ARSENIC BEHAVIOUR IN DIFFERENT TEXTURED SOILS AMENDED WITH PHOSPHATE ROCK AND FARM YARD MANURE

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ABSTRACT

Background Arsenic (As), a contaminant of main concern all over the world, poses severe threat to plant, soil and environment. It must be safely remediate from soil and environment as to lower its potential harmful effects especially to humans and plants. Thus to remediate soils from arsenic contaminants many chemical, physical and biological strategies are available. Among these, phytoextraction is potentially an environment-friendly and cost-effective tool in extracting pollutants by using hyper-accumulator plants. Though, phytoextraction as a successful application to As contaminated soils depends on several factors, amongst bioavailability of As in the soil is the most significant one. For increasing bioavailable fraction of As in contaminated soil, several amendments are used to aid As uptake and accumulation in plants, including application of chelating agents, organic matter and nutrient fertilization especially phosphorus. In this review history, sources, adsorption-desorption reaction in soil, phytoavailability in different textured soils and under different chemical amendments (phosphate rock and organic matter) are presented.

Conclusion The presented data revealed that both organic matter and phosphorus have the potential to remediate arsenic contaminated sites effectively by improving phytoextraction depending upon tested plant and soil environment.

INTRODUCTION

Soils contaminated with arsenic are a major environmental threat due to the toxic and carcinogenic nature of As compounds (Mandal and Suzuki 2002). Both natural and anthropogenic processes result in widespread As contamination of soils and sediments across the globe (Smedley and Kinniburgh 2002). Natural activities such as forest fires, erosion of rocks and volcanic action set up As in the environment (EPA 2001). While, anthropogenic sources include insecticides, herbicides, pesticides, livestock dips and wood preservatives. Arsenic is also added into the environment by blazing of wastes and fuels, mining, production of pulp and paper, glass manufacturing, cement manufacturing, paint industry and detergent production (Kabata-Pendias and Mukherjee 2007).

It is considered as one of the most toxic natural elements (Smith et al. 1998) and currently notified as a Class A carcinogen by the United States (US) EPA. Arsenic impacts on soils may pose an elevated threat to human, animal and plant health. In humans, chronic exposure to As can cause impaired nerve function, skin and organ cancer and damage to liver and kidney (Smith et al. 1998). High As concentrations in soils can induce plant toxicity (phytotoxicity) and in some instances lead to As accumulation in plant biomass in excess of the levels deemed safe for human and animal consumption. An average toxicity threshold of 40 mg kg^{-1} was established for crop plants (Sheppard 1992). More than thirty countries in the world have been found to be affected due to existence of too much As in their environment (Olias et al. 2006). In many countries As contaminant has reached enormous levels including India, Afghanistan, Thailand, Bangladesh, Mongolia, Myanmar, Nepal, Cambodia, China and Vietnam (EIS 2009). It has been estimated that about 200,000 to 270,000 people worldwide have been died

of cancer caused by drinking As-contaminated water (Harvey et al. 2002; Meharg and Rahman 2003).

In the natural environment, As is rarely encountered as a free element. It usually exists as a component of sulfiolic ores as metal arsenide (NAS 1977). Arsenic exists in different oxidation states in the environment i.e., -3, 0, +3 and +5 (Adriano 1986; Welch et al. 1988). Under reduced soil conditions As-III is predominant but in oxic environments As-V is dominant (Ascar et al. 2008). Arsenicals, both trivalent and pentavalent, are soluble over a wide pH range (Bell 1998) and are found routinely in surface as well as ground water (Feng et al. 2001). Arsenic may also exist in organometallic forms such as monomethyl arsenic acid, dimethyl arsenic acid and the more volatile methyl arsines (Jacobs et al. 1970). Arsenic phytotoxicity depends on the form and availability of As in the soil. Organic arsenic compounds are less toxic than inorganic compounds and the toxicity decreases in the following order: arsine > arsenite > arsenate > organic As compounds (Adriano 1986).

