

Discovery, The Student Journal of Dale Bumpers College of Agricultural, Food and Life Sciences

Volume 15

Article 17

Fall 2014

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Chris Wilbanks
University of Arkansas, Fayetteville

Kristofor Brye
University of Arkansas, Fayetteville

David Miller
University of Arkansas, Fayetteville

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Recommended Citation

Wilbanks, C., Brye, K., & Miller, D. (2014). Dilute-acid-extractable phosphorus, arsenic, and selenium in weathered and fresh coal fly ash. *Discovery, The Student Journal of Dale Bumpers College of Agricultural, Food and Life Sciences*, 15(1), 106-111. Retrieved from <https://scholarworks.uark.edu/discoverymag/vol15/iss1/17>

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Dilute-acid-extractable phosphorus, arsenic, and selenium in weathered and fresh coal fly ash

Chris Wilbanks^{}, Kristofor R. Brye[†], and David Miller[§]*

ABSTRACT

Fly ash is a byproduct of the combustion of coal, primarily by coal-fired power plants. Over 97.8 million tonnes of fly ash are produced each year in the United States. Fly ash can contain trace elements in concentrations that can cause health risks. Recent spills have highlighted that fly ash disposal is problematic. The objective of this study was to evaluate the effects of fly-ash type (fresh and weathered) from a local coal-burning power plant and extraction time (2 and 6 h) on dilute-acid extractable concentrations of phosphorus (P), arsenic (As), and selenium (Se). Ash samples were extracted with 0.1 M HCl and shaken for either 2 or 6 h. Extracts were analyzed by inductively coupled argon plasma mass spectrometry. Phosphorus concentrations increased with the longer extraction time, but there was no significant difference between ash type. Arsenic and Se concentrations were greater in fresh ash and decreased with longer extraction time in fresh ash, but no difference between extraction times was observed in weathered ash. It was determined that P concentrations were not related to As and Se concentrations, but were possibly dependent on calcium phosphates because of the high pH of fly ash. The lower As and Se concentration in the fresh ash, 6-h extraction, as compared to the 2-h extraction suggests that a process analogous to environmental weathering occurred during extraction. Research into the behavior and speciation of these insoluble forms will help explain movement and behavior of trace elements in fly ash.

* Chris Wilbanks is a May 2014 graduate who majored in Environmental, Soil, and Water Science, with minors in Sustainability and Geology.

† Kristofor Brye is a faculty mentor and a professor of Applied Soil Physics and Pedology in the Department of Crop, Soil, and Environmental Sciences.

§ David Miller is a faculty mentor and a professor in the Department of Crop, Soil, and Environmental Sciences.

MEET THE STUDENT-AUTHOR



Chris Wilbanks

I grew up in the suburbs of North Texas and was fascinated by nature documentaries and wanted to help protect natural environments. After graduating from Guyer High School in Denton, Texas, in May of 2010, I came to the U of A to study environmental science. Though the coursework was much more concrete than my lofty ideals of saving the planet, I came to enjoy them. Because I came into the program with a number of AP credits, I was able to focus on environmental coursework, particularly the wide variety of courses offered in the department and across the campus. With environmental issues in particular, different perspectives often collide, and the various backgrounds and teaching styles of the faculty helped me understand how agricultural, industrial, environmentalist, and scientific perspectives interact in real world projects. This is something I hope to carry forward as I pursue a Masters in Ecological Science and Engineering at Purdue University starting in the Fall of 2014. I would like to thank everyone in the Crop, Soil, and Environmental Sciences department for excellent teaching. I would also like to particularly thank Drs. Brye and Miller for helping me gain some very valuable lab experience, which I believe served as a controlled introduction to my future as a graduate student.

INTRODUCTION

In February 2014, a spill of coal wastes into the Dan River in North Carolina occurred. This began because of a leak from a retired power plant's ash landfill and took one week to stop (Shoichet, 2014). Cases such as this in recent years have heightened awareness and concern about the disposal of coal wastes and focused attention on the need for disposal methods that limit the potential for coal wastes to contaminate the air, water, and soil (Swan, 2014).

Fly ash is a subset of coal wastes that is produced during the burning of coal for power generation. Fly ash is precipitated from the smoke produced by coal combustion in order to meet air quality standards. Fly ash is predominantly inert, siliceous and aluminous glasses, which is similar to volcanic ash. Significant levels of base-forming cations are present in fly ash, giving the material a relatively high pH. Lower concentrations of trace elements, such as arsenic (As), selenium (Se), cadmium (Cd), and chromium (Cr), are also present (Ahmaruzzaman, 2010). Table 1 summarizes the composition and chemical properties of a typical Class C fly ash produced from a coal-burning power plant in northwest Arkansas.

