

Chapter 25

Remediation of arsenical pesticide applied soils using water treatment residuals: Preliminary greenhouse results

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Abstract

Long-term application of arsenical pesticides in agricultural fields has resulted in increased background concentration of this toxic metalloid in soils. In addition, leaching of arsenic (As) from chromated copper arsenate (CCA)-treated wood found in decks, docks, playground equipment, and garden construction has contributed further to soil As contamination. Arsenic contamination is particularly severe in cattle dipping vat sites, where soil As concentrations range between 700 and 2000 mg kg⁻¹. Plants growing in As-contaminated soils could pose a potential health hazard on human and livestock populations. Several studies have successfully used water treatment residuals (WTRs) to bind phosphorus (P) in soils, resulting in reduced P in runoff from fields, which would otherwise cause P-enrichment, and eutrophication of water bodies. Since P and As exhibit very similar chemical properties, it is logical to assume that As, like P, will be similarly and significantly retained by WTRs. The main objective of this study was to evaluate the use of various WTRs as low-cost chemical amendments to bind As in pesticide-applied soils, reducing As availability to plants. Rice was used as the test crop. Soils contaminated with arsenical pesticides and amended with two types of WTRs (Al and Fe) were used for a greenhouse column study. Rice was grown in the columns for a period of six months. The results obtained in this study show that both Al- and Fe-WTRs are very effective in reducing phytoavailable As in the soils. Addition of WTRs resulted in considerable improvement in the growth of rice plants in comparison to control plants with no WTR added, in which growth of rice was severely impaired. While Al-WTR was more effective in reducing As

concentration in rice plants, Fe-WTR was more effective in improving the growth of rice in As-contaminated soils.

25.1. Introduction

Arsenic is an element of great concern in terrestrial as well as aquatic environments because of the high toxicity and carcinogenicity of some As species. Arsenic has been classified as a Group A human carcinogen (Southworth, 1995). Organic forms of As are considered non-carcinogenic; however, transformation of As from organic to inorganic forms is possible in soil environments (Rodriguez, 1998). USEPA adopted a new drinking water standard in 2001, lowering the maximum contaminant level (MCL) of As from 50 to 10 ppb (USEPA, 2001). Arsenic contamination of the environment can occur from natural as well as anthropogenic sources. The primary natural sources of arsenic include hot springs, igneous rock, sedimentary rock, metamorphic rock, seawater, mineral deposits, and volcanoclastic materials (Bowen, 1979; Cai and Ma, 2003). Anthropogenic sources include indiscriminate disposal of wastes from mining, milling, and smelting of ores (Lindau, 1977), raw and spent oil shale (Shendrikar and Faudel, 1978) and coal fly ash amendments (Hansen et al., 1984). Long-term application of arsenical pesticides in agricultural lands has also resulted in high levels of As residues in certain soils (Murphy and Aucott, 1998). The soil As problem is particularly critical in cattle dipping vat sites, which are almost ubiquitously present in ranches or former ranching areas in various parts of the country, particularly in the southern United States. Ng (1997) assessed soil As to range between 700–2000 mg kg⁻¹ in cattle dip sites. Although the use of arsenical pesticides as dipping solutions has long been banned, there exists a large number of abandoned vat sites in the southern United States that are seriously contaminated by As.

Plants (either wild or cultivated) growing in As-contaminated soils or water could pose a potential health hazard on human and livestock populations. Arsenic is translocated to most plant organs, although highest concentrations are often found in roots and older leaves (Tamaki and Frankenberger, 1992). Pickering et al. (2000) reported that most of As was locked up in plant roots while relatively small quantities translocated into the aboveground tissues. In rice plants, As concentration was reported to be 4–8-fold higher in root tissue when compared to the shoot (Liu et al., 2004). In addition to the As species, toxicity of As to the plants is affected by several biogeochemical factors such as soil texture, organic matter, nature and constituents of minerals, pH, redox potential, and competing ions (Adriano, 2001). Our knowledge on As metabolism in plants is

limited. There are reports of As metabolism in mammals and bacteria involving methylation and biotransformation to As-lipid compounds, but there are no reports of these processes playing a role in As detoxification in higher plants (Nissen and Benson, 1982). While arsenate is a chemical analogue of phosphate and may interfere with oxidative phosphorylation (Terwelle and Slater, 1967), arsenite is a neutral species at natural pH values and inhibits the activity of enzymes by binding to thiol groups. Methylarsonic acid (MMA) and dimethylarsenic acid (DMA) also form anions in soils but are much less toxic than inorganic species (Sohrin et al., 1997) and may block protein synthesis (Sckerl and Frans, 1969).

Water treatment residuals (WTRs) are a by-product of drinking water treatment plants. Metal salts, such as ferric chloride and aluminum sulfate (alum), are commonly used in the municipal water treatment processes to destabilize colloids for subsequent flocculation and water clarification (Butkus et al., 1998; Ippolito et al., 1999). WTRs are generally composed of Fe/Al-oxides, activated C, and high molecular weight, long-chain, water-soluble polymers (Elliott and Dempsey, 1991). Land-filling is a common practice for the disposal of this material; however, recent studies have shown that benefits associated with the reuse of WTR as a soil amendment include improved soil structure (El-Swaify and Emerson, 1975), increased moisture-holding capacity (Bugbee and Frink, 1985), and increased availability of nutrients for various plants (Heil and Barbarick, 1989).