The behavior of As in soil is exceptionally complex (McLaren et al. 2006). Arsenic reacts strongly with the solid phase soil constituents via time-dependent retention and release processes and is often considered as being relatively immobile in soil. Arsenic adsorption and desorption processes are in turn directly related to soil physiochemical properties and consequently vary between different soil types. Adriano (2001) reported that the availability of As is greater in sandy than in clay soils. Sheppard (1992) also reported that inorganic As was five times more toxic to plants in sand than in clay soils. Arsenic is generally adsorbed by soil cations such as iron, aluminum and calcium forming insoluble salts. This immobilization occurs more frequently in clay soils or organic soils. In sandy soils, bound As is prone to movement by erosion of soil particles. Sandy soils generally contain low amounts of Fe and Al oxides and clay minerals thus arsenic phytoavailability and toxicity is expected to be greater in sandy soils than other soil types (Peterson et al. 1981).

Various soil amendments have been used to aid or suppress plant uptake and accumulation of As (Zhou and Wong, 2001). Incorporation of carbon-rich composts into soils has been shown to increase As solubility through formation of soluble As–organic complexes (Zhou and Wong 2001). However Gadepalle et al. (2007) reported that soil organic matter effects on As mobility and solubility are inconsistent. Some studies have revealed that the application of organic matter (OM) reduced the As mobility while in others, As is released into soil solution after the application of compost (Mench et

al. 2003; Clemente et al. 2008). Hence, there is a complex correlation between soil As and OM and depends on numerous factors which comprise of insoluble and stable humus percentage, amount of Mn, Fe and Al present in the OM and the soluble organic carbon proportion (Grafe and Sparks 2006).

Plant phosphorus (P) nutrition has been described as one of the main factors affecting the As bioavailability and uptake by plants (Smith et al. 2010). Arsenic is chemically an analogue of P having similar electron configuration, chemical properties, competes for same binding sites in soil (Wauchope 1983) and uptake carriers in root plasma lemma (Meharg and Macnair 1991). Therefore, the phosphate concentration of the soil solution must be considered as a prime factor determining the uptake and accumulation of As in plants. Tu and Ma (2003) also reported that interaction among phosphate and arsenate is important in order to understand their uptake and buildup by plants as their chemical behavior is similar. However, the interaction of As and P in soil and plant uptake is complex and inconsistent depending upon phosphate/arsenate status and growth environment.

The purpose of this review paper hence is to provide a comprehensive and critical review of the existing information on the effects of P and OM on the phytoavailability and uptake of As using hyper-accumulator plants from soils.

ARSENIC HISTORY

The name 'Arsenic' is derived from the Greek word arsenikon meaning potent (Frost 1984). An Arabian alchemist, Geber was discovered As during the eighth century when he heated orpiment (As_2S_3) (Mellor 1954). A famous Swedish chemist, Scheele discovered arsine (AsH_3), however, its deadly nature was not known until the death of a chemistry professor in Munich who inhaled a minor amount of AsH_3 in 1815 (Nriagu 2002). The era from 1850 to 1950 is considered as the century of As contamination. This was the time when human beings were affected by As in medicine, food, air, water and at work and the world production of arsenic trioxide (As_2O_3) increased from 5,000 to 60,000 tons year^{-1} during this period (Nriagu 2002).

Sources of arsenic
The entry of As in the soil is due to both natural and anthropogenic sources and both type of sources are responsible for the distribution of As in the soil environment (Mahimairaja et al. 2005). In soils, the toxic nature of As presents significant environmental hazards to animals, plants and most critically human

beings. Assumed the carcinogenic and toxic nature of As, the United States Environment Protection Agency has enumerated As as the number one toxin among toxicants.

Natural sources

Arsenic minerals are natural sources of As in the environment. Natural activities such as forest fires, volcanic action and erosion of rocks set up As into the environment (EPA 2001). Moreover, weathering of parent material also releases As in to the environment (Smith et al. 1998). Arsenic contamination in Bangladesh and India is severe with several recent reports indicating approximately 6 million people in the 74 As-affected blocks in West Bengal, India were at risk to As exposure and more than 9% of residents suffered from arsenocosis (Mandal and Suzuki 2002).

