

**Field Testing of Arsenic and Mercury Bioavailability Model from Land-
Applied Coal Combustion Byproducts**

Final Report

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Abstract

The objective of the study was to provide a model to predict the uptake of arsenic and mercury by plants in response to coal combustion byproducts (CCB) application rates to soil, based on CCB/soil characteristics as determined by sequential extraction of the amended soil. Two greenhouse studies were conducted. The first study consisted of sorghum sudan grass, sunflower, and brake fern, an arsenic accumulator, grown in potted soil (Sango series) amended with flyash (0, 10, 25, 50, and 100 g/kg, corresponding to tons/acre), and the second study consisted of corn, soybean, and brake fern grown in soil amended with FGD gypsum (0, 1, 2.5, 5, and 10 g/kg). Immediately before planting, soil samples were analyzed for arsenic and mercury using sequential extraction procedures that employ successively stronger extractants to first remove arsenic and mercury weakly bound to the soil, followed by arsenic and mercury held increasingly more tightly. The largest proportion of arsenic and mercury were found in the more strongly extracted soil fractions for both flyash- and FGD gypsum-amended soils, indicating that arsenic and mercury were not readily available for plant uptake. Plant biomass was detrimentally affected by flyash amendments, decreasing with increasing flyash levels, whereas FGD gypsum amendments increased plant biomass for corn and brake fern. Arsenic concentrations in sorghum sudan grass and brake fern increased up to the 50 and 25 g flyash/kg soil, respectively, and decreased at the higher flyash levels. For corn, soybeans, and brake fern grown in FGD gypsum-amended soil, in general arsenic concentrations did not differ greatly, and little or no arsenic was found in corn cobs and kernels or in soybean pods. Mercury concentrations for plants grown on flyash- and FGD gypsum-amended soil were the same or less than for plants grown on non-amended (control) soil. For model development, multiple linear regression analysis was used to regress plant arsenic and mercury concentrations against concentrations in the soil fractions. Arsenic in sorghum sudan grass grown on flyash-amended soil was found to be significant ($P=0.013$, $R^2=0.689$) for the statistical analysis. The application of this predictive model would be used for sites being considered for amending the soil with flyash or FGD gypsum, to assess the potential for arsenic and mercury plant uptake and resultant bioavailability of these contaminants.

List of Figures

Figure 1. Total arsenic concentration in soil amended with flyash.

Figure 2. Arsenic concentrations in soil fractions from sequential extraction of flyash-amended soil.

Figure 3. Arsenic concentrations of sequential extraction for non-amended soil (0 g/kg flyash), soil amended with 50 g/kg flyash, and flyash alone.

Figure 4. Mature plant weights for sorghum, sunflower, and brake fern grown on flyash-amended soil.

Figure 5. Arsenic concentrations in sorghum and fern grown on flyash-amended soil.

Figure 6. Predicted and measured arsenic concentrations in sorghum sudan grass grown on flyash-amended soil

Figure 7. Total mercury concentration in soil amended with flyash.

Figure 8. Mercury concentrations in soil fractions from sequential extraction of flyash-amended soil.

Figure 9. Mercury concentrations for sequential extraction of non-amended soil (0 g/kg flyash), soil amended with 50 g/kg flyash, and flyash alone.

Figure 10. Mercury concentrations in sorghum and fern grown on flyash-amended soil.

Figure 11. Total arsenic concentration in soil amended with FGD gypsum.

Figure 12. Arsenic concentrations in soil fractions from sequential extraction of FGD gypsum-amended soil.

Figure 13. Mature plant weights for corn, soybean, and brake fern grown on FGD gypsum-amended soil.

Figure 14. Mercury concentrations in soil fractions from sequential extraction of FGD gypsum-amended soil.

List of Tables

- Table 1. Multiple linear regression of arsenic concentration in sorghum sudan grass on arsenic concentrations in sequential extraction fractions from soil amended with flyash.
- Table 2. Multiple linear regression of arsenic concentration in brake fern on arsenic concentrations in sequential extraction fractions from soil amended with flyash.
- Table 3. Multiple linear regression of mercury concentration in sorghum sudan grass on mercury concentrations in sequential extraction fractions from soil amended with flyash.
- Table 4. Multiple linear regression of mercury concentration in brake fern on mercury concentrations in sequential extraction fractions from soil amended with flyash.
- Table 5. Means and standard errors for arsenic and mercury concentrations in mature plants grown on FGD gypsum-amended soil.
- Table 6. Multiple linear regression of arsenic concentration in soybean on arsenic concentrations in sequential extraction fractions from soil amended with FGD gypsum.
- Table 7. Multiple linear regression of arsenic concentration in brake fern on arsenic concentrations in sequential extraction fractions from soil amended with FGD gypsum.

INTRODUCTION

Coal combustion byproducts (CCB) have a number of applications, including concrete amendment, structural fill, road base, and wallboard from gypsum. CCB are also used for application to agricultural land and can provide a number of potential benefits (Korcak, 1998). CCB can supply essential plant nutrients for crop production, modify soil pH, decrease Al toxicity, and increase water infiltration and aggregation of the soil. In 2000, the USEPA concluded that CCB should not be regulated as a potentially toxic solid waste material, and a number of states including Alabama, Kentucky, and Tennessee, allow land application of CCB without any regulatory issues. However, perceptual and regulatory barriers still exist for the use of CCB for application to agricultural land, including the concern over possible leaching and subsequent bioavailability of metals to soil organisms, plants, and possibly animals and man.

As more fossil power plants add air pollution controls, the amount of FGD gypsum will increase. Off-specification gypsum containing flyash, which cannot be used for wallboard, is also produced at a number of plants utilizing FGD scrubbers. Currently this gypsum is ponded or dry stacked. Application of CCB for enhancing agricultural land is one solution for reducing the amount that has to be stored on-site, which should result in operation and maintenance cost savings or in avoided costs for on-site storage.

Soils amended with CCB often show improved chemical and physical properties and increased plant yields. FGD gypsum used as a source of sulfur (S), when applied at a rate to give 30 lbs S acre⁻¹, increased corn grain yield by 18.3% and 6.6% in consecutive years in field test plots in Ohio (Chen et al., 2005b). Improved nitrogen efficiency was also observed, which would provide an economic benefit to the farmer by reducing the cost of nitrogen fertilization, and would also reduce potential nitrogen pollution through run-off. No-tillage corn grain yield increased by 9% when soil was amended with FGD gypsum (Chen et al., 2005b). Increases in biomass also occurred for alfalfa, corn, soybean, radish, and cotton when grown on soil treated with FGD gypsum (Chen et al., 2005a; Punshon et al., 2001). Wheat grown on soil treated with 4, 8, and 12 Mg ha⁻¹ flyash had higher grain yield, leaf area index, and root length density compared to untreated soil (Garg et al., 2005). The soil benefited from the flyash amendments by reduced bulk density, increased hydraulic conductivity, and increased moisture retention capacity. Aboveground biomass increased by 25% for rice on soil amended with 20 tons ha⁻¹ flyash, and grain and straw yield increased by 21% and 18%, respectively, at 17.5 tons ha⁻¹ flyash (Sarangi et al., 2001). Root biomass of turf grass grown on sandy soil amended with fly ash was 1.2 – 1.5 times greater in the amended soil (Pathan et al., 2003).

Coal combustion byproducts are used in combination with other soil amendments, including sewage sludge, paper factory sludge, compost, and crop residue to further improve soil properties and plant growth (Mitra et al., 2003; Tsadilas et al., 2003; Schlossberg and Miller, 2004; Schumann and Sumner, 2004; Smith, 2005). Co-utilization of byproducts allows reduction in both components while maintaining crop yields, so that detrimental effects of a component at a high application rate can be

avoided. Amendment mixtures can be substituted for chemical fertilizers and are usually less costly than using chemical fertilizers.

However, as stated before, one concern with the use of CCB as soil amendments is the potential environmental hazard of trace elements in the CCB, including arsenic and mercury. In addition to leaching of trace elements to the groundwater, uptake by vegetation in sufficient quantities could cause these to become bioavailable to livestock and other herbivores. Several studies have been conducted to assess the uptake of arsenic and mercury by turfgrass on CCB-amended soil, with mixed results for contaminant uptake depending on the type of soil and CCB used. Three soils amended with FGD gypsum had plant-available arsenic concentrations similar to non-amended soil (Kukier et al., 2001), and arsenic concentrations in annual rye grass leaf tissue grown on potted soil mixed with a high gypsum content material were the same as the untreated control soil (Codling and Wright, 1998). Plant-available arsenic was higher in a sandy soil amended with flyash and a flyash/FGD gypsum mixture than in the non-amended soil, but was the same in soils with higher clay contents (Kukier et al., 2001). However, no effect of flyash-amended soil was observed on arsenic and mercury concentrations in the leaf tissue of turfgrass grown in sandy soil (Pathan et al., 2003). Turfgrass grown on soil treated with unweathered flyash showed no increase in mercury concentration in the plant tissue, whereas arsenic concentrations increased significantly for the two highest treatments for both years of the study (Adriano et al., 2002). Similarly, arsenic concentrations for rye grass grown on soil treated with flyash were significantly greater for the highest soil amendment of 80 g kg⁻¹ than for the control Codling and Wright, 1998). However, application rates for flyash used in the field would probably not be this high, since plant growth was inhibited at this amendment level. The authors concluded that the gypsum would be the best amendment for soil applications at high rates, although the levels of arsenic in plant tissue from the fly ash treatments were not considered high enough to present a potential food chain risk.