A significant amount of research work has been performed to investigate the advantages of applying WTR to reduce P in surface runoff for P-enriched soils, which could otherwise end up causing eutrophication of surface water bodies. Moore and Miller (1994) used alum sludge (Al-WTR) to reduce P concentration in runoff from land to which poultry litter was applied. Maurice et al. (1998) reported that partially dried alum sludge used as a component of poultry litter also reduced movement of P. Gallimore et al. (1999) attributed the ability of Al-WTR to reduce P in runoff from poultry litter-amended fields to the P-fixation potential of amorphous Al-oxides in the WTR. Adding WTR at higher ratios, on the other hand, could immobilize bioavailable P and induce P deficiency in crops (Ippolito et al., 1999). However, Jacobs and Teppen (2000) found no yield reductions in corn or decreases in extractable P levels even when Al-WTR was applied at rates as high 135Mg ha^{-1} to soils highly enriched in P from repeated fertilizer and manure applications. Butkus et al. (1998) used Fe-WTR as a soil amendment and showed that the reduction in available P is due to binding of P to both amorphous ferric hydroxide and the cationic polyelectrolyte, a quarternary polyamine.

Since P and As exhibit very similar chemical properties, it is logical to assume that As, like P, will be similarly and significantly retained by WTR

components, such as amorphous Fe/Al-oxides and cationic polymers. Both phosphates and arsenates undergo similar types of retention in soil minerals via primarily inner-sphere surface complexation. Thus, P has demonstrated a strong ability to compete with As for sorption sites in environmentally important pH ranges (Matera and Le Hecho, 2001). The retention of P by WTR is strongly hysteretic (Butkus et al., 1998; Ippolito et al., 1999). Apparently, if Al-WTR and/or Fe-WTR are capable of retaining As in a similar irreversible fashion as P, it may be possible to use WTR as an in-situ amendment in As-contaminated environmental systems. However, there are very few published studies on As retention by WTR.

The objective of this study was to evaluate the use of various WTRs as low-cost chemical amendments in As-contaminated soils. Immokalee series soil from Florida, with minimal As retention capacity was used for the study. The soil was spiked with either sodium arsenate or DMA. Al- and Fe-WTRs were used as amendments to bind As in the soils. Rice (*Oryza sativa* L) plants were used as a test crop to determine the efficacy of WTRs in reducing phytoavailable As in the contaminated soils.

25.2. Materials and methods

To evaluate the role of WTRs in As-phytoavailability, it is important to use a soil that has minimal As retention capacity. Immokalee series soil from Florida was selected to conduct the greenhouse study. Immokalee series soil is sandy with low pH, low extractable Fe/Al, Ca/Mg, and low organic matter content. Being sandy, acidic and lacking positively charged adsorptive surfaces (e.g. amorphous Fe + Al oxides), it is likely to have minimal As retention capacity (Pierce and Moore, 1980; Oscarson et al., 1981), thereby increasing potentially phytoavailability of As. Immokalee series soil was collected from Southwest Florida Research and Education Center, Immokalee, Florida.

The soil was characterized for its texture, pH, EC, cation exchange capacity (CEC), total Fe and Al, oxalate-extractable Fe and Al, total and extractable Ca and Mg, total and extractable P, soil organic matter, and total As (Table 25.1). Standard protocols outlined in the Soil Science Society of America Handbooks for Chemical and Mineralogical Analysis (Klute, 1996; Sparks, 1996) were followed for soil characterization.

The soil was spiked with two As compounds, sodium arsenate and DMA at two rates, 675 and 1500 mg kg⁻¹. This high-soil As concentrations were chosen following the assessment of Ng (1997) who estimated soil As concentrations in cattle dip sites to range between 700 and 2000 mg As per kg. Contaminated soils as well as control samples (soil

Table 25.1. General chemical properties of Immokalee soil

pH		6.0
EC ($\mu\text{S cm}^{-1}$)		59
CEC (cmol kg^{-1})		777
Soil organic matter (g kg^{-1})		8.4
Total-recoverable As (mg kg^{-1})		0.8
P (mg kg^{-1})	Mehlich 3	4.0
	Total	210
Ca + Mg (mg kg^{-1})	Mehlich 3	270
	Total	1200
Fe + Al (mg kg^{-1})	Oxalate	66
	Total	212

EC, electrical conductivity; CEC, cation exchange capacity.

with no pesticide application) were loaded in polyvinyl chloride (PVC) columns 15" high \times 6" diameters in three replicates.

Rice, a fast growing, high-biomass plant was used as the test crop. Rice seeds (thirty seeds per column) were sown into the columns and allowed to grow for a period of six months. The columns were arranged in a randomized block design and rotated periodically to account for variances in temperature and sunlight within the greenhouse and maintained at 80% pot holding capacity. Once every month, the pots were over-watered in order to induce leaching.

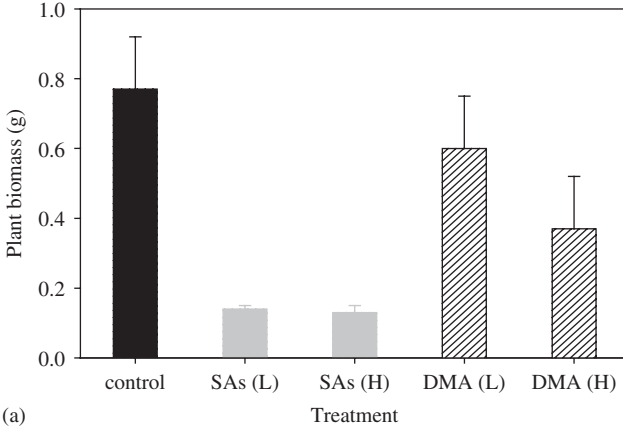
To evaluate the role of WTR-amendment in reducing As phytoavailability in contaminated soils, two types of WTRs were used. Al-WTR was obtained from the Manatee County Water Treatment Plant in Bradenton, FL. Fe-WTR obtained from the Hillsboro River Water Treatment Plant in Tampa, FL. The soils, wetted to 80% of their water holding capacity, were mixed with 1500 mg kg^{-1} of Sodium arsenate and DMA separately. The WTRs were applied at 2 rates of 5% and 10% following the field study of Gallimore et al. (1999). Soils were loaded in PVC columns and rice was grown as described above. All the above treatments were done in triplicates.