Fly ash is disposed of in a variety of ways, the most common being landfilling. Other disposal methods include use in cement and use as a soil amendment. Land-

filling is the dominant form of fly ash disposal (Ahmaruzzaman, 2010), but little scientific research has been undertaken into the status of fly ash landfills. Ash landfills were not required by Arkansas state law to include a liner until recently, and there are still no federal restrictions. Siting is also not restricted, which can lead to spills of material, as in the case of the Dan River. Use of fly ash as an additive in cement is common, where fly ash serves

Table 1. Selected properties of Flint Creek Power Plant fresh fly ash (adapted from Cantrell, 2014).

Ash Property	Value
Silicon	29.9%
Aluminum	18.4%
Iron	6.9%
Calcium	29.1%
Magnesium	6.2%
Potassium	0.3%
Phosphorus	1.3%
Carbon	0.1%
Selenium	9.0 mg/kg
Arsenic	< 1 mg/kg
pH	11.5

Elements were determined by weight in a total digest. pH was determined at 25 °C (1% slurry). Carbon measured is Total Carbon.

both as a pozzolan that provides structure to concrete and as a source of lime that is required in the Portland cement chemical reaction (Helmuth, 1987). Fly ash has two uses when used as a soil amendment. Fly ash can function as a liming material to raise soil pH due to the high amounts of base-forming cations, particularly calcium (Ca), that are present in the ash. Fly ash can also be used as a fertilizer to supply micronutrients, such as sulfur (S) and boron (B) (Pandey and Singh, 2010).

Use of fly ash is often limited by trace element content. Trace elements, some of which are also heavy metals, occur in fly ash due to coal's organic origin. Minute amounts of trace elements that were present in the precursor plant tissue were preserved when the plant tissue underwent lignification to become coal. These elements volatilize when coal is combusted and then condense in the ash that is left over, concentrating the trace elements in coal wastes (Ahmaruzzaman, 2010). These trace elements, such as As, Se, and Cd, can pose environmental health risks. Trace elements differ from other contaminants in soil because, unlike organic compounds or pathogens, they cannot be degraded. Contamination can also persist because trace elements sorb to soil colloids or precipitate into solid phase minerals, which can dissolve and be mobilized with alteration of pH. Both of these mechanisms can replenish the active fraction in the soil solution, which is the fraction that poses the greatest environmental health risk.

Currently, the United States Environmental Protection Agency (USEPA) does not regulate the disposal of coal wastes. The USEPA has considered classifying coal wastes as a hazardous material under the Resource Conservation and Recovery Act of 1976, but in both 1993 and 2000, USEPA determined coal wastes to be non-hazardous (USEPA, 2014a). The USEPA has remained concerned about the potential for coal wastes to cause environmental damage and in 2010 reopened the investigation into classifying coal wastes as hazardous. This investigation is slated to release a final decision by December 2014 (USEPA, 2014a).

In a previous study (Cantrell, 2014) of the same fly ash material used in the present study, As and Se were selected for examination due to their toxicity and similar chemical behavior. Phosphorus (P) was also examined because P and As are both Group 15 elements from the periodic table that exhibit similar chemical behavior and exist as oxyanions in soils. Research has indicated that As and P compete for sorption sites in soil (McDonald et al., 2009). This is of particular concern in northwest Arkansas, as many soils are saturated with P from decades of land application of P-rich poultry litter (Daigh et al., 2010). Research has also suggested that in low pH Ultisols, P is more competitive for soil adsorption sites than As (Violante and Pigna, 2002). However, Se is a Group 16

element and is more mobile than As and P, acting similarly to sulfate in soil, which can threaten groundwater.

The central premise of this study was that land application of fly ash is a viable method of fly ash disposal in northwest Arkansas as long as leaching of As and Se can be shown to be insignificant. It is likely that long-term storage of ash in ash landfills changes the chemical forms and leachability of trace elements, but research on the topic is scarce. The objective of this study was to evaluate the effects of long-term storage and extraction time (2 and 6 h) on dilute-acid extractable concentrations of P, As, and Se in fresh and weathered ash. It was hypothesized that extractable P, As, and Se concentrations would be greater in fresh than weathered ash and that extractable P, As, and Se concentrations would be greater after a 6-h extraction than a 2-h extraction.

MATERIALS AND METHODS

Fly Ash Materials. Samples of fly ash were collected from the Flint Creek Power Plant in Benton County, Ark., which is operated by the American Electric Power-Southwestern Electric Power Company (AEP-SWEPCO; Cantrell, 2014). The plant uses Powder River Basin coal from the Wyodak Beds in Wyoming (Cantrell, 2014). Fresh samples were collected over a 30-d period from 7 July 2013 to 5 August 2013 during normal plant operation from the plant's fly ash collection piping (Cantrell, 2014). Weathered samples were collected from the on-site ash landfill, which has been used to store fly ash since the plant began operation in 1978 (Cantrell, 2014). The actual age of the weathered ash is unknown due to the disposal method, but samples were collected from areas believed to have the oldest ash (Cantrell, 2014).