Anthropogenic sources

Human beings have disturbed nature and exploited natural resources to accomplish their needs. Consequently anthropogenic activities have also contributed to contaminating the soil environments with contaminants especially As. Anthropogenic sources of As include mining and smelting operations, refining of metalliferous ore including by-products such as slag, emissions from industrial manufacturing processes including electroplating, energy and fuel production, copper chromium arsenate (CCA) treatment of wood timber and agricultural inputs such as the application of fertilizers, pesticides, herbicides, fungicides and municipal sludge to land (Smith et al. 1998). Agricultural use of As-based pesticides and herbicides has resulted in the elevated concentrations of As (up to $> 1,000$ mg kg^{-1}) in soils. For example, spraying $PbAsO_4$ on apple orchards has increased the As concentration up to 54.2 mg kg^{-1} in the top-soil (0–15 cm depth) and 20.9 mg kg^{-1} in the subsurface soil depth (15–30 cm) (Smith et al. 2003). Arsenical pesticides such as sodium arsenite were extensively used at cattle dip sites to control cattle ticks in Australia and many other countries of the world including the South Africa, USA and New Zealand. Irrigation with waste effluents is not only the source of As accumulation in soils; in some cases, water itself used for irrigating agricultural crops has led to As deposition in soils (Roberts et al. 2007). The notable example of this occurrence is in Bangladesh where As-contaminated groundwater has resulted in the deposition of As in surface soils with As concentrations in top-soil (0−10 cm) ranging between 11 and 35 mg kg^{-1} (Dittmar et al. 2007). The regular use of As contaminated groundwater for irrigation is resulting in a gradual increase in the concentration of As in soils (Mahimairaja et al. 2005). Arsenic trioxide was the major As compound produced for many industrial uses including ceramic manufacturing, electronics, fireworks preparation, pigments and antifouling agents production, glass manufacturing, cosmetics production, and use in the Cu-based alloys to increase resistance against corrosion.

Arsenic and plants

Arsenic toxicity is a worldwide concern due to enhanced contamination in soil, water and crops especially in South East Asia. Arsenic poses a serious threat of food chain contamination by accumulating in various crops. Roots of plants are capable to take up inorganic as well as organic As [Monomethyl As (MMA) and dimethyl As (DMA)] but the rates of uptake reduce with rising methyl group number. On contrary to uptake efficiency, the translocation from roots to shoots of the As compounds usually increases with the rising methyl group number (Abedin et al. 2002; Li et al. 2009; Carey et al. 2010; Ye et al. 2010). Arsenate enters the plants using phosphate transporters as a phosphate analogue, while undissociated methylated species of As and arsenite enter through nodulin 26-like intrinsic (NIP) aqaporin channels (Zhao et al. 2010). While, Ma et al. (2008) reported that the efflux of both silicon and As (III) mediated by Lsi_2, a silicon transporter from endodermal and exodermal cells toward the stele for xylem loading; Lsi_2 plays a key role in accumulation of As in shoots of rice plant. The movement of As within plants is restricted and the relative order of As concentrations is usually roots > vegetative tissue > seeds and fruit with old likely to contain more As than young ones (Fergusson 1990; Smith et al. 1998). Accumulated As in tissues of plants causes numerous physiological and metabolic disorders (Wells and Gilmor 1997) thus negatively affect growth performance which eventually leads to decline in productivity of plants (Stepanok 1998). From ATP, As displace phosphate to form unstable ADP-Arsenic and as a result disrupt plant cell energy metabolism (Meharg 1994). Biosynthesis of photosynthetic pigments is a basic metabolic process of plant system affected by arsenic. Uptake of As in excessive amount also disrupt enzyme function and reduce flow of phosphate in the plant system with the general tolerance level considered to be around 2 mg kg^{-1} DW plant tissue (Kabata-Pendias and Mukherjee 2007).

Arsenic and soil environment

Arsenic is present in water, soil, air and food (Mandal and Suzuki 2002). On an average, As is present in soils from 0.2 to 40 mg kg^{-1}. Some researchers also

think that 10–40 mg kg^{-1} base concentrations of As present in areas where the Lithology has no known unnatural sources of contamination (Fitz and Wenzel 2002). On the other hand it is estimated that on an average only 5-8 mg kg^{-1} As level exists in the pedosphere (Matschullat 2000). In rare cases either due to natural or anthropogenic sources a few soils are identified to hold extremely high concentration of As i.e. 0.1 and 2% (Chang et al. 2005; Ongley et al. 2007; King et al. 2008). Such soils create a hazard to ecosystem quality in addition to health of humans and if deemed compulsory, these areas must be reclaimed to diminish possible exposure risks. The variation in background soil As levels is mainly related to differences in parent material and soil development; however soil concentrations can also be naturally influenced through atmospheric fluxes (McLaren et al. 2006). The biogeochemical dynamics of As are complex, involving both abiotic, biotic reduction-oxidation reactions and methylation-demethylation reactions.