Plant samples were digested using $\text{HNO}_3/\text{H}_2\text{O}_2$ digestion procedures (Carbonell et al., 1998). The acid digests were analyzed for total As using a graphite furnace atomic absorption spectrophotometer (GFAAS).

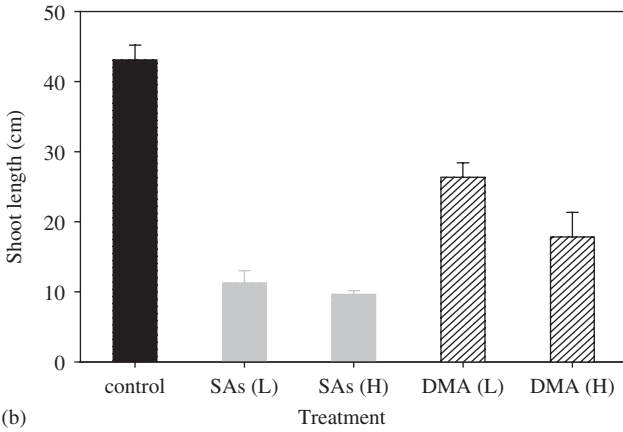
25.3. Results and discussion

25.3.1. Effect of arsenical pesticides on plant growth

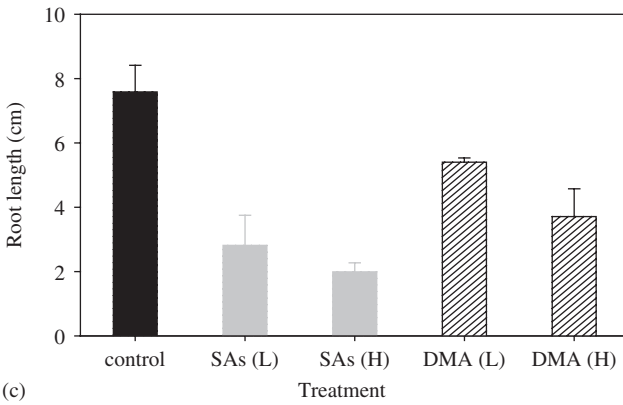
The quantitative effect of organic and inorganic arsenical pesticides on plant growth is shown in Fig. 25.1. The results showed that the growth of rice was more severely impaired by the addition of sodium arsenate



(a)



(b)



(c)

compared to DMA. The average total biomass of the plants grown in either 675 or 1500 mg kg⁻¹ sodium arsenate was 0.13 g in dry weight (± 0.02) compared to 0.6 g (± 0.2) in DMA at the same concentrations (Fig. 25.1a). As expected, the average total biomass of the control plants (grown in soil with no pesticide added) was higher (0.8 g) than the plants grown in pesticide-contaminated soils. Increasing DMA concentration to 1500 mg kg⁻¹ significantly reduced the plant biomass ($p < 0.001$) by about 38% when compared to the plants grown in 675 ppm of DMA and by about 52% when compared to the control plants (Fig. 25.1a). Fig. 25.1b shows that the addition of sodium arsenate caused a significant reduction ($p < 0.0001$) in shoot length by an average of 74% compared to the control plants with no significant difference between low and high concentrations of sodium arsenate applied. On the other hand, addition of 675 and 1500 mg kg⁻¹ DMA to the soils caused a reduction of 39% and 60% respectively, in shoot lengths compared to the control plants. Unlike shoots, roots were less affected by addition of As in soils (Fig. 25.1c). However, the effect of inorganic and organic As on root length followed a similar trend as total biomass and shoot lengths. The root lengths were not very much affected by the lower concentration of sodium arsenate and DMA. At the higher concentration of 1500 mg kg⁻¹ of sodium arsenate and DMA, root lengths decreased by 75% and 53% respectively, compared to control plants (Fig. 25.1c).

Our results indicate that phytotoxicity of As is influenced by the species of As applied. Rice plants treated with sodium arsenate produced lower biomass and reduced plant shoot and root lengths compared to plants treated with DMA with no notable differences between low and high concentrations applied. Milam et al. (1988) and Marin et al. (1993) reported a reduction of biomass/plant growth of rice plants subjected to arsenate. Tsutsumi (1982), on the other hand, observed no reduction in rice plant height at 125 ppm of arsenate applied to the soils. However, increasing arsenate concentration up to 312.5 ppm decreased the plant height by 63% compared to control plants. On the other hand, there are several contradictory reports on the effect of DMA on plant growth. While several reports of varied effects of As on plant growth have been published (Tang and Miller, 1991; Marin et al., 1992; Sneller et al., 1999; Abdein et al., 2002), mechanism of As toxicity in plants remain unclear. The toxicity of inorganic arsenicals such as arsenate is due to interference

Figure 25.1. Effect of arsenical pesticide-contaminated soil on the growth of rice plants. Immokalee soil was contaminated using either sodium arsenate (SAs) or dimethylarsenic acid (DMA) either at 675 mg kg⁻¹ (L) or 1500 mg kg⁻¹ (H) of As. Effect on total biomass (a), shoot length (b) and root length (c) were recorded. Error bars represent \pm SE.

with oxidative phosphorylation (Terwelle and Slater, 1967). On the other hand, organic arsenicals, such as DMA, are less toxic to plants and are likely to block protein synthesis (Sckerl and Frans, 1969).

25.3.2. Arsenic accumulation in plant tissues

The concentration of As in the plant tissues is presented in Fig. 25.2a. The results show that As concentration ranged from $25 \mu\text{g g}^{-1}$ to $271 \mu\text{g g}^{-1}$ in plants treated with DMA and sodium arsenate, respectively (Fig. 25.2a). In general, As concentration in plants treated with 1500 mg kg^{-1} sodium arsenate was 10-fold higher than in the plants treated with DMA at the same concentration. However, at the lower rate of 675 mg kg^{-1} , As concentrations in the plants treated with sodium arsenate were only 2-fold higher than those treated with DMA at the same rate.

