluation of its nitrate removal efficiency. Desalination 256: 120-128.

Jacks G., Bhattacharya P. (1998). Arsenic contamination in the environment due to the use of CCA-wood preservatives. In: Arsenic in Wood Preservatives, Part I, Kemi Report 3/98, pp. 7-75.

Jain P., Yong-Chul J., Thabet T., Witwer M., Townsend T. (2005). Recycling of water treatment plant sludge via land application: assessment of risk. J. Res. Sci. Technol. 2: 13-23.

Jiang Q.Q., Singh B.R. (1994). Effect of different forms and sources of arsenic on crop yield and arsenic concentration. Water, Air, and Soil Pollution 74: 321-343.

Jiménez E.I., Garcia V.P. (1989). Evaluation of City Refuse Compost Maturity: A Review. Biological Wastes 27: 115-142.

Johnson D.L. (1972). Bacterial reduction of arsenate in sea water. Nature 240: 44-45.

Jomova K., Jenisova Z., Feszterova M., Baros S., Liska J., Hudecova D., Rhodesd C.J., Valkoc M. (2011). Arsenic: toxicity, oxidative stress and human disease J. Appl. Toxicol. 31: 95-107.

Jones C.A., Inskeep W.P., Neuman D.R. (1997). Arsenic transport in contaminated mine tailings following liming. J. Environ. Qual. 26: 433-439.

Kannan S. (1998). Decomposition of nitrous oxide over the catalysts derived from hydrotalcite-like compounds. Appl. Clay Sci. 13(5-6): 347-362.

Kannan S., Swamy C.S. (1999). Catalytic decomposition of nitrous oxide over calcined cobalt aluminum hydrotalcites. Catal. Today 53(4): 725-737.

Kapadia A. (2000). Technologies and Costs for Removal of Arsenic from Drinking Water, US, Environmental Protection Agency, EPA 815-R-00-028, Washington, DC.

Kenyon D.J., Elfving D.C., Pakkala I.S., Bache C.A., Lisk D.J. (1979). Residues of lead and arsenic in corps cultured on old orchard soils. Bull. Environ. Contam. Toxicol. 22: 221-223.

Khan A.I., O’Hare D. (2002). Intercalation chemistry of layered double hydroxides: recent developments and applications, J. Mater. Chem. 12: 3191-3198.

Kiso Y., Jung Y.J., Yamada T., Nagai M., Min K.S. (2005). Removal properties of arsenic compounds with synthetic hydrotalcite compounds. Water Sci. Technol.: Water Supply 5(5): 75-81.

Knox A.S., Seaman J.C., Mench M.J., Vangronsveld J. (2000). Remediation of metal and radionuclides-contaminated soils by in situ stabilization techniques. In: Environmental Restoration of Metals-Contaminated Soils (Iskandar I.K., Ed.), Lewis, New York, pp. 21-60.

Kögel-Knabner I. (2002). The macromolecular organic composition of plant and microbial residues as inputs to soil organic matter. Soil Biology & Biochemistry 34: 139-162.

Koljonen T. (ed.) (1992). Geochemical Atlas of Finland, Part 2, Till. Geological Survey of Finland, pp. 218.

Kookana R.S., Naidu R. (2000). Capping contaminated sites with clean cover: Assessing the upward migration of contaminants and the thickness of cap. In: Towards Better Management of Wastes and Contaminated Sites in the Australasia - Pacific Region,Workshop Proceeding, Adelaide, South Australia, pp. 39-40.

Korte N.E., Fernando Q. (1991). A review of arsenic(III) in groundwater. Crit Rev. Environ. Control 21(1): 1-39.

Lantz R.J., MacKenzie F.T. (1979). Atmosphere trace metals. Global cycles and assessment of man’s impact. Geochem. Cosmochim. Acta 43: 511-523.

Lazaridis N.K., Matis K.A., Webb M. (2001). Flotation of metalloaded clay anion exchangers. Part I: The case of chromates. Chemosphere 42(4): 373-378.

Lazaridis N.K., Hourzemanoglou A., Matis K.A. (2002). Flotation of metal-loaded clay anion exchangers. Part II: The case of arsenates. Chemosphere 47: 319-324.

Lazaridis N.K., Pandi T.A., Matis K.A. (2004). Chromium(VI) removal from aqueous solutions by Mg-Al-CO_3 hydrotalcite: sorption-desorption kinetic and equilibrium studies. Ind. Eng. Chem. Res. 43(9): 2209-2215.

Lee D.A., Chen A., Schroeder J.I. (2003). Ars1, an *Arabidopsis* mutant exhibiting increased tolerance to arsenate and increased phosphate uptake. The Plant Journal 35: 637-646.

Leonard A. (1991). Arsenic. In: “Metals and Their Compounds in the Environments: Occurrence, Analysis, and Biological Relevance” (E. Merian, Ed.), 2nd edition, pp. 751-773, Weinheim, VCH.

Li F., Duan X. (2005). Applications of layered double hydroxides. Struct. Bond. 119(1): 193-223.

Li F., Jiang X.R., Evans D.G., Duan X. (2005). Structure and basicity of mesoporous materials from Mg/Al/In layered double hydroxides prepared by separate nucleation and aging steps method. J. Porous Mat. 12(1): 55-63.

Lin T.F., Wu J.K. (2001). Adsorption of arsenite and arsenate within activated alumina grains: equilibrium and kinetics. Water Res. 35: 2049-2057.

Lin Y.J., Li D.Q., Evans D.G., Duan X. (2005). Modulating effect of Mg-Al-CO_3 layered double hydroxides on the thermal stability of PVC resin. Polym. Degrad. Stabil. 88(2): 286-293.

Liu F., De Cristofaro A., Violante A. (2001). Effect of pH, phosphate and oxalate on the adsorption/desorption of arsenate on/from goethite, Soil Sci. 166: 197-208.