Speciation of arsenic

The term speciation is defined as the oxidation states; chemical speciation which deals with determining redox form of an individual element in a system (Akter and Naidu 2006). A variety of inorganic and organic compounds of As formed in soils (Vaughan, 1993) and is exist mainly as inorganic species, either arsenite (As-III) or arsenate (As-V) (Masscheleyn et al. 1991). Among the As species found in the soil environment, compounds of As-III and As-V are the most important inorganic As species in the soil because their compounds are highly soluble in water (Vaughan 1993).These are the most stable form of As in soil having oxidation states of +3 and +5, bonding strongly to either three or four oxygen atoms to form arsenite (AsO_3^{-3}) or arsenate (AsO_4^-), respectively depending on the redox and pH conditions. Oxygen ligands can be replaced by methyl groups to form a variety of organic As forms. Prevalent organic As forms are mono-methylarsonic acid (MMAA) and dimethylarsenic acid (DMAA). In general organic arsenicals account for a minor fraction of total soil soluble As (Miao and Naidu 2006).

Arsenate is the thermodynamically stable form under oxygen rich conditions and represents the dominant form of As in aerobic soils (Masscheleyn et al. 1991). Arsenate is present as $H_2AsO_4^-$ and $HAsO_4^{2-}$ in the soil. In contrast, under moderately reduced and anoxic conditions in the soil in which the pH is less than 6 (Sadiq 1997), As-III increases in prevalence (Masscheleyn et al. 1991). Arsenite exists in a neutral state (H_3AsO_3) and it is considered more soluble and mobile than arsenate due to its typically uncharged nature at normal soil pH values and lower

affinity for Al oxides and phyllosilicate clays (Raab et al. 2007).

Adsorption

The capacity of soil to adsorb As and the kinetics of adsorption-desorption reactions determine its mobility in soil and consequently its phytoavailability and bio-accessibility. Arsenic exhibits a high sorption affinity for soil's solid phase constituents (Szakova et al. 2005). Soil solid constituents proved as capable of adsorbing As include clay minerals, Fe oxides and hydroxides, Mn oxides, Al oxides and calcium carbonate (McLaren et al. 2006). In soils, the distribution of these solids affected by both pH and Eh. Arsenic adsorption studies on pure minerals have shown that Fe and Al oxides and hydroxides exhibit the greatest affinity for As (Dixit and Hering 2003). Retention of As species by aluminosilicate minerals is substantially lower, due to their permanent negative charge and restriction of pH dependent hydroxyl groups to edge surfaces (Goldberg 2002; Lin and Puls 2000). Arsenic adsorption onto oxides depends on the extent of the interface between them and the discharge of As being further difficult as the time of interaction increases (Grafe and Sparks 2006). The rate and magnitude of As adsorption varies between soils and it has been shown that adsorption behavior is influenced by soil constituents, soil pH, redox conditions and soil solution composition. Generally As-V is adsorbed to a greater magnitude than As-III, but the relative affinity is influenced by soil pH, mineral constituents and competing ionic species (Dixit and Hering 2003). Arsenite adsorbs to clay minerals less intensely than does As-V. Soil pH exerts a considerable influence on As sorption largely a reflection of its preferential adsorption by minerals with a pH dependent charge (McLaren et al. 2006). Soil pH directly controls As-V and As-III equilibria as well as modifying the surface charge properties of variable charge constituents with oxides and hydroxides becoming more negatively charged as pH increases. In general sorption of As-V decreases with increasing pH, while adsorption of As-III generally increases with increasing pH (Goldberg 2002).