Although As concentrations were higher in plants treated with sodium arsenate, the plants accumulated more As when treated with the same concentration DMA in the soil (Fig. 25.2b). The highest As accumulation in plant tissues was recorded in the plants treated with 675 mg kg^{-1} of DMA ($57.8 \mu\text{g/plant dry weight}$) followed by 36 and $25 \mu\text{g/plant dry weight}$ when sodium arsenate was added at 1500 and 675 mg kg^{-1} respectively. The lowest accumulation of As in plant tissues was recorded when plants were treated with 1500 mg kg of DMA. Since inorganic arsenicals are more toxic than organic arsenicals (Fowler, 1977; Adriano, 2001), plants grew better in soil contaminated with DMA, hence were able to accumulate more As in their tissues over a time period of six months. Earlier studies by Tlustoš et al. (2002) showed that DMA was adsorbed to a much lesser extent than As(V) in the soils, making it more phytoavailable. These findings are in agreement with the results of Marin et al. (1992) who found that phytoavailability of As is higher when supplied as DMA than As(V) for two rice cultivars grown in solution culture. However, in this study, we observed that As concentrations in plant tissues were higher when plants were treated with sodium arsenate, when compared to DMA (Fig. 25.2a).

25.3.3. Effect of WTRs on As phytoavailability

WTRs were added to the soils contaminated with 1500 mg kg^{-1} of As to evaluate their capacity of irreversibly retain As, thereby reducing its phytoavailability. Soils spiked with 1500 mg kg^{-1} of either sodium arsenate or DMA were amended using two types of WTRs (Fe-WTR

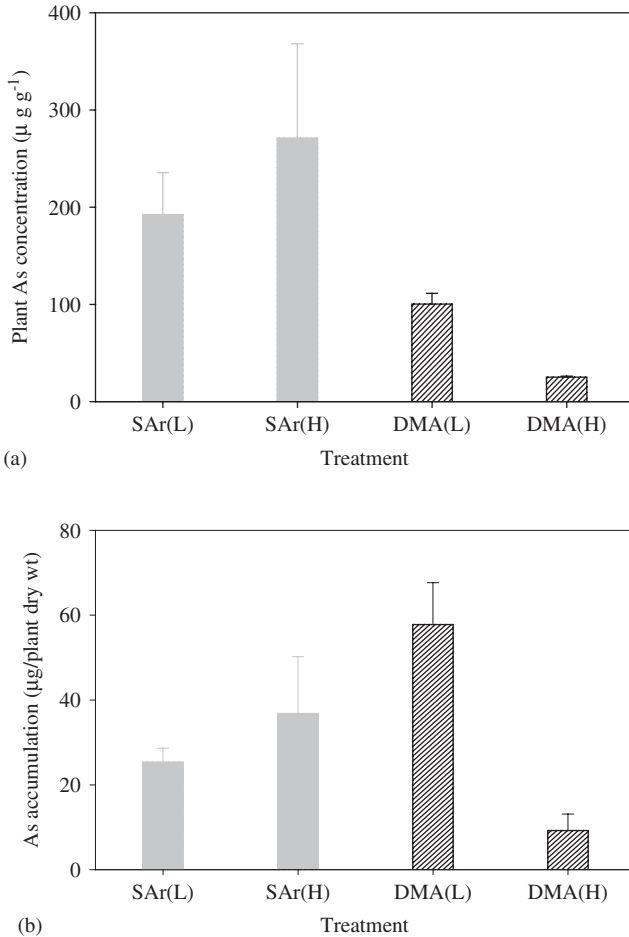
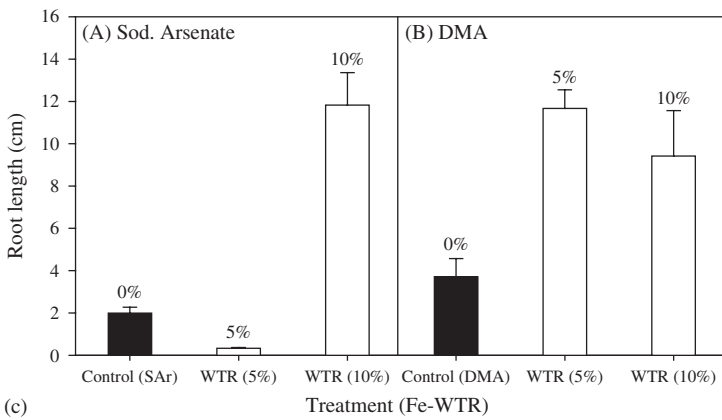
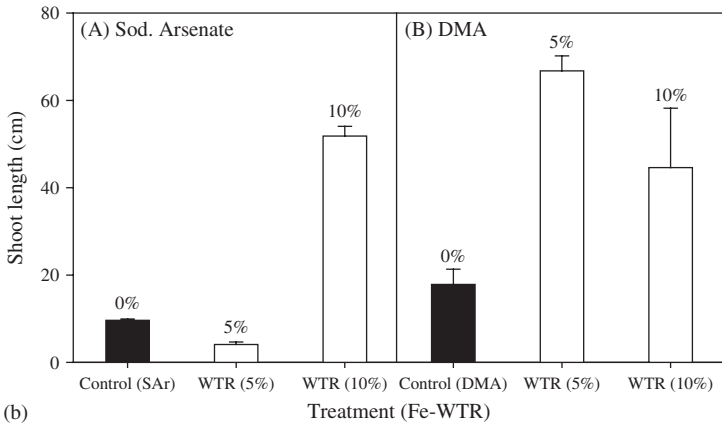
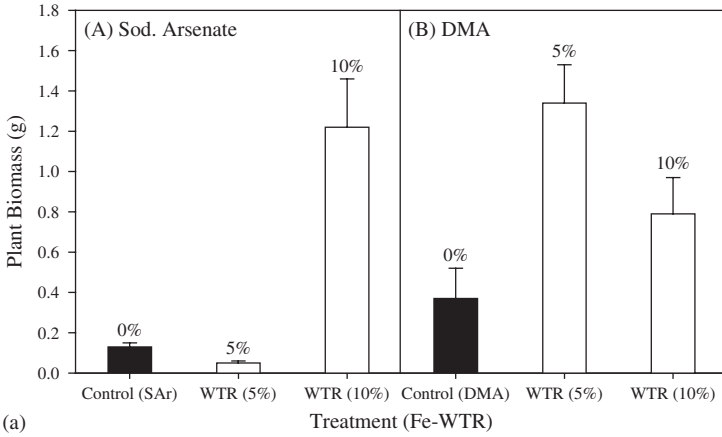