Arsenic increased in soybean, radish, corn, and cotton with increasing levels of FGD applied to the soil (Punshon et al., 2001). Radish had the greatest increase, followed by corn and cotton, and soybean had the least increase in arsenic concentration.. Arsenic was not detected in white clover grown on FGD gypsum-amended soil over three years, whereas alfalfa showed elevated arsenic concentrations for the first two years of the study, but no leaf tissue arsenic in the third year (A. D. Behel, unpublished data, TVA).

The objective of this study is to provide a model to predict the uptake of arsenic and mercury by plants in response to CCB application rates to soil, based on CCB/soil characteristics as determined by sequential extraction of CCB-amended soil. This will provide a measure of contaminant bioavailability for plants and concomitant risk assessment for soils that are being considered for CCB application, eliminating the need to grow plants to maturity at each site to obtain risk assessment data.

Modeled predictions of the environmental fate of arsenic and mercury can provide greater flexibility for offsite land application uses. This will allow the power industry greater latitude in promoting the marketing and utilization of these materials for beneficial reuse

in agricultural applications, which may result in operation and maintenance cost savings or in avoided costs for on-site storage.

Executive Summary

Coal combustion byproducts (CCB) have a number of applications, including soil amendments to agricultural land to enhance crop production. CCB are not regulated as a toxic solid waste material; however, perceptual and regulatory barriers still exist for CCB application to agricultural land, including the concern over possible leaching and subsequent bioavailability of metals to soil organisms, plants, and possibly animals and man. However, increased agricultural use could offset the expected increased production of FGD gypsum as more fossil power plants add air pollution controls.

The objective of this study is to provide a model to predict the uptake of arsenic and mercury by plants in response to CCB application rates to soil, based on CCB/soil characteristics as determined by sequential extraction of CCB-amended soil. Modeled predictions of the environmental fate of arsenic and mercury can provide greater flexibility for offsite land application uses, which can result in operation and maintenance cost savings or in avoided costs for on-site storage.

Two greenhouse studies were conducted. The first study consisted of sorghum sudan grass, sunflower, and brake fern, an arsenic accumulator, grown in potted soil (Sango series) amended with flyash (0, 10, 25, 50, and 100 g/kg, corresponding to tons/acre), and the second study consisted of corn, soybean, and brake fern grown in soil amended with FGD gypsum (0, 1, 2.5, 5, and 10 g/kg). Immediately before planting, soil samples were analyzed for arsenic and mercury using sequential extraction procedures. This method employs successively stronger extractants to first remove arsenic and mercury weakly bound to the soil, followed by arsenic and mercury held increasingly more tightly. The extractants for arsenic were 1 M ammonium chloride, 0.5 M ammonium fluoride, 0.1 M sodium hydroxide, and 0.5 M sulfuric acid. The arsenic fractions removed in this way were water-soluble and exchangeable As, Al-bound As, Fe- and organic-bound As, and Ca-bound As, respectively. For mercury, the extractants consisted of water, followed in succession by 0.1 N hydrochloric acid solution, 1 N sodium hydroxide, 12 N nitric acid, and aqua regia solution (4:1 HCl:HNO₃).

For the first greenhouse study, sequential extraction of the soil/flyash mixes showed that the highest concentrations of arsenic were in the NaOH and H₂SO₄ soil fractions, suggesting that most of the arsenic was not readily available for plant uptake. Sorghum sudan plant weights were adversely affected by addition of flyash to the soil, and fern growth was limited at higher flyash application rates. However, arsenic concentrations increased in sorghum up to the 50 g/kg flyash application rate and in fern to the 25 g/kg rate. Sunflower had very poor growth and further results could not be obtained.

The multiple linear regression analysis for arsenic concentrations in sorghum sudan grass regressed on the arsenic concentrations in the sequential extraction fractions was significant at P=0.013 (R²= 0.689). The model used to predict arsenic concentrations in mature sorghum sudan plants is:

As concentration mature plant = $6.44 + (-345.23)(\text{As conc. H}_2\text{O-sol/exchangeable fraction}) + (32.72)(\text{As conc. Al bound fraction}) + (-14.51)(\text{As conc. Fe and Org-bound fraction}) + (19.16)(\text{As conc. Ca-bound fraction})$

Predicted arsenic concentrations using the above equation corresponded closely with the measured values obtained in this study, indicating that this equation should be useful in estimating arsenic uptake by plants on soil that has been amended with flyash.

For the mercury sequential analysis, most of the mercury was in the 0.1N KOH extraction, with the remaining mercury in the 12N HNO₃ fraction. These results suggest that mercury in flyash-amended soil is not readily available for plant uptake. Mercury concentrations in sorghum sudan grass and brake fern decreased with increasing flyash in the soil, so in this case flyash soil amendments would not be a concern for mercury bioavailability. Regression analyses for both sorghum sudan grass and brake fern were not significant.

In the second greenhouse study, due to the lower application rates of FGD gypsum and lower arsenic concentration in gypsum compared to flyash in the first study, arsenic concentrations in soil amended with the FGD gypsum were much lower, and were only slightly higher than concentrations in the non-amended soil. Almost all the arsenic was in the NaOH and H₂SO₄- extracted fractions, indicating that very little of the arsenic was available for plant uptake. Gypsum provided a significant increase in plant biomass for corn, with biomass at the highest gypsum application rate triple that of the non-amended soil, and for brake fern. Corn showed little or no arsenic uptake in the stems, cobs, and grain, whereas soybean stems had arsenic uptake at every level of FGD gypsum treatment. Arsenic concentrations in the soybean stem increased approximately three-fold from the control treatment to the 1 g/kg FGD gypsum amendment, suggesting that FGD gypsum application increased arsenic uptake by soybeans. However, no arsenic was detected in the soybean pods grown in FGD gypsum-amended soil. Corn data did not contain sufficient points above the detection limit to conduct regression analysis, and regression analysis for soybean and fern were not significant at P=0.05.

Sequential extraction results for mercury in FGD gypsum-amended soil did not show the expected pattern of increasing mercury with increasing FGD gypsum application, and multiple linear regression analysis was not conducted. Plants grown on FGD gypsum-amended soil did not have higher mercury concentrations than plants grown on non-amended soil in stems, grain, or fruit.

Further studies are needed to refine and validate these results with sorghum sudan grass. In addition, since this model appears to work for sorghum sudan grass, further studies to determine whether this method can be applicable to dicot species may be beneficial to pursue. The application of the predictive model for sorghum sudan grass and subsequent models would be to screen sites for application of CCB. This could ensure that plants growing on the site will not accumulate sufficient arsenic and mercury, so that these contaminants would not become bioavailable to animals and humans.

EXPERIMENTAL

Greenhouse Experiment I

For this study, sorghum sudan grass (*Sorghum vulgare var. sudanense*), sunflower (*Helianthus annuus*), and brake fern (edenfern™, Edenspace Systems Corporation, Dulles, VA) were planted in pots containing 3 kg of soil (Sango series) amended with either 0, 10, 25, 50, or 100 g flyash/kg soil, which corresponds to tons/acre of flyash added. Each flyash rate/plant species combination was replicated three times, and pots were arranged in a randomized complete block experimental design. Three replicates of unplanted pots at 0 and 50 g flyash/kg soil were also included.

Before planting, bulk soil for sorghum sudan grass and sunflower was fertilized with NH_4NO_3 (333 mg N/kg soil), concentrated superphosphate (CSP) (167 mg P/kg soil), and K_2SO_4 (267 mg K/kg soil). Soil fertilization for the brake fern was urea (50 mg N/kg soil), CSP (17 mg P/kg soil), and KCL (33 mg K/kg soil). The soil was limed to bring the pH to 5.9. After the bulk soil was fertilized, flyash was added and mixed into the soil, and the soil was subjected to alternate mixing, wetting, and air drying over the course of several weeks. The amended soils were then analyzed immediately before planting for arsenic and mercury using sequential extraction techniques. The extractants for arsenic were 1 M ammonium chloride, 0.5 M ammonium fluoride, 0.1 M sodium hydroxide, and 0.5 M sulfuric acid, with a saturated sodium chloride solution wash after each extraction (Onken and Adriano, 1997), and the arsenic fractions removed from the amended soil in this way were water-soluble and exchangeable As, Al-bound As, Fe- and organic-bound As, and Ca-bound As, respectively. For mercury, the extractants consisted of water, followed in succession by 0.1 N hydrochloric acid solution, 1 N sodium hydroxide, 12 N nitric acid, and aqua regia solution (4:1 HCl:HNO₃) (Cussen and Hensman, 2006). This procedure fractionates arsenic into water soluble, weak acid-dissociable, organo-complexed, strongly complexed or strong acid-dissociable, and mineral bound.