Liu J. (2000). Composting and use of compost as a soil amendment. Doctoral Dissertation. Natural Resources and Environmental Management Department, University of Hawaii, pp.138.

Liu R., Frost R.L., Martens W.N. (2009). Absorption of the selenite anion from aqueous solutions by thermally activated layered double hydroxide. Water Res. 43: 1323-1329.

Loeppert R.H., Inskeep W.P. (1996). Iron. In: Sparks D.L., Page A.L., Helmke P.A., Loeppert R.H., Soltanpour P.N., Tabatabai M.A., Johnston C.T., Summer M.E. (eds.) Method of soil analysis. Part 3. Chemical methods, pp. 639-664, SSSA, Madison, WI.

Lokeshwari H., Chandrappa G.T. (2006). Impact of Heavy Metal Contamination of Bellandur Lake on Soil and Cultivated Vegetation. Current Science 91(5): 622-627.

Loukidou M.X., Matis K.A., Zouboulis A.I., Kyriakidou M.L. (2003). Removal of As (V) from wastewaters by chemically modified fungal biomass. Wat. Res. 37: 4544-4552.

Lu F.J. (1990). Blackfoot disease: Arsenic or humic acid? Lancet 336: 115-119.

Lv L., He J., Wei M., Evans D.G., Duan X. (2006). Uptake of chloride ion from aqueous solution by calcined layered double hydroxides: equilibrium and kinetic studies. Water Res. 40: 735-743.

Lynn S., Shiung J., Gurr J., Yan K. (1998). Arsenic stimulates poly (adp-ribosylation) by generation of nitric oxide. Free Radical Biology and Medicine 24: 442-449.

Ma L.Q., Komar K.M., Tu C., Zhang W.H., Cai Y., Kennelley E.D. (2001). A fern that hyperaccumulates arsenic: A hardy, versatile, fast-growing plant helps to remove arsenic from contaminated soils. Nature 409: 579.

MacPhee M.J., Charles G.E., Cornwell D.A., Sorg T.J. (2001). Management of residuals containing arsenic. WEF/AWWA/CWEA joint residuals and biosolids management conference Biosolids 2001: Building Public Support. CD-ROM, Water Environment Federation, Alexandria, VA.

Maeda S., Nakashima S., Takeshita T., Higashi S. (1985). Bioaccumulation of arsenic by freshwater algae and the application to the removal of inorganic arsenic from an aqueous phase. 2. By *Chlorella vulgaris* isolated from arsenic-polluted environment. Separation Sci. Technol. 20: 153-161.

Maeda S., Inoue R., Kozono T., Tokuda T., Ohki A., Takeshita T. (1990). Arsenic metabolism in a freshwater food chain. Chemosphere 20: 101-110.

Maest A.S., Pasilis S.P., Miller L.G., Nordstrom D.K. (1992). Redox geochemistry of arsenic and iron in Mono Lake, California. In: Kharaka Y.K., Maest A.S. (eds.), Water-Rock Interaction. Balkema A.A., pp. 507-511, Rotterdam, The Netherlands.

Mahimairaja S., Bolan N.S., Adriano D.C., Robinson B. (2005). Arsenic contamination and its Risk management in complex Environmental settings. Advances in agronomy vol. 86.

Makris K.C., Harris W.G., O'Connor G.A., Obreza T.A. (2004). Phosphorus immobilization in micropores of drinking water treatment residuals: implications for long-term stability. Environ. Sci. Technol. 38: 6590-6596.

Makris K.C., Harris W.G., O'Connor G.A., Obreza T.A., Elliott H.A. (2005). Physicochemical properties related to long-term phosphorus retention by drinking-water treatment residuals. Environ. Sci. Technol. 39: 4280-4289.

Makris K.C., Sarkar D., Datta R. (2006). Evaluating a drinking-water waste by-product as a novel sorbent for arsenic. Chemosphere 64: 730-741.

Makris K.C., Sarkar D., Parsons J.G., Datta R., Gardea-Torresdey J.L. (2007). Surface arsenic speciation of a drinking-water treatment residual using X-ray absorption spectroscopy. J. Colloid Interf. Sci. 311: 544-550.

Makris K.C., O'Connor G.A. (2007). Beneficial utilization of drinking-water treatment residuals as contaminant mitigating agents. In: Sarkar D., Datta R., Hannigan R. (eds.) Concepts and applications in environmental geochemistry, pp. 609-636, Elsevier, Amsterdam, The Netherlands.

Makris K.C., Sarkar D., Parsons J.G., Datta R., Gardea-Torresdey J.L. (2009). X-ray absorption spectroscopy as a tool investigating arsenic(III) and arsenic(V) sorption by an aluminum-based drinking-water treatment residual. J. Hazard. Mater. 171: 980-986.

Mandal B.K., Suzuki K.T. (2002). Arsenic around the world: a review. Talanta 58: 201-235.

Mappes R. (1977). Experiments on excretion of arsenic in urine. Int. Arch. Occup. Environ. Health 40: 267-272.

Marin A.R., Masscheleyn P.H., Patrick W.H. Jr. (1992). The influence of chemical form and concentration of arsenic on rice growth and tissue arsenic concentration. Plant Soil 139: 175-183.

Marques I.A., Anderson L.E. (1986). Effects of arsenite, sulphite, and sulphate on photosynthetic carbon metabolism in isolated pea (*Pisum sativum* L., Cv. Little Marvel) chloroplasts. Plant Physiol. 82: 488-493.

Martell A.E., Smith R.M. (1977). Critical stability constants, vol. 3, other organic ligands, Plenum Press, New York, USA.

Masscheleyn P.H., Delaune R.D., Patrick W.H. Jr. (1991). Effect of redox potential and pH on arsenic speciation and solubility in a contaminated soil. Environ. Sci. Technol. 25: 1414-1418.