Figure 25.2. Arsenic uptake and accumulation in rice plants grown in arsenical pesticide-contaminated soils. Immokalee soil was contaminated using either sodium arsenate (SAs) or dimethylarsenic acid (DMA) either at 675 mg kg^{-1} (L) or 1500 mg kg^{-1} (H) of As. Arsenic concentration in plant tissues (a) and As accumulation per plant (b) was determined after acid digestion of the plant tissues and analyzing the digests using a graphite furnace atomic absorption spectrophotometer. Error bars represent \pm SE.

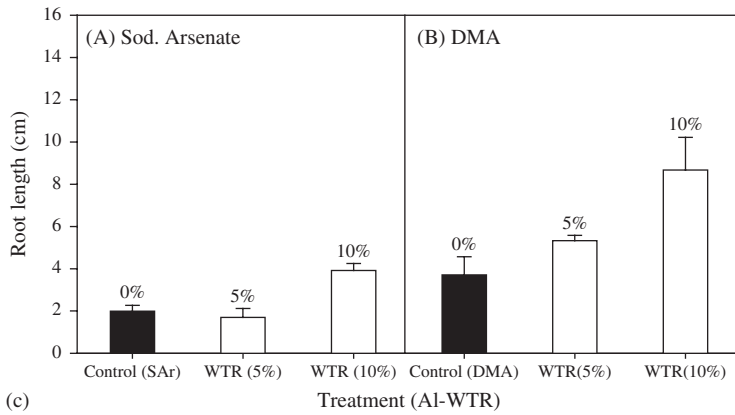
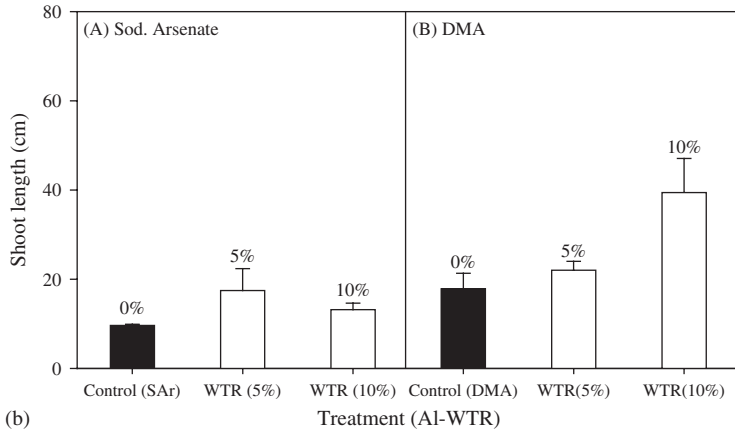
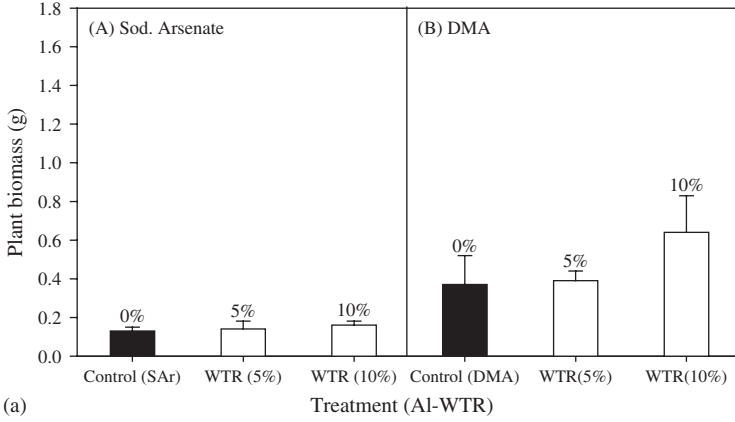
and Al-WTR) at two rates (5% and 10%). The addition of Fe-WTRs had a marked effect on the growth of rice plants. It was observed that plant biomass increased significantly ($p < 0.001$) when Fe-WTR was added at the rate of 10% to the soils contaminated with 1500 mg kg^{-1} sodium arsenate (Fig. 25.3a). Compared to the control



(0% of Fe-WTR), the total plant biomass increased by 90% while shoot and root lengths increased by the average of 82% (Fig. 25.3b, 3c). Addition of 5% Fe-WTR did not improve the growth of rice plants in soils contaminated with sodium arsenate. In case of DMA, the plant growth was significantly increased ($p < 0.001$) when Fe-WTR was applied compared the control (0% WTR). Addition of 5% Fe-WTR resulted in an increase in total plant biomass by 96% (Fig. 25.3a) when compared to the control plants. Shoot and root lengths were increased by an average of 71% compared to the controls (Fig. 25.3b, 3c). At 10% Fe-WTR amendment, the total plant biomass increased by an average of 50% (Fig. 25.3a), and shoot and root lengths increased by an average of 60% when compared to control (Fig. 25.3b, 3c). Increased iron concentration in the soils due to Fe-WTR amendment was found to result in improved plant growth. Iron is essential for the functioning of a number of redox proteins in the electron transport chains of respiration and photosynthesis; it is a component of antioxidant enzymes such as catalases and peroxidases; it is essential also in iron-sulfur proteins such as ferredoxin, superoxide dismutase and aconitase (Marschner, 1995). Despite its abundance on the earth surface, soil iron is almost exclusively present in its oxidized form, which has very low solubility in water. Transgenic lettuce plants accumulating higher levels of iron exhibited enhanced growth resulting in higher biomass compared to control plants (Goto et al., 2000).