Ten seeds were planted in each pot, and after three and half weeks all the plants except one per pot were harvested. The remaining plants were grown to maturity and harvested 10 weeks after planting. The plant leaf tissue was dried, weighed, and ground. For sample analysis, 0.2-0.3 grams of the ground material were digested in concentrated nitric acid. After digestion, samples were brought to volume with a 0.5% bromine chloride solution for arsenic analysis and with distilled water for arsenic analysis.

Soil and plant extracts were analyzed for arsenic on a Varian 220Z atomic absorption spectrometer. Extracts were analyzed for arsenic with a Tekran Model 2600 CVAFS Mercury Analyzer (CVAFS – cold vapor atomic fluorescence spectrometry).

Plant and soil analysis data were used to obtain the parameters in the following regression model for predicting arsenic bioavailability:

$$\text{MPC} = b_0 + b_1(\text{WS/Ex}) + b_2(\text{Al}) + b_3(\text{Fe/Org}) + b_4(\text{Ca})$$

where the parameters are the arsenic concentrations in the soil sequential extraction procedure (WS/Ex - water-soluble and exchangeable; Al – aluminum-bound ; Fe/Org – Fe and organic bound; Ca – calcium bound). Parameters that were not significant in the regression analysis were removed from the model. Regression analysis was conducted in the same way for arsenic, using the results of the sequential extraction and plant analysis.

Greenhouse Experiment II

Corn (*Zea mays*), soybean (*Glycine max*), and brake fern were planted in pots containing 3 kg of soil (Sango series) amended with either 0, 1, 2.5, 5, or 10 g FGD scrubber gypsum by-products/kg soil. The FGD by-products were collected from a TVA fossil power plant, and in addition to FGD scrubber gypsum contained approximately 12-20% fly ash. Each FGD gypsum/plant species combination was replicated three times, and pots were arranged in a randomized complete block experimental design. Three replicates of unplanted pots at 0 and 5 g FGD gypsum/kg soil were also included. The procedures used for this study were the same as for Greenhouse Experiment I above.

Results and Discussion

Greenhouse Experiment I: Soil Amended with Flyash

Arsenic

The concentration of arsenic in the flyash used in this experiment was 49.3 mg As/kg flyash, and the amount in each soil/flyash mixture is shown in Figure 1. Non-amended soil contained slightly more than 4 mg As/kg soil, and the highest addition of flyash approximately doubled the arsenic concentration in the soil. For the sequential extraction analysis, very little arsenic was in the NH₄Cl fraction, which contains the water-soluble and exchangeable arsenic and is most available for plant uptake (Figure 2). The next fraction, which is the NH₄ extraction, contains Al-bound As, which is the next most plant-available arsenic. The highest concentrations of arsenic were in the NaOH and H₂SO₄ extracted soil fractions, which contained 70-90% of the soil arsenic. These results suggest that most of the arsenic in this flyash-amended soil is not readily available for plant uptake. Figure 3 compares the extraction patterns of non-amended soil (0 g/kg) and soil amended with 50 g/kg flyash to the extraction of flyash alone. For the flyash alone, about one-half of the arsenic is in the NH₄F-extracted fraction, and another 10% is in the NH₄Cl fraction, so approximately 60% of the arsenic is in the two most plant-available fractions. However, by mixing the flyash with soil, a large percentage of the arsenic is transferred to the less plant-available fractions, which is beneficial in limiting the arsenic that can be taken up by plants and introduced into the food cycle.

Sorghum sudan plant weights were adversely affected by addition of flyash to the soil. (Figure 4). Fern biomass increased at the lowest rate of 10 g/kg soil over that of non-

amended soil, but at higher application rates plant growth was limited. However, arsenic concentrations increased in sorghum up to the 50 g/kg flyash application rate and in fern to the 25 g/kg rate (Figure 5). Sunflower had very poor growth even on non-amended soil and further results could not be obtained for this species. Flyash soil amendments usually benefit plant growth and soil properties (Pathan et al., 2003; Garg et al., 2005), but at higher rates can become detrimental to plant growth.

The multiple linear regression analysis for arsenic concentrations in sorghum sudan grass regressed on the arsenic concentrations in the sequential extraction fractions was significant at $P=0.013$ (Table 1). The P -values for all of the soil fractions were significant at $P=0.05$ level, indicating that all of the coefficients should be included in the model. The model used to predict arsenic concentrations in mature sorghum sudan plants is:

$$\text{As concentration mature plant} = 6.44 + (-345.23)(\text{As conc. H}_2\text{O-sol/exchangeable fraction}) + (32.72)(\text{As conc. Al bound fraction}) + (-14.51)(\text{As conc. Fe and Org-bound fraction}) + (19.16)(\text{As conc. Ca-bound fraction})$$

where the fraction extracted with NH_4Cl = As concentration in the H_2O -sol/exchangeable fraction, NH_4F extraction = Al-bound fraction, NaOH extraction = Fe and Org-bound fraction, and the H_2SO_4 extraction = Ca-bound fraction.

Predicted arsenic concentrations using the above equation corresponded closely with the measured values obtained in this study (Figure 6), indicating that this equation should be useful in estimating arsenic uptake by plants on soil that has been amended with flyash.

Regression analysis for fern was not significant at $P=0.207$, and a model to accurately predict arsenic uptake in ferns could not be developed.

Mercury

Total mercury in non-amended soil was approximately 100 $\mu\text{g}/\text{kg}$ soil, and addition of flyash to the soil only increased mercury concentrations to 114 $\mu\text{g}/\text{kg}$ at the highest rate of flyash amendment (Figure 7). For the sequential analysis, very little mercury was in the first two extractants, which would be the mercury that is most available for plant uptake (Figure 8). Most of the mercury was in the 0.1N KOH extraction. For each extraction, the mercury is expected to increase with increasing flyash levels, similar to that observed for the arsenic sequential extraction (Figure 2). However, mercury levels decreased with increasing flyash levels for the 0.1N KOH extraction. The reason for this anomaly is not known. The remaining mercury was extracted in the 12N HNO_3 fraction. These results suggest that mercury in flyash-amended soil is not readily available for plant uptake. The extraction patterns of non-amended soil (0 g/kg), soil amended with 50 g/kg flyash, and flyash alone show that most of the mercury in flyash is in one of the least plant-available fractions (Figure 9). Mercury appears to remain in this fraction when added to soil, as indicated by the increase in this fraction from the non-amended soil (0 g/kg flyash) to the soil amended with 50 g/kg flyash.

Mercury concentrations in sorghum sudan grass decreased with increasing flyash in the soil, so in this case flyash soil amendments would not be a concern for mercury bioavailability (Figure 10). Mercury concentrations in brake fern also decreased slightly in soil amended with flyash.

Regression analysis for both sorghum sudan grass and brake fern in Tables 3 and 4 were not significant ($P=0.370$ for sorghum and $P=0.864$ for brake fern), and models were not developed for mercury with these plants.

Greenhouse Experiment II: Soil Amended with FGD Scrubber Gypsum

Arsenic

The concentration of arsenic in the FGD gypsum used in this experiment was 3.46 mg As/kg gypsum (Figure 11), which is a much lower concentration of arsenic than the 49.3 mg/kg in the flyash used in greenhouse experiment I discussed above. Application rates of FGD gypsum were also much lower than for flyash. Because of this, arsenic concentrations in soil amended with the FGD gypsum differ very little from concentrations in the non-amended soil. Almost all of the arsenic was in the NaOH and H₂SO₄- extracted fractions, indicating that very little of the FGD gypsum/soil arsenic was available for plant uptake (Figure 12).

Commercial gypsum is used as a source of sulfur for plant fertilization, to decrease soil aluminum toxicity, and improve water infiltration and aggregation of the soil, which benefits plant growth. This is seen in the significant increase in plant weight for corn and brake fern with FGD gypsum application (Figure 13). This response was not observed for soybean, however.