Mazumder D.N.G., Chakraborty A.K., Ghose A., Gupta J.D., Chakraborty D.P., Dey S.B., Chattopadhyay N. (1988). Chronic arsenic toxicity from drinking tube well water in rural West Bengal. Bull. World Health Organ. 66: 499-506.

McBride G.L., Holland P., Wilson K. (1998). Investigation of contaminated sheep dipping sites in the Waikato. In: Proceedings of Waste Management Institute New Zealand Conference, pp. 129-137, Waste Management Institute, New Zealand Inc., Rotorua.

McKeague J.A., Brydon J.E., Miles N.M. (1971). Differentiation of forms of extractable iron and aluminum in soils. Soil Sci. Soc. Am. Proc. 35: 33-38.

McLaren R.G., Naidu R., Smith J., Tiller K.G. (1998). Fractionation and distribution of arsenic in soils contaminated by cattle dip. J. Environ. Qual. 27: 348-354.

McLaughlin M.J., Tiller K.G., Naidu R., Stevens D.P. (1996). The behaviour and environmental impact of contaminants in fertilizers. Aust. J. Soil Res. 34: 1-54.

Meharg A.A., Macnair M.R. (1991). The mechanisms of arsenate tolerance in *Deschampsia cespitosa* (L.) Beauv and *Agrostis capillaris* L. The New Phytologist 119: 291-297.

Meharg A.A., Macnair M.R. (1992). Suppression of the high affinity phosphate uptake system a mechanism of arsenate tolerance in *Holcus lanatus* L. Journal of Experimental Botany 43: 519-524.

Meharg A.A. (1994). Integrated tolerance mechanisms constitutive and adaptive plant responses to elevated metal concentrations in the environment. Plant, Cell & Environment 17: 989-993.

Meharg A.A., Hartley-Whitaker J. (2002). Arsenic uptake and metabolism in arsenic resistant and non resistant plant species. The New Phytologist 154: 29-43.

Meharg A.A. (2005). Mechanism of plant resistance to metal and metalloid ions and potential biotechnological applications. Plant Soil 274: 163-174.

Mench M., Bussiere S., Boisson J., Castaing E., Vangronsveld J., Ruttens A., De Koe T., Bleeker P., Assuncao A., Manceau A. (2003). Progress in remediation and revegetation of the barren Jales gold mine spoil after *in situ* treatments. Plant Soil 249: 187-202.

Merry R.H., Tiller K.G., Alston A.M. (1983). Accumulation of copper, lead, and arsenic in some Australian orchard soils. Aust. J. Soil Res. 21: 549-561.

Meyn M.M., Beneke K., Lagaly G. (1990). Anion-exchnage reactions of layered double hydroxides. Inorg. Chem. 29: 5201-5207.

Miller W.H. Jr, Schipper H.M., Lee J.S., Singer J., Waxman S. (2002). Mechanisms of action of arsenic trioxide. Cancer Res. 62: 3893-3903.

Minato H., Morimoto T., Wada N. (2000). Mineral techniques for the remediation of contaminated water and geology. In: Proceedings of the Workshop on Towards Better Management of Wastes and Contaminated Sites in the Australasia - Pacific Region, pp. 128-129, Adelaide, South Australia.

Miteva E., Merakchiyska M. (2002). Response of chloroplasts and photosynthetic mechanism of bean plants to excess arsenic in soil. Bulg. J. Agric. Sci. 8: 151-156.

Miyata S. (1975). The syntheses of hydrotalcite-like compounds and their structure and physico-chemical properties. The systems Mg^{2+}-Al^{3+}-NO^{3-}, Mg^{2+}-Al^{3+}-CI^{-}, Mg^{2+}-Al^{3+}-CIO^{4-}, Ni^{2+}-AI^{3+}-Cl^{-} and Zn^{2+}-Al^{3+}-CI^{-}. Clays Clay Miner. 23: 369-375.

Miyata S., Okada A. (1977). Synthesis of hydrotalcite-like compounds and their physico-chemical properties - the systems Mg^{2+}-Al^{3+}-SO_4^{2-} and Mg^{2+}-$Al^{3+}CrO_4^{2-}$. Clays Clay Miner. 25: 14-18.

Miyata S. (1983). Anion-exchange properties of hydrotalcite-like compounds. Clays Clay Miner. 31: 305-311.

Moore J.N., O'Callaghan C.A., Berylne G. (1994). Acute arsenic poisoning: Absence of polyneuropathy after treatment with 2,3-dimercaptopropanesulphonate (DMPS). J. Neurol. Neurosurg. Psychiatry 57: 1133-1135.

Mulchi C.L., Adamu C.A., Bell P.F., Chaney R.L. (1991). Residual heavy metal concentrations in sludge-amended coastal plain soils. I. Comparison of extractans. Commun. Soil Sci. Plant Anal. 22(9-10): 919-941.

Murphy M.J., Lyon L.W., Taylor J.W. (1981). Subacute arsenic neuropathy: Clinical and electrophysiological observations. J. Neurol. Neurosurg. Psychiatry 44: 896-900.

Myers D.J., Heimbrook M.E., Osteryoung J., Morrison S.M. (1973). Arsenic oxidation state in the presence of micro-organism by differential pulse polarography. Environ. Lett. 5: 53-61.

Nagar R., Sarkar D., Makris K.C., Datta R., Sylvia V.L. (2009). Bio-availability and bioaccessibility of arsenic in soil amended with drinking-water treatment residuals. Arch. Environ. Contam. Toxicol. 57: 755-766.

Nagar R., Sarkar D., Makris K.C., Datta R. (2010). Effect of solution chemistry on arsenic sorption by Fe- and Al-based drinking-water treatment residuals. Chemosphere 78: 1028-1035.

Naidu R., Smith E., Smith J., Kookana R.S. (2000). Is there potential for using strongly weathered oxidic soils as reactive landfill barriers? In: Proceedings of Workshop on Towards Better Management of Wastes and Contaminated Sites in the Australasia-Pacific Region, pp. 130-133, Adelaide, South Australia.