Application of Al-WTR to the soils amended with 1500 mg kg^{-1} of sodium arsenate or DMA caused no major improvement in plant growth (Fig. 25.4). Generally, when Al-WTR was applied to soils amended with 1500 mg kg^{-1} of sodium arsenate, there was no major effect on plant biomass, shoot, and root lengths. On the other hand, when Al-WTR was applied to the soils amended with 1500 mg kg^{-1} of DMA, while there was no significant effect on plant biomass (Fig. 25.4a), addition of 5% Al-WTR to the DMA-contaminated soil increased shoot length by 17% (Fig. 25.4b) and root length by 30% (Fig. 25.4c). Application of 10% Al-WTR to DMA-contaminated soils caused a significant increase in shoot and root lengths by an average of 56% (Fig. 25.4b,c).

Figure 25.3. Effect of water treatment residual (WTR)-amendment on growth of rice plants on arsenical pesticide-contaminated soil. Immokalee soil was contaminated using either sodium arsenate (A) or DMA (B) at 1500 mg kg^{-1} of As and amended with Fe-WTR at two rates (5% or 10%). Control plants were grown in soils spiked with 1500 mg kg^{-1} of As using either sodium arsenate or DMA with no WTR amendment. Effect on total biomass (a), shoot length (b), and root length (c) were recorded. Error bars represent \pm SE.



Application of WTRs into highly As-contaminated soils had a significant effect in reduction of As concentration in plant tissues compared to control plants. Arsenic concentration was substantially decreased by an average of 90% and 98% when Fe- or Al-WTR was added into soils amended with 1500 mg kg^{-1} of sodium arsenate respectively (Fig. 25.5a) with no significant difference between low and high rate of WTR applied. In case of DMA-contaminated soils, As concentration in plant tissues increased from $25 \text{ } \mu\text{g g}^{-1}$ (in the control plants) up to $39 \text{ } \mu\text{g g}^{-1}$ when 5% of Fe-WTR was applied (Fig. 25.5a). Increasing the percentage of Fe-WTR applied up to 10% caused a reduction of As concentration to $14 \text{ } \mu\text{g g}^{-1}$ (Fig. 25.5a). Al-WTR had an opposite effect on As concentration in plant tissues compared to the effect of Fe-WTR. At 5% of Al-WTR, As concentration in plants decreased significantly from $25 \text{ } \mu\text{g g}^{-1}$ (in control plants) to $5.7 \text{ } \mu\text{g g}^{-1}$ in plants treated with 5% Al-WTR, while there was no significant reduction observed when Al-WTR rate increased up to 10% (Fig. 25.5b).

The results obtained in this study indicate the beneficial effects of WTR amendment on growth of rice plants in As-contaminated soils. Both Al and Fe-WTRs were very effective in reducing phytoavailable As in the soils, and as a result, the growth of the plants improved. In general, Al-WTR was slightly more effective in reducing As concentration in rice plants. However, Fe-WTR was more effective in increasing the growth of rice plants when compared to Al-WTRs. This effect could be due to the toxicity of Al to plants. Aluminum toxicity has been reported to result in a reduced and damaged root system, which in turn causes the affected plants to be susceptible to mineral nutrient deficiencies (Foy, 1988). Aluminum toxicity is one of the most important yield-limiting factors for rice grown on acid upland and lowland acid sulphate soils (IRRI, 1978). On the other hand, Fe is an essential micro-nutrient in plants, and crop plants widely suffer from Fe deficiency (Marschner, 1995). Excess iron can also cause loss in crop yield, especially in acid soils (Fageria and Rabelo, 1987). Hence, it is essential to carefully calibrate the rate of WTR amendment to the As-contaminated soil for optimum plant growth and reduced phytoavailability of As.

Figure 25.4. Effect of water treatment residual (WTR)-amendment on growth of rice plants on arsenical pesticide-contaminated soil. Immokalee soil was contaminated using either sodium arsenate (A) or DMA (B) at 1500 mg kg^{-1} of As and amended with Al-WTR at two rates (5% or 10%). Control plants were grown in soils spiked with 1500 mg kg^{-1} of As using either sodium arsenate or DMA with no WTR amendment. Effect on total biomass (a), shoot length (b), and root length (c) were recorded. Error bars represent \pm SE.

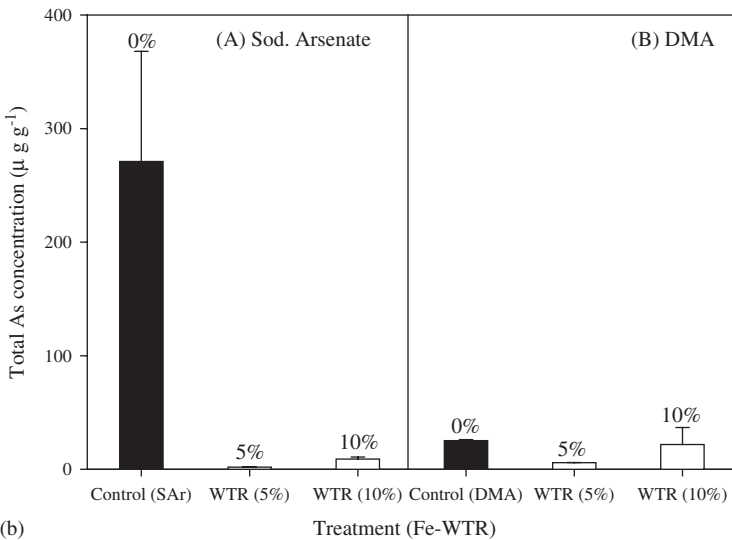
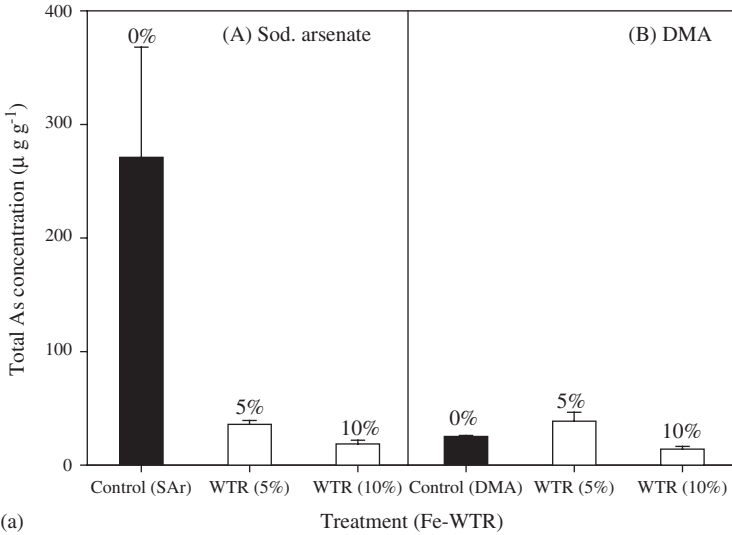