Desorption

Arsenic release has not been studied as extensively as sorption. Desorption of As from pure mineral systems and soils is highly hysteretic, rates of desorption being substantially lower than those of adsorption with significant proportions of As appearing as irreversibly bound (Zhang and Selim 2005). Furthermore, the rate of release decreases with increasing residence time (O'Reilly et al. 2001). This phenomenon is commonly ascribed to continued slow

diffusion of As into the soil matrix and sorption to less kinetically favorable sites (Zhang and Selim 2005). In addition it has been suggested that the solid-phase precipitation and complexation reactions are time dependent such as rearrangement of bonding mechanisms to higher binding strengths or growth of three-dimensional As solid phase minerals (Arai and Sparks 2002). While desorption of Asarsenic is commonly limited, considerable proportions of initially adsorbed As have been desorbed from soils with low affinity for As or following leaching with P solutions (Carbonell-Barrachina et al. 1996). For instance, As-III initially adsorbed by three soils with low sorption capacities was fully released after 36 hours (Carbonell-Barrachina et al. 1996). Significant rates of As desorption have also been achieved using P displacement and anion exchange resins suggesting that As can under certain conditions become labile (McLaren et al. 2006).

Phytoavailability of arsenic

Phytoavailable form is that fraction of As in soil which is available for the uptake of plants. Determination of availability and solubility of As in soil is vital which is thought to be related to different pools in the soil system. Wenzel et al. (2001) showed that the concentration of As in the soil is the sum of the As fractions within the following five pools:

- Weakly adsorbed or exchangeable–As present as free ions or in soluble form (outer-sphere complexed)

- Arsenic specifically sorbed to the mineral surfaces, such as Al/Fe (oxy) hydroxides. This phase is also termed as the phosphate extractable As, as As is desorbed due to phosphate ions (inner-sphere complexed)

- Arsenic bound to hydrous oxides of Fe and Al (inner-sphere complexed)

- Arsenic associated with crystalline Fe/Al oxides

- Residual As

Availability of As is chiefly determined by the equilibrium between As in soil solution and the solid phase. Generally, the equilibrium is affected by a variety of reactions consisting of adsorption, complexation and ion-exchange with inorganic and organic ligands, redox reactions and precipitation dissolution (Morel 1997). These reactions can potentially affect the free ion concentration of As at the soil-water interface thereby affecting the solubility of As. The fraction of As available to plants is not alike as the entire concentration in the soil; As is mainly bound to the solid phase. The phytoavailable form of As is either in soil solution (weakly association with solid phase) or specifically

sorbed to the solid phase but during plant growth capable of transferring it to soil solution. Therefore, of these five pools, the first three are considered bioavailable in terms of As availability for plant uptake. The unavailable or the least available fractions (those rendered immobile or least mobile) are strongly bound within the mineral matrix (McLaren et al. 1998; Wenzel et al. 2001). It is essential to recognize that high concentrations of As may not necessarily indicate its release in soil and/or availability for plant uptake (Devesa-Rey et al. 2008; Ko et al. 2008).

Arsenic toxicity

The element As is an environmental toxin that is exit naturally in all soils (Cullen and Reimer 1989; Smedley and Kinniburgh 2002). It is one of the most harmful and a notorious poisonous metalloids found in nature (Adriano 2001). The distribution of As in soils may vary with soil type depending on the nature of the parent material. Background concentrations do not generally exceed 15 mg As kg^{-1} (NRCC 1978), although concentrations ranging from 0.2 to 40 mg As kg^{-1} soil have been reported (Walsh et al. 1977). The speciation of As in the soil environment is of critical value as toxicity of inorganic and organic compounds vary largely (Leonard 1991). The toxicity of As is also affected by the rate at which it is metabolized within the plant body and the extent to which it accumulates by tissues (Jiang and Singh 1994). In general, organic arsenicals are less toxic than inorganic arsenicals and the pentavalent oxidation state is less toxic than the trivalent oxidation state due to its greater cellular uptake (NRCC 1978). Arsenic is abundant trace element with 5 mg kg^{-1} mean lithosphere concentration. Usually 1-20 mg kg^{-1} As concentration present in uncontaminated agricultural soils (Wauchope 1983) while in industrial or mining areas where contaminated soils may contain As concentration as high as 45-2600 mg kg^{-1} (Brandsetter et al. 2002). However, for crop plants toxicity threshold of 40 mg kg^{-1} on an average was established (Sheppard 1992). Humans might be exposed to As from a diverse environmental sources but food constitutes the largest source of As intake, with minor contributions from drinking water and air (Chen and Lin 1994).