Naidu R., Bolan N.S., Owens G. (2003). Risk based land management: A cost effective tool for contaminated land management. In: Environmental Management using Soil-Plant Systems (Currie L.D., Stewart R.B., Anderson C.W.N., Eds.), pp. 5-19, Occasional Report No. 16. Fertilizer and Lime Research Centre, Massey University, Palmerston North.

Neku A., Tandukar N. (2003). An overview of arsenic contamination in groundwater of Nepal and its removal at household level. J. De Physique 107: 941-944.

Newman S.P., Jones W. (1998). Synthesis, characterization and applications of layered double hydroxides containing organic guests. New J. Chem. 22(2): 105-115.

Nordstrom D.K. (2000). In: Young C., ed. Minor Elements: Arsenic, Antimony, Selenium, Tellurium and Bismuth. Soc. Mining Metallurgy and Exploration, pp. 21-30.

NRC (1997). National Research Council. Arsenic. National Academy Press, Washington, DC.

Nriagu J.O., Pacyna J.M. (1988). Quantitative assessment of worldwide contamination of air, water, and soils by trace metals. Nature 333: 134-139.

O'Melia C.R. (1989). Particle-particle interactions in aquatic systems. Colloids Surf. 39: 255-271.

O'Neill P. (1995). Arsenic. In: Heavy Metals in Soil (Alloway B.J., ed.). Blackie Academic & Professional, Glasgow.

Orloff K., Mistry K., Metcalf S. (2009). Biomonitoring for environmental exposures to arsenic. J. Toxicol. Environ. Health B Crit. Rev. 12: 509-524.

Osborne F.H., Ehrlich H.L. (1976). Oxidation of arsenite by a soil isolate of alcaligenes. J. Appl. Bacteriol. 41: 295-305.

Pacyna J.M. (1986). Atmospheric trace elements from natural and anthropogenic sources. Toxic metals in the atmosphere. Adv. Environ. Sci. Technol. 17: 33-52.

Paliouris G., Hutchinson T.C. (1991). Arsenic, cobalt and nickel tolerances in two populations of *Silene vulgaris* (Moench) Garcke from Ontario, Canada. The New Phytologist 117: 449-459.

Palomares A.E., López-Nieto J.M., Lázaro F.J., López A., Corma A. (1999). Reactivity in the removal of SO_2 and NO_x on Co/Mg/Al mixed oxides derived from hydrotalcites. Appl. Catal. B. Environ. 20(4): 257-266.

Palomares A.E., Prato J.G., Rey F., Corma A. (2004). Using the ‘‘memory effect’’ of hydrotalcites for improving the catalytic reduction of nitrates in water. J. Catal. 221(1): 62-66.

Palm C.A., Gachengo C.N., Delve R.J., Cadish G., Giller K. (2001). Organic inputs for soil fertility management in tropical agro-ecosystems: application of organic resource database. Agric., Ecosystems and Environ. 83: 27-42.

Pane C., Spaccini R., Piccolo A., Scala F., Bonanomi G. (2011). Compost amendments enhance peat suppressiveness to *Pythium ultimum, Rhizoctonia solani* and *Sclerotinia minor.* Biological Control 56: 115-124.

Paris P., Robotti A. (1981). Il recupero agricolo dei residui urbani a base organica. Genio Rurale 7-8: 21-33.

Paris P., Lucianer A. (1986). Tra caratteristiche del suolo e ioni metallici cento equilibri mutevoli. Genio Rurale 11: 21-28.

Peak D. (2006). Adsorption mechanisms of selenium oxyanions at the aluminum oxide/water interface. J. Colloid Interface Sci. 303: 337-345.

Perez-de-Mora A., Burgos P., Cabrera F., Madejon E. (2007). *In situ* amendments and revegetation reduce trace element leaching in a contaminated soil. Water Air Soil Pollut. 185: 209-222.

Pérez-Ramírez J., Kapteijn F., Moulijn J.A. (1999). High activity and stability of the Rh-free Co-based ex-hydrotalcite containing Pd in the catalytic decomposition of N_2O. Catal. Lett. 60(3): 133-138.

Peryea F.J., Creger T.L. (1994). Vertical distribution of lead and arsenic in soils contaminated with lead arsenate pesticide residues. Wat. Air Soil Pollut. 78: 297-306.

Petersen C., Drinkwater L.E., Wagoner P. (1999). The Rodale Institute Farming Systems Trial: The first fifteen years. Kutztown, PA.

Peterson P.J., Benson L.M., Zieve R. (1981). Metalloids, section: Arsenic. In: Effect of Heavy Metal Pollution on Plants (Lepp N.W., ed.), pp. 299-322, Applied Science Publishers, London.

Petruzzelli G., Vigna-Guidi G., Lubrano L., Canarutto S., Aiello M. (1991). Agronomic utilization of a low metal sewage sludge: results from field experiments. Proc. Int. Conf. Heavy metals in the Environment. CEP consultants, pp. 383-386, Edinburgh.

Phillips S.E., Taylor M.L. (1976). Oxidation of arsenite to arsenate by *Alcaligenes faecalis*. Appl. Environ. Microbiol. 32: 392-399.

Pigna M., Krishnamurti G.S.R., Violante A. (2006). Kinetics of arsenate sorption-desorption from metal oxides: effect of residence time. Soil Sci. Soc. Am. J. 70: 2017-2027.

Pigna M., Cozzolino V., Violante A., Meharg A.A. (2009). Influence of Phosphate on the Arsenic Uptake by Wheat (*Triticum durum* L.) Irrigated with Arsenic Solutions at Three Different Concentrations. Water Air Soil Pollut 197: 371-380.

Pohman A.A., McColl J.G. (1988). Soluble organics from forest litter and their role in metal dissolution. Soil Sci. Soc. Am. J. 52: 265-271.