Arsenic concentrations in the mature plants in response to soil treatments with FGD gypsum are shown in Table 5. Corn showed little or no arsenic uptake in the stems, cobs, and grain, whereas soybean stems had arsenic uptake at every level of FGD gypsum treatment. Arsenic concentrations in the soybean stem increased approximately three-fold from the control treatment to the 1 g/kg FGD gypsum amendment, suggesting that FGD gypsum application increased arsenic uptake by soybeans. However, no arsenic was detected in the soybean pods, except for the non-amended control (0 g/kg FGD gypsum). Soils contain background levels of arsenic, and this may account for the arsenic concentration in the control pods. As expected, arsenic concentrations in the brake fern were much higher, about three times that in the soybeans, since brake fern is an arsenic accumulator.

Corn data did not contain sufficient points above the detection limit to conduct regression analysis. Regression analysis for soybean and fern were not significant at $P=0.05$ (Tables 6 and 7).

Mercury

Sequential extraction results for mercury in FGD gypsum-amended soil did not show the expected pattern of increasing mercury with increasing FGD gypsum application (Figure 14). For this reason, multiple linear regression analysis was not conducted for corn, soybean, and brake fern. Mercury was detected in corn stems, cobs, and kernels, and in soybean stems and pods; however, the concentrations in plants grown on amended soil was not significantly higher than plants grown on the non-amended soil (0 g/kg). This also occurred in the brake fern. This indicates that plants grown on soil amended with FGD-gypsum should not have higher mercury concentrations than plants grown without amendment.

Conclusions

This project was designed to assess whether a relatively simple method could be developed to predict uptake of arsenic and mercury by plants grown on soil that had been amended with coal combustion byproducts, in this case flyash and FGD scrubber gypsum. To do this, various plant species (sorghum sudan grass, sunflower, brake fern, corn, and soybean) were grown in the greenhouse in pots amended with different levels of either flyash or gypsum. The amended soil was analyzed using sequential extraction techniques, starting with mild extractants that would first remove arsenic and mercury that is weakly held by the soil, followed by increasingly stronger extractants to remove the arsenic and mercury that are more tightly bound to the soil. The portion of the total arsenic and mercury that is weakly held by the soil is more easily taken up by plants, whereas the arsenic and mercury that are not removed until strong extractants are used are not readily plant-available. The hypothesis of this study is that by comparing the concentrations of arsenic and mercury in the different soil fractions to the concentration of the chemicals in the mature plant leaves and stems, a model could be developed to estimate arsenic and mercury concentrations in plants based on the sequential soil extraction analyses. This was done using multiple linear regression analysis to regress plant arsenic and mercury concentrations against concentrations in the soil fractions.

The application of the resultant predictive model would be used for sites being considered for amending the soil with flyash or FGD gypsum. Soil from the site could be mixed with the coal combustion byproduct, analyzed using sequential extraction, and these results used in the predictive model to estimate the amount of arsenic and mercury that would be taken up by plants grown on the site. In this way, sites could be screened for application of CCB to assure that plants growing on the site will not accumulate sufficient arsenic and mercury in the plant tissues so that these chemicals would not become bioavailable to animals and humans.

The plant species used in the study were selected to provide both monocots (sorghum sudan grass, corn) and dicots (sunflower, soybean). Brake fern, which is an arsenic accumulator, was included as a plant that would take up sufficient arsenic to provide detectable amounts for analysis in the event that arsenic in the amended soil would be too low for detectable amounts to accumulate in the other species. Multiple

regression analysis was conducted on sorghum sudan grass, sunflower, and brake fern grown in soil amended with flyash, and corn, soybean, and brake fern grown in FGD gypsum-amended soil. Only arsenic in sorghum sudan grass grown on flyash-amended soil was found to be significant ($P=0.013$, $R^2=0.689$) for the statistical analysis. Predicted arsenic concentrations using the model corresponded closely with the measured values of arsenic in the mature sorghum plants, indicating that this equation should be useful in estimating arsenic uptake by plants on soil that has been amended with flyash..

Several other results from this study are of note. Mixing flyash with soil increases arsenic concentration in the less soluble fraction of the soil/flyash mix, indicating that arsenic may be moving from the more easily extracted fractions in the flyash itself to less soluble fractions in the soil. Almost all of the arsenic in FGD gypsum-amended soil was in the two most strongly extracted fractions. Mercury was also in the more strongly extracted fractions both in flyash itself and in the soil/flyash mix. These results all indicate that both arsenic and mercury from coal combustion byproducts are not easily available for plant uptake in CCB-amended soils.

For the plants, little or no arsenic was found in corn cobs, and no arsenic was detected in kernels for plants grown on FGD gypsum-amended soil, although arsenic was low in the corn leaves and stems also. No arsenic was detected in soybean pods from plants grown in amended soil. These results indicate that arsenic in FGD gypsum-amended soil is not transported to the grain or fruit of crop plants. Mercury was found in corn cobs and kernels and in soybean pods from plants grown on FGD-gypsum amended soil, but the concentrations were the same as those found for plants grown on non-amended soil. Mercury concentrations in corn, soybean, and brake fern leaves and stems were also the same in plants grown on amended and non-amended soil. This indicates that FGD-gypsum soil amendments did not cause increased mercury in plants greater than found with untreated soil.

Further studies are needed to refine and validate these results with sorghum sudan grass. In addition, since this model appears to work for sorghum sudan grass, further studies to determine whether this method can be applicable to dicot species may be beneficial to pursue.

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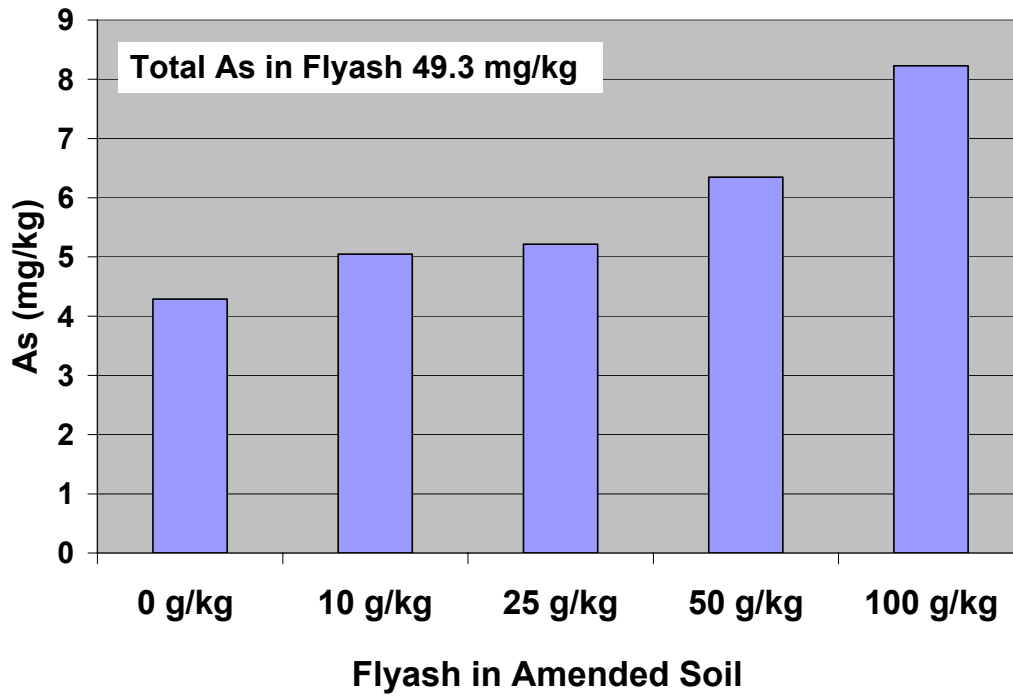


Figure 1. Total arsenic concentration in soil amended with flyash.

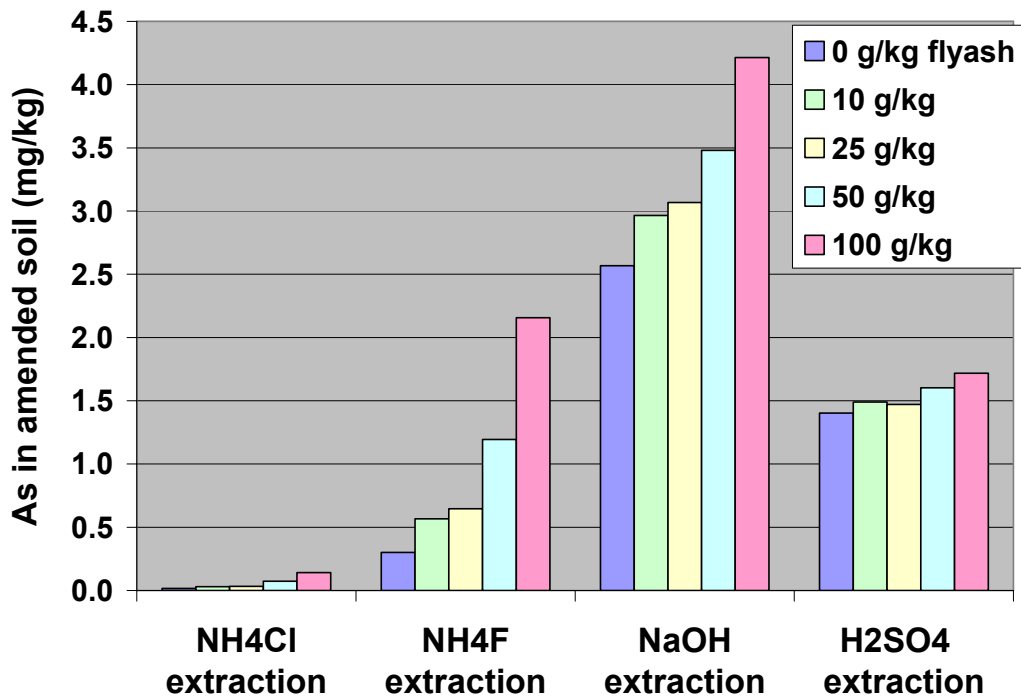


Figure 2. Arsenic concentrations in soil fractions from sequential extraction of flyash-amended soil.