Figure 25.5. Effect of water treatment residual (WTR)-amendment on As uptake in rice plants grown on arsenical pesticide-contaminated soil. Arsenic concentration was determined in the tissues of rice plants grown in soils spiked with 1500 mg kg^{-1} of sodium arsenate (A) or DMA (B) and amended with Fe-WTR (a) or Al-WTR (b) at two rates (5% or 10%). Control plants were grown in soils spiked with 1500 mg kg^{-1} of sodium arsenate or DMA with no WTR-amendment. Arsenic concentration in plant tissues was determined after acid digestion of the plant tissues and analyzing the digests using a graphite furnace atomic absorption spectrophotometer. Error bars represent $\pm \text{SE}$.

REFERENCES

- Abdein, 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., 2001. Trace elements in terrestrial environments: Biogeochemistry, bio-availability, and risks of metals. Springer, New York, NY.
- Bowen, H.J.M., 1979. Environmental chemistry of the elements. Academic Press, New York, NY.
- Bugbee, G.J., Frink, C.R., 1985. Alum sludge as soil amendment: Effects on soil properties and plant growth. *New Haven Connecticut Agric. Exp. Stn. Bull.* 827, .
- Butkus, M.A., Grasso, D., Schulthess, C.P., Wijnja, H., 1998. Surface complexation modeling of phosphate adsorption by water treatment residual. *J. Environ. Qual.* 27, 1055–1063.
- Cai, Y., Ma, L.Q., 2003. Metal tolerance, accumulation, and detoxification in plant with emphasis on arsenic in terrestrial plants. In: Cai, Y., Braids, O.C. (Eds.), *Biogeochemistry of Environmentally Important Trace Elements*. ACS symposium series 835. Washington DC, American Chemical Society, pp. 95–114.
- Carbonell, A., Aarabi, A.M.A., DeLaune, R.D., Gambrell, R.P., Patrick, W.H. Jr., 1998. Arsenic in wetland vegetation: Availability, phytotoxicity, uptake and effects on plant growth and nutrition. *Sci. Total Environ.* 217, 189–199.
- Elliott, H.A., Dempsey, B.A., 1991. Agronomic effects of land application of water treatment sludges. *J. AWWA* 83, 126.
- El-Swaify, S.A., Emerson, W.W., 1975. Changes in the physical properties of soil clays due to precipitated aluminum and iron hydroxides: I. Swelling and aggregate stability after drying. *Soil Sci. Soc. Am. J.* 39, 1056–1063.
- Fageria, N.K., Rabelo, N.A., 1987. Tolerance of rice cultivars to iron toxicity. *J. Plant Nutr.* 10, 653–661.
- Fowler, B.A., 1977. Toxicology of environmental arsenic. In: Goyer, R.A. and Mehlan, M.A. (Eds.), *Toxicology of Trace Elements*. Wiley, New York, pp. 79–122.
- Foy, C.D., 1988. Plant adaptation to acid aluminum-toxic soils. *Commun. Soil Sci. Plant Anal.* 19, 959–987.
- Gallimore, L.E., Basta, N.T., Storm, D.E., Payton, M.E., Huhnke, R.H., Smolen, M.D., 1999. Water treatment residuals to reduce nutrients in surface runoff from agricultural land. *J. Environ. Qual.* 28, 1474–1478.
- Goto, F., Yoshihara, T., Saiki, H., 2000. Iron accumulation and enhanced growth in transgenic lettuce plants expressing the iron-binding protein ferritin. *Theor. Appl. Genet.* 100, 658–664.
- Hansen, L.D., Gilberman, D., Fisher, G.L., Eatough, D.J., 1984. Chemical speciation of elements in stack-collected, respirable size, coal fly ash. *Environ. Sci. Technol.* 18, 181–186.
- Heil, D.M., Barbarick, K.A., 1989. Water treatment sludge influence on the growth of Sorghum-Sudan grass. *J. Environ. Qual.* 18, 292–298.
- International Rice Research Institute, 1978. Annual Report for 1977. Los Bamos, The Philippines.
- Ippolito, J.A., Barbarick, K.M., Redente, E.F., 1999. Co-application effects of water treatment residuals and biosolids on two range grasses. *J. Environ. Qual.* 28, 1644–1650.
- Jacobs, L.W., Teppen, B.J., 2000. WTR as a soil amendment to reduce non-point source pollution from phosphorus-enriched soils. Fourteenth Annual Residuals and Biosolids Management Conference. Water Environment Federation. February 27–March 1, Boston, MA.