Prakash P., Sengupta A.K. (2003). Selective coagulant recovery from water treatment plant residuals using Donnan membrane process. Environ. Sci. Technol. 37: 4468-4474.

Quirk J.P. (1955). Significance of surface area calculated from water vapor sorption isotherms by use of the B.E.T. equation. Soil Sci. 80: 423-430.

Rahman, M.A., Hasegawa H., Rahman M.M., Rahman M.A., Miah M.A.M. (2007). Accumulation of arsenic in tissues of rice plant (*Oryza sativa* L.). Chemosphere 69: 942-94.

Rahman M.B.A., Basri M., Hussein M.Z., Idris M.N.H., Rahman R.N.Z.R.A., Salleh A.B. (2004). Immobilization of lipase from *Candida rugosa* on layered double hydroxides of Mg /Al and its nanocomposite as biocatalyst for the synthesis of ester, Catal. Today 93-95: 405-410.

Raskin I., Smith R.D., Salt D.E. (1997). Phytoremediation of metals: Using plants to remove pollutants from the environment. Curr. Opinion Biotech. 8: 221-226.

Ravenscroft P., Brammer H., Richards K. (2009). Arsenic pollution; A global synthesis 2008 RGS-IBS Book Series, Wiley-Blackwell.

Redman A.D., Macalady D.L., Ahmann D. (2002). Natural organic matter affects arsenic speciation and sorption onto hematite. Environ. Sci. Technol. 36: 2889-2896.

Reed J.F., Sturgis M.B. (1963). Toxicity from arsenic compounds to rice on flooded soils. J. Am. Soc. Agron. 28: 432-436.

Reidel F.N., Eikmann T. (1986). Natural occurrence of arsenic and its compounds in soil and rocks. Wiss Umwelt 3-4: 108-117.

Reina S.V., Esteban E., Goldsbrough P. (2005). Arsenate-induced Phytochelatins in white lupin: influence of phosphate status. Physiology plantarum, 124: 41.

Reynolds W.D., Elrich D.E., Young E.G., Amoozegar A., Booltink H.W.G., Bouma J. (2002). Methods of soil analysis, part 4: physical methods, Dane J.H., Topp G.C., (Eds.) Soil Sci. Soc. Am. No. 5. Madion, WI, 797.

Rimstidt J.D., Chermak J.A., Gagen P.M. (1994). Rates of reaction of galena, sphalerite, chalcopyrite and arsenopyrite with Fe(III) in acidic solutions. In: Alpers C.N., Blowes D.W., eds. Environmental Geochemistry of Sulfide Oxidation. ACS Symposium Series 550: 2-13.

Rives V. (2001). Layered Double Hydroxides: Present and Future. Nova Science Publishers Inc., New York.

Rives V. (2002). Characterization of layered double hydroxides and their decomposition products. Mater, Chem. Phys. 75: 19-25.

Robertson F.N. (1989). Arsenic in groundwater under oxidizing conditions, southwest United States. Environ. Geochem. Health 11: 171-185.

Robinson B.H., Brooks R.R., Outred H.A., Kirkman J.H. (1995). The distribution and fate of arsenic in the Waikato River System, North Island, New Zealand. Chem. Spec. Bioavail. 7: 89-96.

Robinson B.H., Green S., Mills T. (2003). Assessment of phytoremediation as best management practice for degraded environments. In: Environmental Management using Soil-Plant Systems (Currie L.D., Stewart R.B., Anderson C.W.N., Eds.), pp. 39-49, Fertilizer and Lime Research Centre, Massey University, Palmerston North, New Zealand. Occasional Report No. 16.

Roe N.E., Stoffella P.J., Bryan H.H. (1993). Utilization of MSW compost and other organic mulches on commercial vegetable crops. Compost Sci. Utilization 1(3): 73-84.

Ryberg D., Haugen A. (1992). Helsefare ved Saltimpregnering med CCA (kobber, krom, arsen). In: Träskyddsinstitutets Miljöprojekt 1990-1994. Report 170, Swedish Wood Preservation Institute, Stockholm, Sweden, pp. 201-236 (in Norwegian).

Saha K.C. (2003). Review of arsenicosis in West Bengal, India: A clinical perspective. Crit. Rev. Environ. Sci. Technol. 33: 127-163.

Sanders J.G., Windom H.L. (1980). The uptake and reduction of arsenic species by marine algae. Estuar. Coast. Mar. Sci. 10: 555-567.

Sanders J.G. (1983). Role of marine phytoplankton in determining the chemical speciation and biogeochemical cycling of arsenic. Can. J. Fish. Aquat. Sci. 40: 192-196.

Sato T., Wakabayashi T., Shimada M. (1986). Adsorption of various anions by magnesium aluminum oxide ($Mg_{0.7}$ $Al_{0.3}$ $O_{1.15}$). Ind. Eng. Chem. Fund. 25(1): 89-92.

Schat H., Llugany M., Vooijs R., Hartley-Whitaker J., Bleeker P.M. (2002). The role of phytochelatins in constitutive and adaptive heavy metal tolerances in hyperaccumulator and nonhyperaccumulator Metallophytes. Journal of experimental botany 53: 2381-2392.

Schmoger M.E., Oven M., Grill E. (2000). Detoxification of arsenic by phytochelatins in plants. Plant physiology 122: 793-801.

Seidel A., Waypa J.J., Elimelech M. (2001). Role of charge (Donnan) exclusion in removal of arsenic from water by a negatively charged porous nanofiltration membrane. Environ. Eng. Sci. 18: 105-113.

Seyler P., Martin J.M. (1991). Arsenic and selenium in a pristine river-estuarine system: the Krka (Yugoslavia). Mar. Chem. 34: 137-151.

Shannon I.J., Maschmeyer T., Sankar G., Thomas J.M., Oldroyd R.D., Sheehy M., Madill D., Waller A.M., Townsend R.P. (1997). A new cell for the collection of combined EXAFS/XRD data in situ during solid/liquid catalytic reactions. Catal. Lett. 44(1-2): 23-27.

