

ARSENIC DISTRIBUTION IN SOIL PROFILES AMENDED WITH COAL COMBUSTION BY-PRODUCTS

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Abstract. Combustion of coal in the generation of electric power produces large quantities of waste ash that is typically landfilled or stockpiled on site. This material may be applied to agricultural land, thereby avoiding disposal costs, if no adverse environmental consequences result. Several trace elements such as arsenic, boron, and selenium have been found in high concentrations in some fly ashes.

In this study, fly ash and a desulfurization gypsum by-product produced by power plants were applied to two soils in the field at rates of 20 mt/ha, both singly and in mixture. Soybean followed by corn was grown on the plots, and soils sampled with depth at the end of the second season and analyzed for extractable arsenic (As).

Arsenic was found to be quite immobile in both soils studied as assayed by acid extraction, although more mobile in the sandier Lakeland than in the Cecil soil. Extractable As in Cecil soil was not different on amended plots vs. controls due to the high pesticide-derived As levels. In sandier Tifton soils, fly ash tended to increase extractable As in topsoils above control levels, but low levels (< 100 ppb) were found below 50 cm depth. Desulfurization gypsum added much less As to soils than did fly ash. We conclude that on very sandy soils, some increase in As availability and leaching potential may occur with high loadings of fly ash materials; plant uptake studies are underway to assess the magnitude of this effect.

INTRODUCTION

Waste disposal in the electric power generating industry is becoming an increasing problem; ash and other wastes are commonly lagooned on-site near coal-fired power plants, with the possible result of groundwater contamination and runoff to surface waters. Land application of these coal-combustion by-products (CCBP) has been suggested as an economical disposal alternative to landfilling, provided that trace contaminants such as

arsenic, selenium, and mercury do not pose an environmental hazard either through excessive plant uptake and food chain contamination, or by movement to ground- or surface waters (Adriano et al., 1980).

Fly ash and flue gas desulfurization gypsum (FDG) are the major by-products generated by coal-fired electric power plants. Fly ash results from the removal of solid particles from the furnace flue gas, while FDG is produced from SO₂ removal in wet (slurry) limestone scrubbers on some power plants. Fly ash is composed largely of aluminosilicate minerals, while FDG is nearly pure CaSO₄. Some power plants may produce a mixed fly ash-FDG waste product if the scrubber is also used for fly ash collection.

As an amendment for field crops, gypsum has been shown to enhance rooting into subsoil horizons of acidic Georgia soils and potentially increase crop yield (McCray et al., 1991). Preliminary results with FDG show similar effects (Alva et al., 1994). However, trace metal contaminants may be a significant problem with both fly ash and FDG application to arable lands. Trace contaminants may be adsorbed to external surfaces of aluminosilicate minerals in fly ash, and hence have high solubility, increasing the potential for movement through the soil. Arsenic (As) is present in ashes in fairly high concentrations, and is highly toxic to humans via either food or water contamination. This study was conducted in order to assess the potential mobility of As in CCBP-amended soils by studying solubility of As in CCBP-amended soils by studying solubility of As the ashes, and in field soils amended with CCBP materials.

MATERIALS AND METHODS

Experimental Design

Experimental plots were located in Tifton on Lakeland loamy sand soil, and in Athens on the Cecil sandy loam soil. The experimental design included a control where no coal combustion by-products were applied and three coal by-

product treatments: FDG applied alone at the rate of 20 mt/ha, fly ash applied alone at the rate 20 mt/ha and fly ash-FDG 1:1 mixture applied at the rate 20 mt/ha. Three replicates of each treatment were arranged in a randomized block design. Coal combustion by-products were surface applied on the experimental plots (4 x 7 m) and mixed with 0-20 cm soil layer.

The experiment was started in the Spring of 1993. Soybeans were planted immediately after treatment application. Corn was planted in the next growing season. Both crops were irrigated during both growing seasons.

Sampling and Analysis

Soil samples were collected from the 0-20 cm soil layer and then in increments of 10 cm up to depth 70 and 80 cm from Cecil and Lakeland plots, respectively, in July 1994. Ten deep samplings were performed on each plot and then combined in average sample representative for each soil layer within plot.

Soil samples were air dried and sieved through 1 mm screen. Arsenic in soil samples was extracted with mixture of 0.03 N NH_4F and 0.025 N HCl (Bray solution) at soil to solution ratio 1:7 (Olsen and Sommers, 1982). Bray solution used for assessment of mobile As was originally designed for evaluation of available soil phosphorus, but the chemical similarity of both elements makes this solution suitable for As extraction.