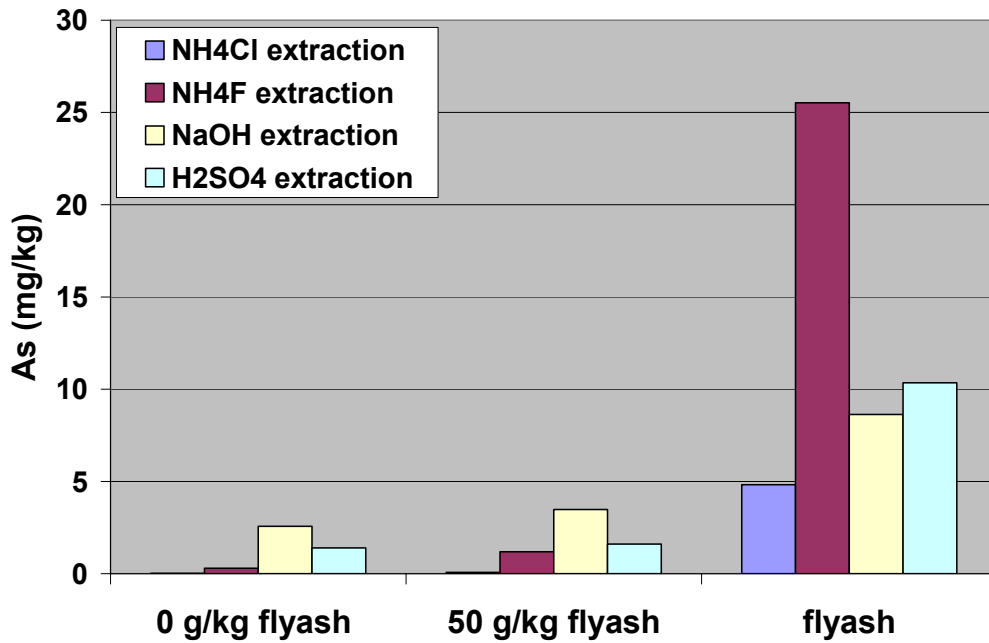


Figure 3. Arsenic concentrations of sequential extraction for non-amended soil (0 g/kg flyash), soil amended with 50 g/kg flyash, and flyash alone.

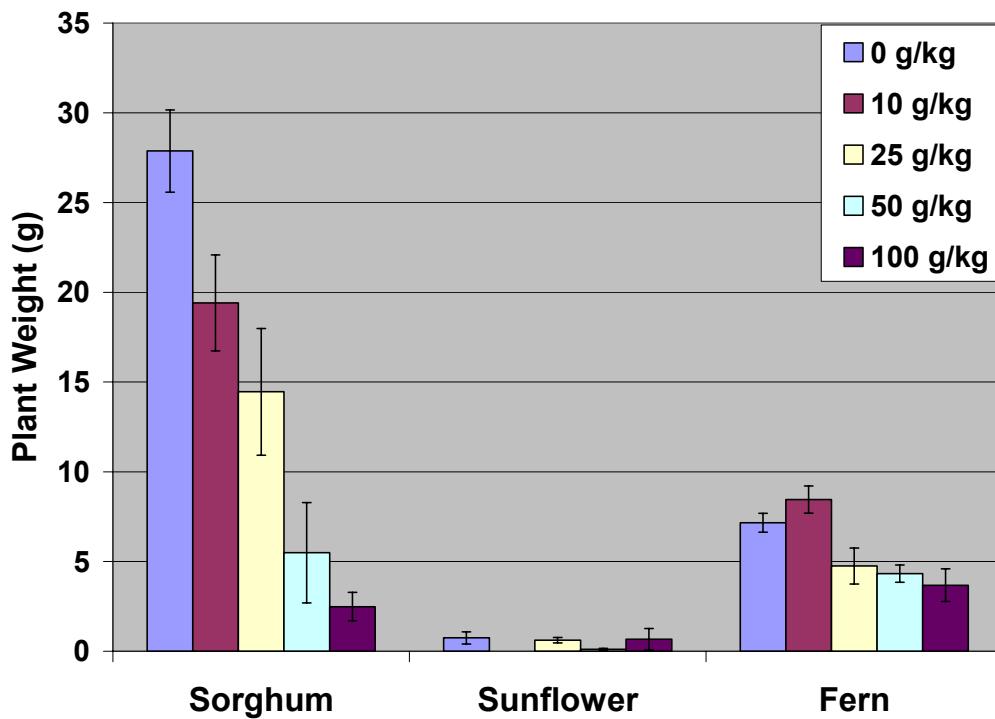


Figure 4. Mature plant weights for sorghum, sunflower, and brake fern grown on flyash-amended soil.

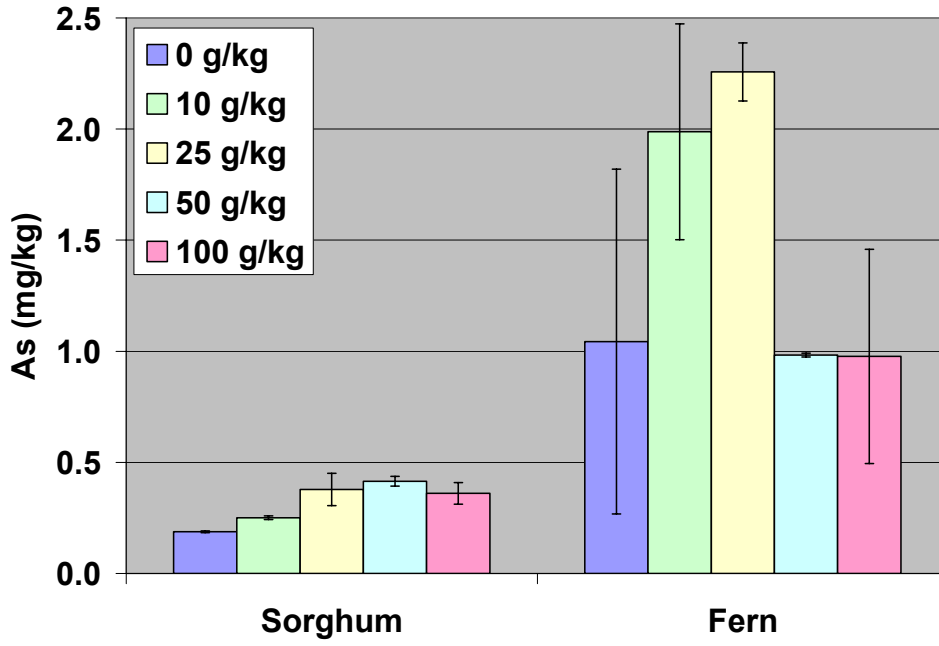


Figure 5. Arsenic concentrations in sorghum and fern grown on flyash-amended soil.