Shen Y.S. (1973). Study of arsenic removal from drinking water. Am. Wat. Works Assoc. J. 65: 543-548.

Sheppard S.C. (1992). Summary of phytotoxic levels of soil arsenic. Wat. Air Soil Pollut. 64: 539-550.

Shi L., Li D.,Wang J., Li S., Evans D.G., Duan X. (2005). Synthesis, flame-retardant and smoke-suppressant properties of a borate-intercalated layered double hydroxide. Clay. Clay Miner. 53(3): 294-300.

Smedley P.L., Kinniburgh D.G. (2002). A review of the sources, behavior and distribution of arsenic in natural waters. Appl. Geochem. 17: 517-568.

Smedley P.L., Nicolli H.B., Macdonald D.M.J., Barros A.J., Tullio J.O. (2002). Hydrogeochemistry of arsenic and other inorganic constituents in groundwaters from La Pampa, Argentina. Appl. Geochem. 17: 259-284.

Smith A.H., Goycolea M., Haque R., Biggs M.L. (1998). Marked increase in bladder and lung cancer mortality in a region of northern Chile due to arsenic in drinking water. Am. J. Epidemiol. 147: 660-669.

Smith A.H., Lingas O.E., Rahman M. (2000). Contamination of drinking water by arsenic in Bangladesh: A public health emergency. Bull. World Health Organ. 78: 1093-1103.

Smith L.A., Means J.L., Chen A., Alleman B., Chapman C.C., Tixier J.S., Brauning S.E., Gavaskar A.R., Royer M.D. (1995). Contaminant fate and migration. In: Remedial Options for Metal Contaminated Sites. Boca Raton, FL: CRC Press, pp. 17-34.

Sparks D.L. (1995). Environmental Soil Chemistry. Academic Press, San Diego, CA.

Sposito G. (1984). The Surface Chemistry of Soils. Oxford University Press, New York.

Sugimoto M. (1999). The past, present, and future of ferrites. J. Am. Ceram. Soc. 82(2): 269-279.

Tamaki S., Frankenberger W.T. Jr. (1992). Environmental biochemistry of arsenic. Rev. Environ. Contam. Toxicol. 124: 79-110.

Taylor G.F. (1996). Exploration, mining and mineral processing. In: Contaminants and the Soil Environment in the Australasia - Pacific Region (Naidu R., Kookana R.S., Oliver D.P., Rogers S., McLaughlin M.J., Eds.), pp. 213-266, Kluwer Academic Publishers, London.

Tezuka S., Chitrakar R., Sakane K., Sonoda A., Ooi K., Tomida T. (2004). The synthesis and phosphate adsorptive properties of Mg(II)-Mn(III) layered double hydroxides and their heat-treated materials. Bull. Chem. Soc. Jpn. 77(11): 2101-2107.

Tu C., Ma L.Q. (2002). Effects of arsenic concentrations and forms on arsenic uptake by the hyperaccumulator ladder brake. J. Environ. Qual. 31: 641-647.

Tu C., Ma L.Q., Bondada B. (2002). Arsenic accumulation in the hyperaccumulator Chinese brake and its utilization potential for phytoremediation. J. Environ. Qual. 31: 1671-1675.

Tuin B.J.W., Tels M. (1991).Continuous treatment of heavy metal contaminated clay soils by extraction in stirred tanks and counter current column. Environ. Technol. 12: 178-190.

Turekian K.K. (1968). Oceans. Englewood Cliffs, NJ: Prentice-Hall. Voldner E., Smith L. Production, usage and atmospheric emissions of 14 priority toxic chemicals. Report of the Joint Water Quality Board/Science Advisory Board/International Air Quality Advisory of the International Joint Commission. Workshop on Great Lakes Atmospheric Deposition.

Tyler G., Olsson T. (2001). Plant uptake of major and minor mineral elements as influenced by soil acidity and liming. Plant Soil 230: 307-321.

Ulibarri M.A., Pavlovic I., Barriga C., Hermosin M.C., Cornejo J. (2001). Adsorption of anionic species on hydrotalcite-like compounds: effect of interlayer anion and cristallinity. Appl. Clay Sci. 18: 17-27.

UN/ECE (1999). Strategies and Policies for Air Pollution Abatement. ECE/EB.AIR/65, pp. 104-105.

U.S. composting council (1997). Compost enhancement guide. Alexandria, VA.

USDHHS, United States Department of Health and Human Services (2000). Toxicological Profile for Arsenic. Agency for Toxic Substances and Disease Registry, Division of Toxicology/Toxicology Information Branch, Atlanta, GA.

USDA, United States Department of Agriculture (2000). Composting. Part 637, National Engineering Handbook, NRCS, Washington, D.C.

USEPA, United States Environmental Protection Agency (1988). Special Report on Ingested Inorganic Arsenic. Skin Cancer; Nutritional Essentiality. EPA/625/3-87/013, Washington, DC.

USEPA, United States Environmental Protection Agency (1993). Integrated Risk Information System on Arsenic. Office Health Environ Assess, Cincinnati, OH.

USEPA, United States Environmental Protection Agency (1994). Review Draft of the Health Effects Notebook for Hazardous Air Pollutants (USEPA Contract # 68-D2-0065). Research Triangle Park, NC: Air Risk Information Support Center.

USEPA, United States Environmental Protection Agency (1997). Recent development for *in situ* treatment of metal contaminated soils. Office of Solid Waste and Emergency Response, EPA-542-R-97-004, p8.

USEPA, United States Environmental Protection Agency (2000). Test methods for evaluating solid waste, physical/chemical methods. USEPA-65 FR 70678. Draft update IVB SW-846, U.S. Governmental Printing Office, Washington, DC.