Arsenic phytoavailability and phosphorus interaction

Phosphorus has both synergistic and antagonistic effects on As uptake by plants depending upon soil and plant characteristics (Otte et al. 1990). Clarkson and Lutteg (1991) found that the effect of P on As uptake appears to depend on the P demand of the plant and the sensitivity of plant species for As which

Table 1 Effect of phosphorus (P) on arsenic availability and uptake by plants

Crop	Treatment	Growth medium	P effects on As availability and uptake	Mechanism	References
Wheat (*Triticum aestivum* L.)	As @ 0, 5, 25, 125 and 625 mg L^{-1} (Na_3AsO_4. $12H_2O$) and P @ 0 and 5.6 mM pot^{-1} as K_2HPO_4	Soil spiked with As (total 5.53 mg As kg^{-1})	P significantly decreased As concentration in all plants parts @ 5 and 25 mg As L^{-1}. Non-significant differences were found at 125 and 625 mg As L^{-1}.	Restricting translocation of As from roots to shoots.	Karimi et al. (2014)
Keshkeni Luvelou (*Ocimum basilicum* L.)	P @ 50, 150, and 250 mg Kg^{-1} and As @ 15 mg kg^{-1} (Arsenic sulphate)	Sandy loam soil spiked with As	P @ 250 mg kg^{-1} reduces the level of As uptake by plants.	Antagonistic effect of P with As.	Rahimi et al. (2013)
Barley (*Hordeum vulgare* L.)	As @ 0 and 10 μM as $NaAsO_2$ and P as ammonium phosphate @ 0, 50, 250 and 500 μM.	Hydroponic experiment	With the increase in P concentration, As uptake reduced by plant.	Preferential uptake of P over As.	Shaibur et al. (2013)
Chinese brake fern (*Pteris vittata* L.)	Oxalic acid, citric acid, EDTA, SPA, PR, SSP, and compost were applied @ 0.54, 1.15, 1.75, 2, 5 and 10 g kg^{-1}, respectively.	Arsenic contaminated soil (144 mg As kg^{-1})	PR and SPA significantly increased As accumulation by the fern by 25% and 31%, respectively.	Competitive anion exchange mechanism.	Yan et al. (2012)
Silverback fern (*Pityrogramma calomelanos* L.)	0 and 100 mg kg^{-1} P in soil as KH_2PO_4.	Total As 270 μg g^{-1} soil. Green house and field experiment	P increased uptake of As in fronds > 59% in field experiment; no significant effect of P in green house.	P displaced As from soil adsorption sites into soil solution.	Jankong et al. (2007)
Chinese brake fern (*Pteris vittata* L.)	0 and 50 ppm P in the form of PR (14.7% P) and As (Sodium arsenate), Cd, Pb and Zn @ 0 and 50 ppm.	As-contaminated Sandy soil with green house conditions.	PR increased As up take in fronds from 608 to 1530 mg kg^{-1} in a multi-metals condition.	Competitive anion exchange mechanism.	Fayiga and Ma (2006)
Chinese brake fern (*Pteris vittata* L.)	As @ 670, 2670, or 5340 μmol kg^{-1} and P @ 800, 1600, or 3200 μmol kg^{-1}	Sandy soil (9.2 μmol total As kg^{-1}) with green house conditions.	WS-As was slightly increased only by 3200 μmol kg^{-1} P levels. Arsenic @ 5340 μmol kg^{-1} and P @ 1600 μmol kg^{-1} decreased As concentrations by 23–25% in the roots and fronds.	Ion exchange mechanism or dilution effects from larger biomass production.	Tu and Ma (2003b)
Chinese brake fern (*Pteris vittata* L.)	Phosphate rock at the rate of 15 g kg^{-1} soil. MSW and BS @ 50 g kg^{-1}.	CCA (135 mg As kg^{-1}) and ASC-soils (125 mg As kg^{-1}).	P increased WE-As > 23% from the CCA soil and > 12% from the ASC soil.	P displaced soil As into the soil solution.	Cao et al. (2003)
Chinese brake fern (*Pteris vittata* L.)	P @ 20, 100, and 500 μM ($NH_4H_2PO_4$), As @ 0, 83, 416, and 2080 μM (Na_2HAsO_4)	Hydroponic experiment.	Increasing level of P from 20 to 100 μM decreased root and shoot As levels by 73% and 41% at 416 μM As level and 76% and 46% at 83 μM As, respectively.	Arsenate has a lesser affinity to the uptake system in the roots than phosphate.	Wang et al. (2002)