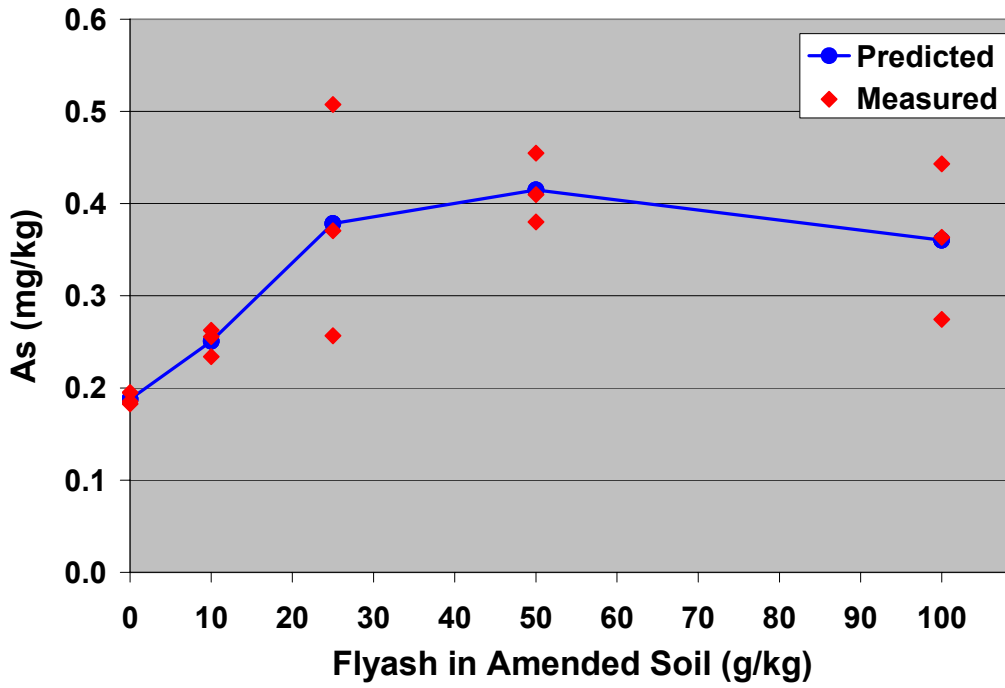


Figure 6. Predicted and measured arsenic concentrations in sorghum sudan grass grown on flyash-amended soil

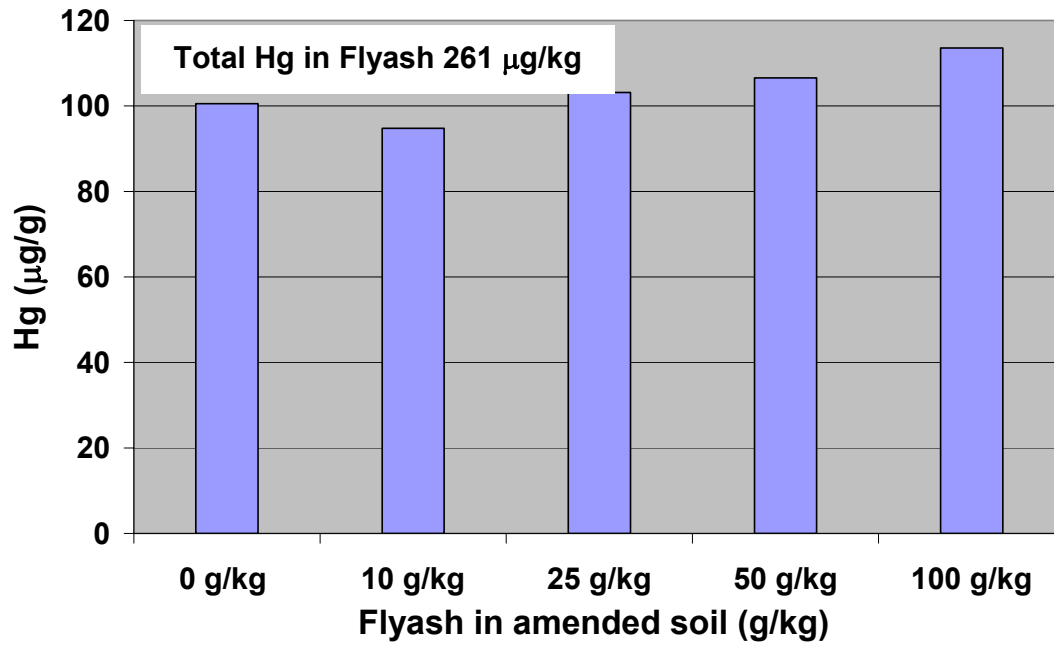


Figure 7. Total mercury concentration in soil amended with flyash.

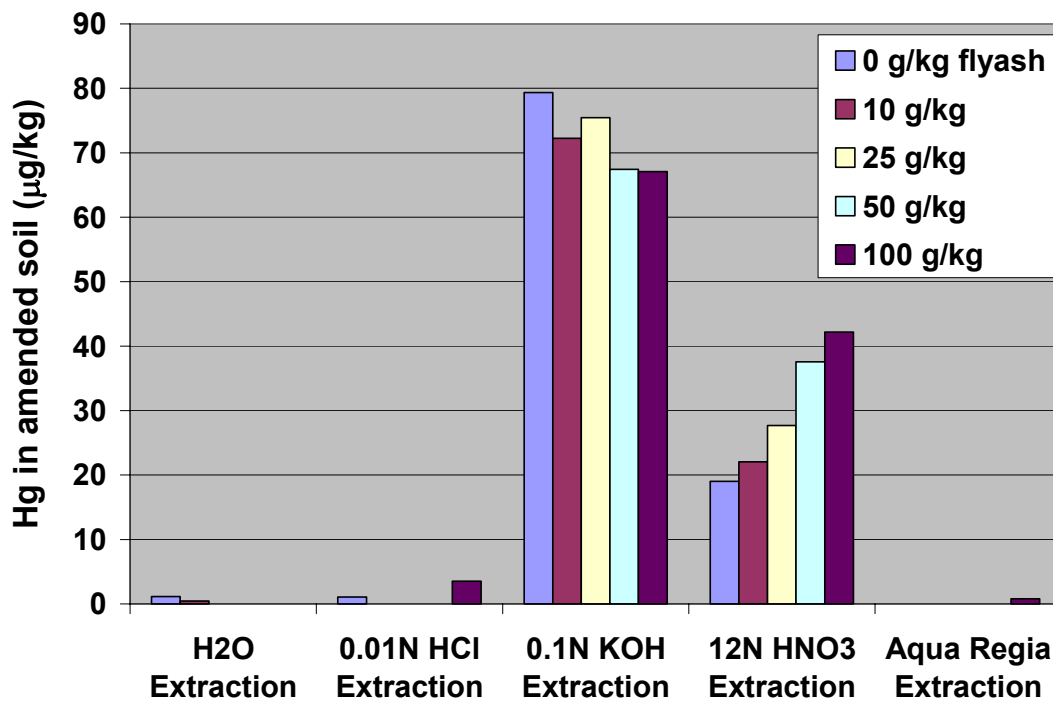


Figure 8. Mercury concentrations in soil fractions from sequential extraction of flyash-amended soil.

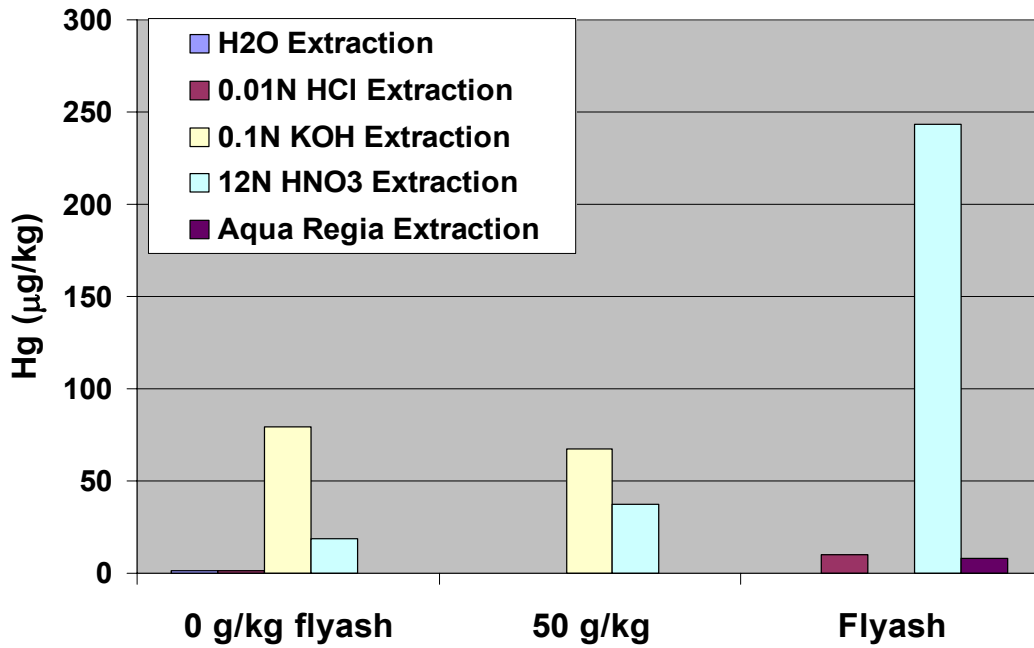


Figure 9. Mercury concentrations for sequential extraction of non-amended soil (0 g/kg flyash), soil amended with 50 g/kg flyash, and flyash alone.