USEPA, United States Environmental Protection Agency (2006). Drinking Water Standard: Maximum Contaminant Level for Arsenic, January 23, 2006.

Vaccari A. (1998). Preparation and catalytic properties of cationic and anionic clays. Catal. Today 41: 53-71.

Van Der Ven L., Van Gemert M.L.M., Batenburg L.F., Keern J.J., Gielgens L.H., Koster T.P.M., Fischer H.R. (2000). On the action of hydrotalcite-like clay materials as stabilizers in polyvinylchloride. Appl. Clay Sci. 17(1-2): 25-34.

Vangronsveld J., Cunningham S.D. (1998). Introduction to the concepts. In: Vangronsveld J. (ed.), “Metal-contaminated Soils: In-situ Inactivation and Phytorestoration”, pp. 1-15, Springer, Berlin.

Vaughan G.T. (1993). The environmental chemistry and fate of arsenical pesticides in cattle tick dip sites and banana plantations. CSIRO, Division of Coal and Energy Technology Centre for Advanced Chemistry. Investigation Report CET / LHIRI 148, Sydney, Australia.

Vigna-Guidi G., Petruzzelli G., Vallini G., Peru A. (1990). Plant productivity and heavy metal contamination. Biocycle 31(6): 46-48.

Violante A., Huang P.M. (1993). Formation mechanisms of aluminum hydroxide polymorphs. Clays Clay Miner. 41: 590-597.

Violante A., Pigna M. (2002). Competitive sorption of arsenate and phosphate on different clay minerals and soils. Soil Sci. Soc. Am. J. 66: 1788-1796.

Violante A., Del Gaudio S., Pigna M. (2005). Adsorption-desorption processes of arsenate in soil environments. In: Huang P.M., Violante A., Bollag J.M., Vityakon P. (eds.), Soil abiotic and biotic interactions and impact on the ecosystem and human welfare, pp. 269-299, Science Publishers, Enfield, NH, USA.

Violante A., Ricciardella M., Del Gaudio S., Pigna M. (2006). Coprecipitation of arsenate with metal oxides: nature, mineralogy and reactivity of aluminum precipitates. Environ. Sci. Technol. 40: 4961-4967.

Violante A., Pigna M., Del Gaudio S., Ricciardella M., Banerjee D. (2007). Coprecipitation of arsenate within metal oxides: nature, mineralogy and reactivity of iron(III) precipitates. Environ. Sci. Technol. 41: 8275-8280.

Violante A., Krishnamurti G.S.R., Pigna M. (2008). Mobility of trace elements in soil environments. In: Violante A., Huang P.M., Gadd G.M. (eds.), Biophysico-chemical processes of metals and metalloids in soil environments, pp. 169-213, John Wiley & Sons, Hoboken, NJ, USA.

Violante A., Pucci M., Cozzolino V., Zhu J., Pigna M. (2009). Sorption/desorption of arsenate on/from Mg-Al layered double hydroxides: influence of phosphate. J. Colloid Interface Sci. 333: 63-70.

Voldner E., Smith L. (1989). Production, usage and atmospheric emissions of 14 priority toxic chemicals. Report of the Joint Water Quality Board/Science Advisory Board/International Air Quality Advisory of the International Joint Commission. Workshop on Great Lakes Atmospheric Deposition, 29-31 Oct 1986.

Wakao N., Koyatsu H., Komai Y., Shimokawara H., Sakurai Y., Shiota H. (1988). Microbial oxidation of arsenite and occurrence of arsenite-oxidizing bacteria in acid-mine water from a sulfur-pyrite mine. Geomicrobiol. J. 6: 11-24.

Walsh L.M., Keeney D.R. (1975). Behaviour and phytotoxicity of inorganic arseninicals in soils. In: Arsenical Pesticides (Woolson E.A., ed.), Am. Chem. Soc., pp. 35-53, Washington, DC.

Walsh P.R., Duce R.A., Fasching J.L. (1979). Consideration of the enrichment, sources, and flux of arsenic in the troposphere. J. Geophys. Res. 84: 1719-1723.

Wang G. (1984). Arsenic poisoning from drinking water in Xinjiang. Chin. J. Prevent. Med. 18: 105-107.

Wang J.R., Zhao F.J., Meharg A.A., Raab A., Feldmann J., McGrath S.P. (2002). Mechanisms of arsenic hyperaccumulation in *Pteris vittata*: Uptake kinetics, interactions with phosphate, and arsenic speciation. Plant Physiol. 130: 1552-1561.

Wang Y., Morin G., Ona-Nguema G., Juillot F., Guyot F., Calas G., Brown G.E. Jr. (2010). Evidence for different surface speciation of arsenite and arsenate on green rust: an EXAFS and XANES study. Environ. Sci. Technol. 44: 109-115.

Wang Z., Han E., Ke W. (2005). Influence of nano-LDHs on char formation and fire-resistant properties of flame-retardant coating. Prog. Org. Coat. 53(1): 29-37.

Webster J.G., Nordstrom D.K., Smith K.S. (1994). Transport and natural attentuation of Cu, Zn, As and Fe in the acid mine drainage of Leviathan and Bryant Creeks. In: Alpers C.N., Blowes D.W. (eds.), Environmental Geochemistry of Sulfide Oxidation. ACS Symposium Series, vol. 550, pp. 244-260, Washington, DC.

Wells B., Gilmor J. (1997). Sterility in rice cultivars as influenced by MSMA rate and water management. Agron. J. 69: 451-454.

Wenzel W.W., Kirchbaumer N., Prohaska T., Stingeder G., Lombi E., Adriano D.C. (2001). Arsenic fractionation in soils using an improved sequential extraction procedure. Anal. Chim. Acta 436: 309-323.

WHO, World Health Organization (2004). Guidelines for Drinking Water, 3rd edition.