For total As determination in fly ash and FDG 0.5 and 1.0 g samples, respectively, were digested in an aqua regia- HF mixture in a Parr bomb. Solutions were diluted with deionized water up to 100 mL and As was determined using a Perkin Elmer 4100 ZL graphite furnace atomic absorption spectrometer with Zeeman background correction. This method was applied for all As determinations carried out in this study. For assessment of As associated with surfaces of fly ash particles, a method similar to that used by Hansen and Fisher (1980) was used. Two g samples of fly ash were shaken with 10 mL of 0.05, 0.1, 0.3 and 1 M HNO_3 for 21 hours, the suspension centrifuged, filtered through No 42 Whatman filter paper; As and Al in the solutions were determined. Two g samples of fly ash were also digested for 3 hours on a hot plate in 20 mL of concentrated (6M) nitric acid, diluted to 100 mL and both As and Al were determined in the filtrate. Inductively coupled plasma spectrometry (ICP) was used for Al determination.

RESULTS AND DISCUSSION

Total As concentrations in fly ash and FDG were 46 and 6.4 mg kg^{-1} , respectively. With 20 mt/ha of fly ash applied,

0.9 kg As was incorporated into the 0-20 cm soil layer, and 0.13 kg with the same rate of FDG.

A batch solubility study showed that initial increases of HNO_3 concentration up to 1 M caused a rapid increase in As solubilization (Figure 1). As acid concentration increased up to 6 M, As continued to solubilize, but at a diminishing rate. The 1 M HNO_3 treatment released about 60% of the total As while at the same acid concentration, less than 5% of the Al, which is component of aluminosilicate matrix, was dissolved. Therefore, As solubilized by 1M HNO_3 may be considered associated with surface of the fly ash particles. Digestion of fly ash with concentrated nitric acid released almost 100% of the As, but only about 10% of the Al present. This means that the major portion of fly ash As is easily accessible to the soil solution, and therefore dissolution-precipitation and sorption become important factors regulating As mobility in soil.

Cecil Soil. Arsenic in well aerated soils occurs in anionic form as AsO_4^{3-} , and as such is adsorbed predominantly on hydrated oxides of iron and aluminum which occur in the soil clay fraction (O'Neill, 1990). In this

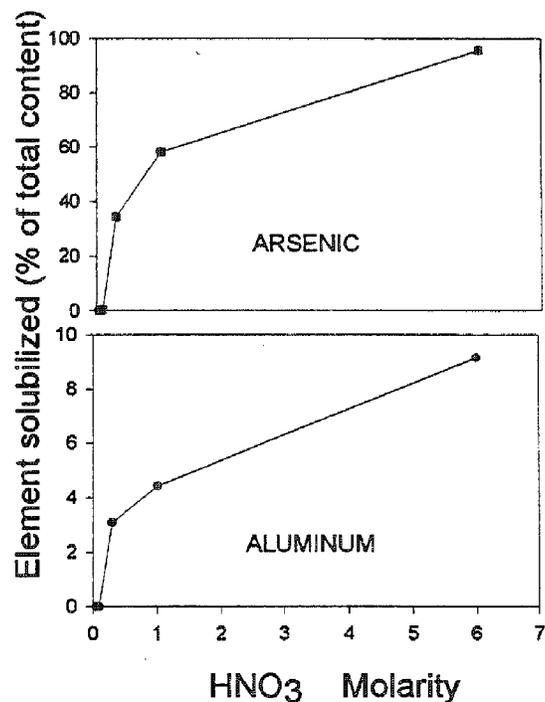


Figure 1. Relationship between element solubilized from fly ash and HNO_3 concentration.