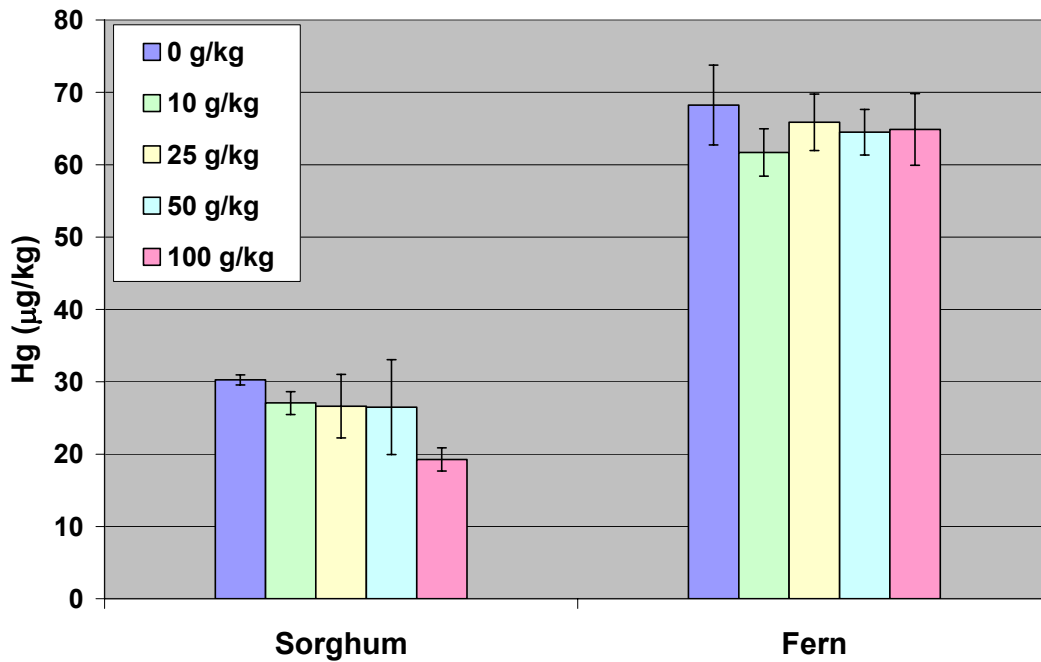


Figure 10. Mercury concentrations in sorghum and fern grown on flyash-amended soil.

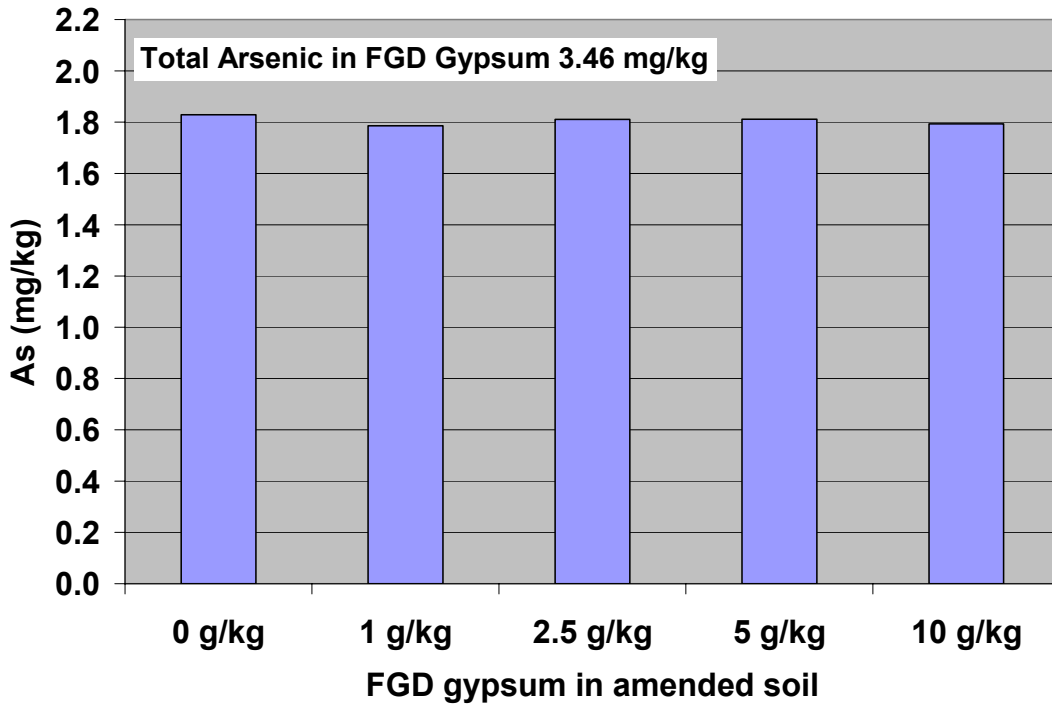


Figure 11. Total arsenic concentration in soil amended with FGD gypsum.

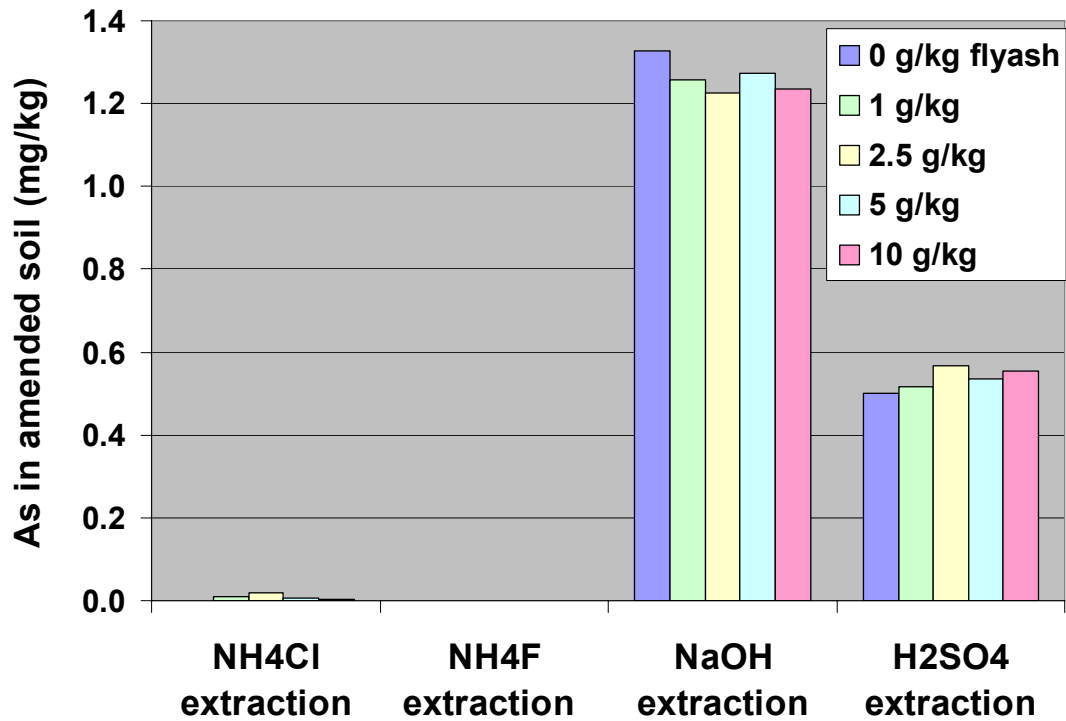


Figure 12. Arsenic concentrations in soil fractions from sequential extraction of FGD gypsum-amended soil.

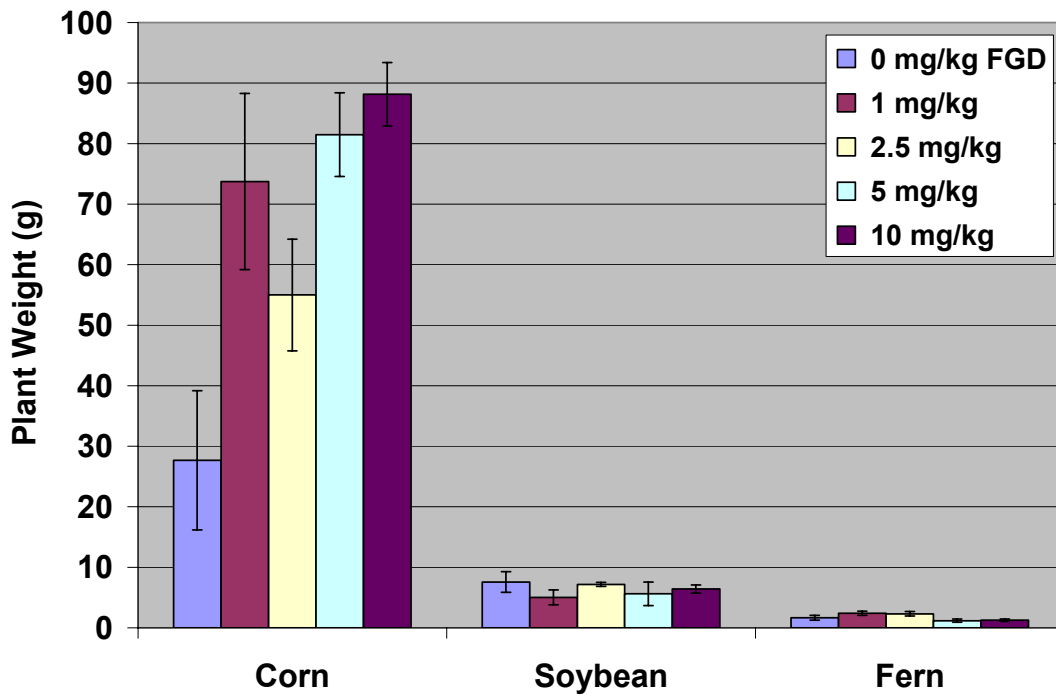


Figure 13. Mature plant weights for corn, soybean, and brake fern grown on FGD gypsum-amended soil.