Williams D.E., Vlamis J., Pukite A.H., Corey J.E. (1980). Trace element accumulation, movement, and distribution in the soil profile from massive applications of sewage sludge. Soil Sci. 129(2): 119-132.

Woolson E.A., Axely J.H., Kearney P.C. (1973). The chemistry and phyto-toxicity of arsenic in soil. II. Effect of time and phosphorus. Soil Sci. Soc. Am. Proc. 37: 254-258.

Xu H., Allard B., Grimvall A. (1991). Effects of acidification and natural organic materials on the mobility of arsenic in the environment. Water Air Soil Pollut. 57-58: 269-278.

Yamanaka K., Ohtsubo K., Hasegawa A. (1996). Exposure to dimethylarsenic acid, a main metabolite of inorganic arsenic, strongly promotes tumorigenesis initiated by 4-nitroquinolone 1 oxide in the lungs of mice. Carcinogenesis 17: 767-770.

Yan-Chu H. (1994). Arsenic distribution in soils. In: “Arsenic in the Environment, Part I: Cycling and Characterization” (Nriagu J.O., ed.), pp. 17-49, Wiley, New York.

Yang H.S., Janssen B.H. (1997). Analysis of impact of farming practices on dynamics of soil organic matter in northern China. Eur. J. Agron. 7: 211-219.

Yang L., Shahrivari Z., Liu P.K.T., Sahimi M., Tsotsis T.T. (2005). Removal of trace levels of arsenic and selenium from aqueous solutions by calcined and uncalcined layered double hydroxides (LDH). Ind. Eng. Chem. Res. 44 (17): 6804-6815.

Yang L., Dadwhal M., Shahrivari Z., Ostwal M., Liu P.K.T., Sahimi M., Tsotsis T.T. (2006). Adsorption of arsenic on layered double hydroxides: effect of the particle size. Ind. Eng. Chem. Res. 45(13): 4742-4751.

Yokota H., Tanabe K., Sezaki M., Akiyoshi Y., Miyata T., Kawahara K., Tsushima S., Hironaka H., Takafuji H., Rahman M., Ahmad S.A., Sayed M.H.S.U., Faruquee M.H. (2001). Arsenic contamination of ground and pond water and water purification system using pond water in Bangladesh. Eng. Geology 60: 323-331.

You Y.W., Zhao H.T. Vance G.F. (2001a). Removal of arsenite from aqueous solutions by anionic clays. Environ. Technol. 22(12): 1447-1457.

You Y.W., Vance G.F., Zhao H.T. (2001b). Selenium adsorption on Mg-Al and Zn-Al layered double hydroxides. Appl. Clay Sci. 20(1-2): 13-25.

Yurtsever M., Sengil I.A. (2009). Biosorption of Pb(II) ions by modified quebracho tannin resin. J. Hazard. Mater. 163: 58-64.

Zamborlini M., Facco S., Canepa D., Franzin F. (1989). Metalli pesanti da concimi minerali e compost: assorbimento in alcune specie vegetali. In: Istituto Agrario di San Michele, editor. Compost: Production and Use. Proc. Int. Symp. Compost: Production and Use, pp. 465-470, Istituto Agrario di San Michele, 20-23 June 1989, Trento, Italy.

Zheng B., Yu X., Zhand J., Zhou D. (1996). Environmental geochemistry of coal and endemic arsenism in southwest Guizhou, P.R. China. 30th Int Geol Cong, Abstracts, vol. 3, pp. 410.

Zhu J., Pigna M., Cozzolino V., Caporale A.G., Violante A. (2011). Sorption of arsenite and arsenate on ferrihydrite: Effect of organic and inorganic ligands. J. Hazard. Mater. 189: 564-571.

Zou B.J. (1986). Arsenic in soil. Tarangxue Jin Zhan. 14(2): 8-13.

Zucconi F., De-Bertoldi M. (1982). Utilizzazione in agricoltura dei prodotti di trasformazione dei residui solidi urbani. Ingegneria Ambientale 11(2): 110-114.

ACKNOWLEDGEMENTS

Looking back throughout these years of my Ph.D. course, I am very grateful for all I have received by numerous kind people. Their contribute has certainly shaped me as a better person and has led me where I am now. So, it is my pleasure show them my heartfelt gratitude for their invaluable support, encouragement and friendship.

First of all, I would like to thank my tutor, Dr. Massimo Pigna, for competently guiding me through my Ph.D. course, for his many advises of all kinds and, above all, for his friendly approach he has always had with me. I appreciate so much his great human value, he is surely been the older brother I have never had and he has definitely contributed to my personal and professional growth.

My acknowledgement also goes to my supervisor, Prof. Antonio Violante, for his valuable and professional help during my Ph.D. studies. He gave me a strong scientific support, I am also thankful for the excellent example he has provided as a competent professor with a great passion for the research.

I wish to thank Dr. Enza Cozzolino for allowing me to discovery my interest in research during my Master thesis and for her many friendly chats during free-time.

I also thank Ms. Alessia Sommella for her considerable help in carrying out the experiment on bean plants, presented in this Ph.D. dissertation.

My Ph.D. studies were made enjoyable in large part due to the many colleagues-friends that became a part of my life. I am grateful for time spent with each of them, thank you all for your encouragement, support and most of all your joy and humor. I am so happy to have shared my Ph.D. course with special persons like you guys, I hope that we will be able to stay in touch in future, perhaps remembering these pleasant years together. I would like to express my gratitude to Ms. Susanna Nuzzo, a dear colleague-friend, with

whom I shared pleasantly, most of my free-time, for her sweetness and amazing friendship.

I also acknowledge Dr. Dybiendu Sarkar, who hosted me in his lab, at the Earth and Environmental Studies Department of the Montclair State University (Montclair, NJ, USA) and his group of research.

Last, but by no means least, my special acknowledgement goes to my parents, my sisters and their own family, who have given me their love, encouragement and unequivocal support throughout, as always, for which my mere expression of thanks likewise does not suffice.