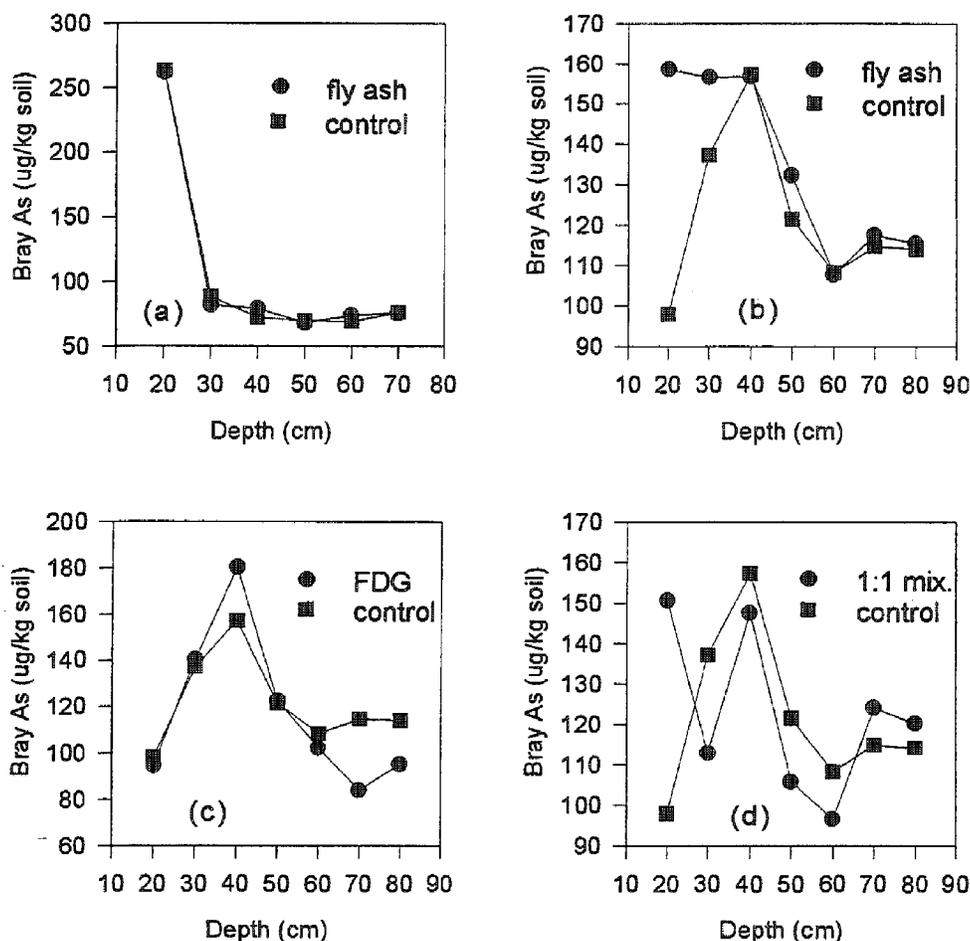


Figure 2. Extractable As in Cecil soil amended with fly ash (a) and Lakeland soil amended with fly ash (b), FDG (c), or fly ash-FDG 1:1 mixture (d).

respect, the Cecil soil is expected to bind As more strongly than the sandy Lakeland soil. The texture of the surface 0-20 cm layer of Cecil soil is sandy loam with a clay content in the range of 10-25%. The clay fraction increases to 40% in the deeper soil horizons. Soil pH is in the range of 5.0-6.0. The Cecil soil has a relatively high anion exchange capacity due to the large positive charge typical for highly weathered soils.

Lakeland Soil. The Lakeland soil, with pH in the same range as the Cecil, has a much sandier texture, with a clay content typically less than 5% within the entire soil profile (Perkins, 1987). Bray extractable As in the profile of Lakeland soil control plots exhibited the highest value at a depth of 30-40 cm, while in the control plots of Cecil soil the top layer 0-20 cm contained the highest mobile As level,

over twice that in the deeper horizons with a very rapid decrease of As concentrations with depth (Figure 2 a and b). This distribution of As is very likely to be a result of As-containing pesticides widely used in Georgia in the past. In the sandy Lakeland soil with low anion exchange capacity and high water permeability, As applied in the past decades has probably moved down the soil profile. In the Cecil soil, which has a higher anion adsorption capacity, As still remains in the upper horizon. The mixture of HCl and NH_4F used for extraction of mobile As forms complexes with aluminum and iron and is expected to extract As sorbed onto iron and aluminum hydroxy surfaces. Therefore, if As migration occurred any time after coal combustion by-product application to the soil, it would result in elevated mobile As over control levels in deeper

soil horizons.

Levels of Bray extractable As in the entire profile of the Cecil soil were not affected by fly ash amendment (Figure 2a). Fly ash application increased extractable As in the 0-20 cm layer of Lakeland soil with no effect on the As content in soil profile below 30 cm (Figure 2b). Arsenic in the Ap horizon of this soil was bound much more weakly than in the Cecil soil, but there is no direct evidence for migration into subsoil during the experimental period. Flue gas desulfurization gypsum contained too little As to change the soil As levels appreciably (Figure 2c), but applied in mixture with fly ash it may have promote leaching of As down the soil profile, due to the large concentration of SO_4^{2-} anions added in the highly soluble gypsum which may result in competition for adsorption sites on the soil. Comparison of the extractable As in the 0-20 cm layer of Lakeland soil amended with fly ash only (Figure 2b) and fly ash-FDG 1:1 mixture (Figure 2d) suggests the possibility of such a competition. The total amount of As incorporated with mixed by-products was about half of that incorporated with fly ash alone, but there was only a small difference in Bray extractable As between both treatments.

CONCLUSIONS

Fly ash applied at the rate of 20 mt/ha to field plots increased Bray extractable As in the upper 0-20 cm layer of sandy Lakeland soil, but had little effect on the heavier Cecil soil two years after application. Flue gas desulfurization gypsum applied alone did not affect As levels in soil, but applied as a mixture with fly ash increased extractable As, probably due to competition with SO_4^{2-} ions for the adsorption sites. There was no evidence of leaching of As incorporated with coal combustion by-products to deeper soil horizons but a longer period of monitoring is necessary in order to make any final conclusions. Further

measurements are underway to assess actual plant uptake of As on these plots, and relate such uptake to As solubility.

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