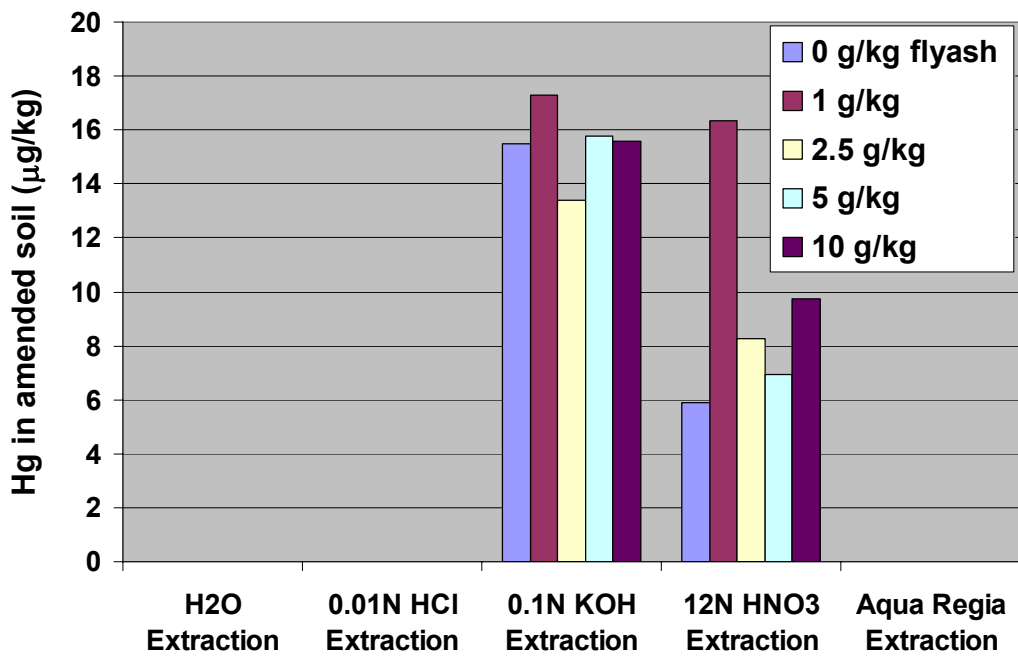


Figure 14. Mercury concentrations in soil fractions from sequential extraction of FGD gypsum-amended soil.

Table 1. Multiple linear regression of arsenic concentration in sorghum sudan grass on arsenic concentrations in sequential extraction fractions from soil amended with flyash.

R^2	0.689				
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>
Regression	4	0.109	0.027	5.537	0.013
Residual	10	0.049	0.005		
Total	14	0.158			
	<i>Coefficients</i>	<i>P-value</i>			
Intercept	6.44	0.100			
H ₂ O-sol/exchangable	-345.23	0.040			
Al-bound	32.72	0.043			
Fe and Org-bound	-14.51	0.049			
Ca-bound	19.16	0.042			

Table 2. Multiple linear regression of arsenic concentration in brake fern on arsenic concentrations in sequential extraction fractions from soil amended with flyash.

R^2	0.485				
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>
Regression	4	3.815	0.954	1.884	0.207
Residual	8	4.050	0.506		
Total	12	7.866			
	<i>Coefficients</i>	<i>P-value</i>			
Intercept	-31.5	0.428			
H ₂ O-sol/exchangable	1490.1	0.353			
Al-bound	-147.9	0.340			
Fe and Org-bound	73.3	0.304			
Ca-bound	-96.8	0.284			

Table 3. Multiple linear regression of mercury concentration in sorghum sudan grass on mercury concentrations in sequential extraction fractions from soil amended with flyash.

R^2	0.323				
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>
Regression	4	195.7	48.94	1.198	0.370
Residual	10	408.5	40.85		
Total	14	604.2			
	<i>Coefficients</i>	<i>P-value</i>			
Intercept	-2.599	0.972			
H ₂ O	6.195	0.462			
0.01N HCl	-2.332	0.266			
0.1N KOH	0.302	0.715			
12N HNO ₃	0.233	0.721			

Table 4. Multiple linear regression of mercury concentration in brake fern on mercury concentrations in sequential extraction fractions from soil amended with flyash.

R^2	0.111				
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>
Regression	4	67.6	16.9	0.311	0.864
Residual	10	544.0	54.4		
Total	14	611.7			
	<i>Coefficients</i>	<i>P-value</i>			
Intercept	-14.752	0.862			
H ₂ O	4.016	0.676			
0.01N HCl	-0.538	0.819			
0.1N KOH	0.862	0.374			
12N HNO ₃	0.563	0.458			

Table 5. Means and standard errors for arsenic and mercury concentrations in mature plants grown on FGD gypsum-amended soil.

Plant	FGD gypsum Treatment g/kg soil	As			Hg		
		— $\mu\text{g/kg}$ plant tissue —			— $\mu\text{g/kg}$ plant tissue —		
		<i>stems</i> ¹	<i>cobs</i>	<i>grain</i>	<i>stems</i>	<i>cob</i>	<i>grain</i>
Corn	0	ND ²	ND	ND	27.8 ± 4.7	8.2 ± 2.1	11.6
Corn	1	ND	63 ± 31	ND	24.3 ± 5.7	7.6 ± 1.4	5.6 ± 2.2
Corn	2.5	160 ± 51	94 ± 62	ND	38.6 ± 10.6	10.9 ± 1.5	5.2 ± 1.9
Corn	5	N.D.	ND	ND	25.8 ± 4.7	6.7 ± 0.4	1.5 ± 0.6
Corn	10	52 ± 20	ND	ND	27.7 ± 1.8	5.3 ± 0.9	0.4 ± 0.3
		<i>stems</i>	<i> pods</i>		<i>stems</i>	<i> pods</i>	
Soybean	0	68 ± 35	45 ± 13		144 ± 13	17.6 ± 7.4	
Soybean	1	237 ± 102	ND		134 ± 10	5.6 ± 0.2	
Soybean	2.5	225 ± 27	ND		129 ± 4	--	
Soybean	5	236 ± 89	ND		150 ± 6	7.4 ± 1.1	
Soybean	10	123 ± 30	ND		155 ± 9	7.8 ± 0.4	
Brake Fern	0	727 ± 92			165 ± 5		
Brake Fern	1	696 ± 148			180 ± 15		
Brake Fern	2.5	683 ± 177			151 ± 6		
Brake Fern	5	394 ± 295			131 ± 17		
Brake Fern	10	579 ± 83			143 ± 11		

¹consists of stems and leaves

²ND – not detectable

Table 6. Multiple linear regression of arsenic concentration in soybean on arsenic concentrations in sequential extraction fractions from soil amended with FGD gypsum.

R^2	0.279				
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>
Regression	4	0.043	0.011	1.034	0.453
Residual	8	0.110	0.014		
Total	12	0.153			

	<i>Coefficients</i>	<i>P-value</i>
Intercept	3.351	0.450
H ₂ O-sol/exchangable	5.767	0.485
Al-bound	0.000 ¹	0.000
Fe and Org-bound	-1.675	0.476
Ca-bound	-2.064	0.508

¹Collinearity

Table 7. Multiple linear regression of arsenic concentration in brake fern on arsenic concentrations in sequential extraction fractions from soil amended with FGD gypsum.

R^2	0.059				
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>
Regression	4	0.068	0.017	0.229	0.916
Residual	11	1.090	0.099		
Total	15	1.159			

	<i>Coefficients</i>	<i>P-value</i>
Intercept	1.66	0.879
H ₂ O-sol/exchangable	11.87	0.508
Al-bound	0.00 ¹	0.000
Fe and Org-bound	0.37	0.949
Ca-bound	-2.99	0.702

¹Collinearity