CCA: Chromated-Copper arsenate, ASC: Arsenic spiked contaminated, PR: Phosphate rock, SPA: Sodium polyacrylate, WS-As: Water soluble Arsenic, MSW: Municipal solid wastes, BS: Biosolids

are both plant specific (Table 1). Fitz and Wenzel (2002) reported that the effects of P on the uptake and toxicity of As in plants is unpredictable because it depends on plant species, chemical speciation of As, growth medium and experimental conditions. According to Woolson (1973) the application of P fertilizer in soils contaminated by As, mobilized up to 77% of total As found in the soil and increased the As availability to plants. Phosphorus fertilization may also enhance As accumulation of plants by alleviating oxidative stress and stimulating the phosphate uptake mechanisms which cannot discriminate well between phosphate and arsenate. Basically, the uptake of arsenate and phosphate has been reported to be competitive (Tu and Ma 2003b) due to chemical similarity and sorption of phosphate and arsenate occurs by the same mechanisms, but arsenate is generally sorbed less strongly than phosphate. On the other hand, Creger and Peryea (1994) demonstrated that in soil system, phosphate may reduce As concentration in plant through competition for uptake sites in plant roots and/or enhanced plant growth by alleviating As phytotoxicity depending on relative phosphate/arsenate levels and/or soil conditions.

Soil arsenic availability and organic matter interaction

Soil organic residues originating from different sources may influence the mobility and phytoavailability of As. Organic residues can form complexes with Fe or Al, thus releasing As into the soil solution. . They might boost As accessibility by blocking As adsorption sites on soil particles or forming complexes on soil mineral surfaces with cations (Table 2). The presence of organic matter in soil has been reported to compete with As for adsorption sites on hematite, ferrihydrite and gibbsite and nano-sized zero valent iron thus inhibiting As adsorption in soil. Organic matter has two major portions: fulvic acid (FA) and humic acid (HA) which affect the adsorption of As in soil and water systems (Smith et al. 1998; Grafe et al. 2001; Grafe et al. 2002). These HA and FA may compete strongly with As (V) and As (III) for active adsorption sites on surfaces of mineral thus effecting the As mobility. The competition among organic acids and As species for active binding sites on mineral surfaces might result in decreasing the extent of As retention particularly under acidic environment (Wang and Mulligan 2006). The presence of FA showed a great influence on the adsorption of As-V on alumina between pH 3 and 7.5. Fulvic acid may be adsorbed on alumina by columbic interaction or directly forms complexes with As (Smith et al. 1998) which decrease the adsorption of As. Several studies have revealed that HA and FA compete with As on oxides

and mineral surfaces and enhance its mobility and availability in soil solution (Gustafsson 2006; Wang and Mulligan 2006; Sisr et al. 2007; Gadepalle et al. 2008; Lin et al. 2008). These studies have suggested that organic matter addition in soil may enhance As mobility and availability either by reducing As adsorption and/or increasing As desorption from soil (McLaren et al. 2006). Organic matter may also alter speciation of As by reducing As (V) to the more mobile and toxic As (III) form and thus increases threat to environment and human (Balasoiu et al. 2001). The effect of organic matter on As phytoavailability may vary with the qualitative composition of the organic matter. A large molecular weight fraction of organic matter may more efficiently retain trace elements including As, while a lighter and more soluble fraction tends to dissolve elements either by displacing (anions) or chelating (metals) them.

CONCLUSION

Background acquaintance of the sources, chemistry and possible risks of noxious heavy metals in polluted soils is essential for the selection of appropriate remediation option. Remediation of soil polluted by heavy metals is indispensable to decrease the related risks and make the soil reserve accessible for production of agricultural crops, boost food security and trim land tenure problems. Phytoremediation, particularly phytoextraction is potentially a lucrative and environment-friendly tool in extracting pollutants by using hyper accumulator plants in order to clean up contaminated soils. However, for As-contaminated soils, successful application of phytoextraction affected by various factors and among these As bioavailability in soil is the most important one. In order to increase bio-available fraction of As in soil, a variety of soil amendments including organic amendment, chelating agents and nutrient fertilization particularly of P are important. For decontamination of sites polluted with As, phosphate rock is most effective one as firstly improved growth of plant and secondly, from soil it mobilized exchangeable As consequently enhanced uptake of total As by hyper accumulators and thus help to extract more As from soil. Furthermore, application of organic amendments boost up the solubility of As by forming complexes with Fe and Al, and by adsorbing on the exchange sites and thus releasing As in to soil solution.