- Klute, A., 1996. Methods of Soil Analysis. Part 1: Physical and Mineralogical Methods. SSSA Publications, Madison, WI.
- Lindau, L., 1977. Emissions of As in Sweden and their reduction. *Environ. Health Perspect.* 19, 25–30.
- Liu, W.J., Zhu, Y.G., Smith, F.A., Smith, S.E., 2004. Do phosphorus nutrition and iron plaque alter arsenate (As) uptake by rice seedlings in hydroponic culture? *New Phytol.* 162, 481–488.
- Marin, A.R., Masscheleyn, P.H., Patrick, W.R., Jr., 1992. The influence of chemical form and concentration of arsenic on rice growth and tissue arsenic concentration. *Plant Soil* 139, 175–183.
- Marin, A.R., Masschenlyn, P.H., Patrick, W.H., Jr., 1993. Soil redox-potential stability of arsenic species and its influence on arsenic uptake by rice. *Plant Soil* 152, 245–253.
- Marschner, H., 1995. Mineral Nutrition of Higher Plants, second ed.. Academic Press, London, UK.
- Matera, V. and Le Hecho, I., 2001. Arsenic behavior in contaminated soils: Mobility and speciation. In: Selim, H.M. and Sparks, D.L. (Eds.), Heavy metal release in soils. Lewis Publishers, Boca Raton.
- Maurice, D.V., Lightsey, S.F., Hamrick, E., Cox, J., 1998. Alum sludge and zeolite as components of broiler litter. *J. Appl. Poultry Res.* 7, 263–267.
- Milam, M.R., Marin, A.R., Sedberry, J.E., Jr., Bligh, D.P., Sheppard, R., 1988. Effect of water management, arsenic and zinc on selected agronomic traits and rice grain yield. In: Annual Progress Report. Northeast Ridge Research Station: Baton Rouge, LA, pp. 105–108.
- Moore, P.A. Jr., Miller, D.M., 1994. Decreased phosphorus solubility in poultry litter with aluminum, calcium, and iron amendments. *J. Environ. Qual.* 23, 325–330.
- Murphy, E.A., Aucott, M., 1998. An assessment of the amounts of arsenical pesticides used historically in a geographic area. *Sci. Total. Environ.* 218, 89–101.
- Ng, J.C., 1997. Speciation, bioavailability, and toxicology of arsenic in the environment. Ph.D. Dissertation, University of Australia, Queensland.
- Nissen, P., Benson, A.A., 1982. Arsenic metabolism in freshwater and terrestrial plants. *Physiol. Plant* 54, 446.
- Oscarson, D.W., Huang, P.M., Defosse, C., Herbillon, A., 1981. Oxidative power of Mn(IV) and Fe(III) oxides with respect to As(III) in terrestrial and aquatic environments. *Nature* 291, 50–51.
- Pickering, I.J., Prince, R.C., George, M.J., Smith, R.D., George, G.M., Salt, D.E., 2000. Reduction and coordination of arsenic in Indian mustard. *Plant Physiol.* 122, 1171–1178.
- Pierce, M.L., Moore, C.B., 1980. Adsorption of arsenite on amorphous iron hydroxide from dilute aqueous solution. *Environ. Sci. Technol.* 14, 214–216.
- Rodriguez, R.R., 1998. Bioavailability and biomethylation of arsenic in contaminated soils and solid wastes. Ph.D. Dissertation, Oklahoma State University, Stillwater, OK.
- Sckerl, M.M., Frans, R.E., 1969. Translocation and metabolism of MAA-14C in johnson-grass and cotton. *Weed Sci.* 17, 421–427.
- Shendrikar, A.D., Faudel, G.B., 1978. Distribution of trace metals during oil shale retorting. *Environ. Sci. Technol.* 12, 332–334.
- Sneller, F.E.C., Van Heerwaarden, L.M., Kraaijeveld-Smit, F.J.L., Ten Bookum, W.M., Koevoets, P.L.M., Schat, H., Verkleij, J.A.C., 1999. Toxicity of arsenate in *Silene vulgaris*, accumulation and degradation of arsenate-induced phytochelatins. *New Phytol.* 144, 223–232.
- Sohrin, Y., Matsui, M., Kawashima, M., Hojo, M., Hasegawa, H., 1997. Arsenic biogeochemistry affected by eutrophication in Lake Biwa, Japan. *Environ. Sci. Technol.* 31, 2712–2720.

- Southworth, R.M., 1995. Land Application Pollutant Limit for Arsenic. Part 503 USEPA, Washington, DC.
- Sparks, D.L., 1996. Methods of Soil Analysis. Part 3: Chemical Methods. SSSA Publications, Madison, WI.
- Tamaki, S., Frankenberger, W.T.J., 1992. Environmental biochemistry of arsenic. *Rev. Environ. Contam. Toxicol.* 124, 79–110.
- Tang, T., Miller, M., 1991. Growth and tissue composition of rice grown in soil treated inorganic copper, nickel and arsenic. *Commun. Soil Sci. Plant Anal.* 22, 2037–2045.
- Terwelle, H.F., Slater, E.C., 1967. Uncoupling of respiratory-chain phosphorylation by arsenate. *Biochim. Biophys. Acta* 143, 1–17.
- Tlustoš, P., Goessler, W., Száková, J., Balik, J., 2002. Arsenic compounds in leaves and roots of radish grown in soil treated by arsenite, arsenate and dimethylarsenic acid. *Appl. Organometal. Chem.* 16, 216–220.
- Tsutsumi, M., 1982. Comparative toxicity of arsenite and arsenate to rice seedlings under various levels of phosphate supply. *Soil Sci. Plant Nutr.* 26, 561–569.
- USEPA, 2001. National Primary Drinking Water Regulations; Arsenic and Clarifications to Compliance and New Source Contaminants Monitoring. Final Rule Federal Register/ Vol. 66, No. 14 (40 CFR Parts 9, 141, and 142). Available at http://www.epa.gov/safewater/ars/arsenic_finalrule.html