REFERENCES

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Table 2 Effect of organic matter (OM) on arsenic availability and uptake by plants

Crop	Treatments	Growth medium	Effect of OM on As availability and uptake	Mechanisms	References
Cress plant	As @ 0, 20 and 40 mg kg^{-1} and OM (rotten and powdered sheep manure) @ 0 and 10 ton/ha	Soil (Clay loam) Spiked with As (Na$_2$HAsO$_4$. 7H$_2$O)	Organic matter @ 10 tons ha^{-1} with As @ 40 mg kg^{-1} increased As uptake by > 40%.	WS–As and the conversion of arsenate (V) to arsenite (III).	Gholami et al. (2012)
Chinese brake fern (*Pteris vittata* L.)	Oxalic acid, citric acid, EDTA, SPA, PR, SSP, and compost were applied @ 0.54, 1.15, 1.75, 2, 5 and 10 g kg^{-1}, respectively.	Arsenic contaminated soil (144 mg As kg^{-1})	Enhanced L-As and Al–As by 150% and 12%, and reduced Fe–As by 26%.	Complexation of Fe or Al, thus releasing As into the soil solution	Yan et al. (2012)
Giant reed (*Arundo donax* L.)	AA, CA and EDTA @ 0, 1.25, 2.5 and 5.0 mmol kg^{-1} soils. Sepiolite and phosphogypsum @ 0, 4.0, 20 and 40 g kg^{-1} soil and 0, 2, 4 and 8 g kg soil, respectively.	As, Cd and Pb contaminated soil (13.7 mg As kg^{-1}, 1.07 mg Cd kg^{-1} and 52.4 mg Pb kg^{-1})	Acetic acid increased 4.68 times As in plant compared with control. Increasing level of CA reduced As level in plant. Saprolite @ 4 g kg^{-1} increased As concentration by 2.18 times.	Increase As availability by blocking As adsorption sites on soil particles or forming complexes with cations on soil mineral surfaces.	Miao et al. (2012)
Maize (*Zea mays* L.)	Poultry manure, cow dung and natural rubber processing sludge @ 0, 2, 5, 10 and 20 % w/w	CCA contaminated soil (39.55± 0.21 mg As kg^{-1})	Effectiveness of immobilization varied in the order of poultry manure > rubber processing sludge > cow dung.	Immobilization of As in the soil due to CEC, P content and organic matter of amendments	Okieimen et al. (2011)
Cuscus Grass (*Vetiveria Zizanioides* L.)	As @ 500, 1000 and 1500 mg kg^{-1} and organic amendment @ 50 tons/ha	Soil spiked with As (Na$_2$HAs$_2$O$_4$)	Organic amendment at 500 mg As kg^{-1} increased As uptake > 60%	Complexation of Fe or Al, thus releasing As into soil solution.	Singh et al. (2007)
Carrot (*Daucus carota* L.) and Lettuce (*Lactuca sativa* L.)	Bio-solid @ 10% (w/w)	Two As contaminated soils with total As content of 26.0 and 43 mg kg^{-1}	Bio-solid lowered WS, exchangeable, and Ca bounded As in soil by 45% over untreated control.	As adsorbed by bio-solid and reduced WS As.	Cao and Ma et al. (2004)
Chinese brake fern (*Pteris vittata* L.)	Municipal solid wastes (MSW) and Bio-solids (BS) @ of 50 g kg^{-1} soil.	Soil spiked with Na$_2$HAsO$_4$ @ 125 mg As kg^{-1} dry soil.	Plants with compost amendments removed < 8% As from ASC soil.	Enhanced As uptake is related to WS–As increases and transformation of As (V) to As (III).	Cao et al. (2003)

ASC: Arsenic spiked contaminated, WS–As: Water soluble arsenic, AA: Acetic acid, CA: Citric acid, L-As: Labile arsenate, Al–As: Aluminum bound arsenic, Fe–As, Iron-bound arsenic

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