Ash Extraction Procedures. Ash samples were extracted following procedures similar to those outlined by Daigh et al. (2010) and McDonald et al. (2009), using a solid:solution ratio of 1:10 (mass:vol) or 3 g fly ash in 30 mL of 0.1 M HCl, dispensed into 50-mL plastic centrifuge tubes. Ten samples each of fresh and weathered ash were further divided into a 2- and a 6-h shake time on an end-over-end shaker, for a total of five samples in each ash type-extraction time combination. For each group of samples, three control samples of 30 mL HCl with no fly ash were run under the same experimental conditions to serve as method blanks for quality control. After being removed from the shaker, samples were centrifuged at 6000 revolutions per minute and filtered through 0.45- μ m Suppor-450 membrane filter (Pall Life Science, Port Washington, N.Y.) into 20-mL scintillation vials. Immediately following the filtration, samples were stored at 4 °C until they were shipped the following week to the University of Georgia for analysis, where a Perkin-Elmer

Elan 6000 inductively coupled plasma mass spectrometer was used to measure As, Se, and P concentrations.

Statistical Analyses. A two-factor analysis of variance was conducted using SAS (version 9.3, SAS Institute Inc., Cary, N.C.) to evaluate the effects of ash type, extraction time, and their interaction on concentrations of As, Se, and P. Means were separated by least significant difference at the 0.05 level.

RESULTS AND DISCUSSION

Ash type and extraction time affected the extractability of all three elements evaluated in this study (Table 2). Dilute-acid-extractable P varied only by extraction time ($P = 0.049$), while As and Se concentrations varied by extraction time within ash type ($P < 0.001$). The mean extractable P concentration was 9.6 mg/kg for the 2-h extraction and 19.3 mg/kg for the 6-h extraction time. One possible cause for this observed trend is the dissolution of calcium phosphates, which are soluble at low pH. With

a longer extraction time, it is possible that the reaction was allowed to continue to equilibrium in the 6-h extraction, while in the 2-h extraction, equilibrium had not yet been reached. However, the experimental procedure used in this study did not include measurements of the rate of P release. Phosphorus concentration showed no statistically significant relationship to As or Se with ash type or extraction time (Table 2). Due to the experimental design not including interaction with soil, it is unclear how P amendment from fly ash could affect the solubility of As, particularly in Northwest Arkansas.

Dilute-acid-extractable As concentrations were greatest from the fresh ash with a 2-h extraction (18.2 $\mu\text{g As/kg}$; Fig. 1), while all other treatment combinations had a lower mean As concentration and did not differ among themselves (Fig. 1). Similar to As, dilute-acid-extractable Se was greatest from the fresh ash with a 2-h extraction time (258 $\mu\text{g Se/kg}$; Fig. 1). However, in contrast to As, extractable Se was also greater from the fresh ash with a 6-h extraction time than from the weathered ash at either extraction times, which did not differ (Fig. 1).

Table 2. Analysis of variance summary of the effects of ash type, extraction time, and their interaction on dilute-acid extractable phosphorus (P), arsenic (As), and selenium (Se).

Source of Variation	P	As	Se
Ash Type	0.684	< 0.001	< 0.001
Extraction Time	0.049	< 0.001	< 0.001
Ash Type * Extraction Time	0.690	< 0.001	< 0.001

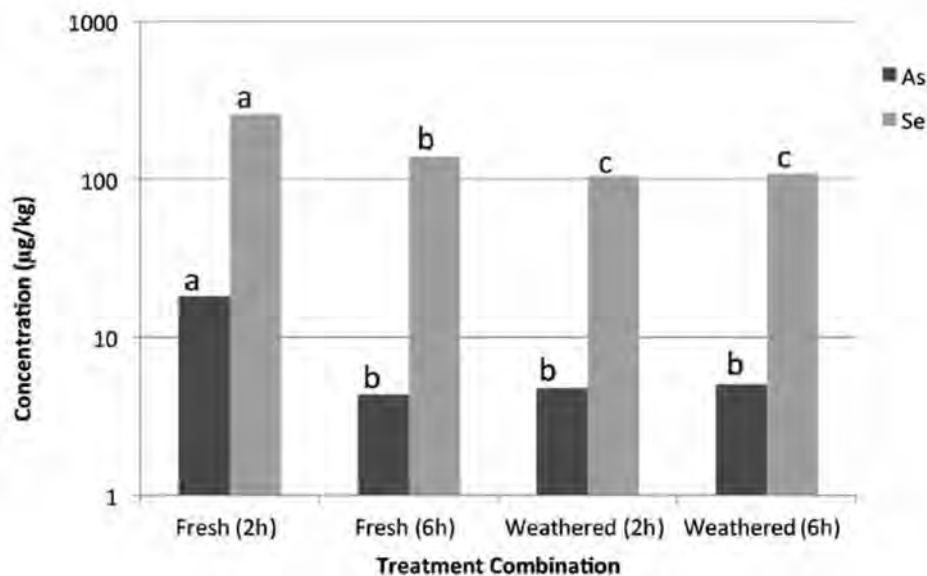


Fig. 1. The effects of ash type (i.e., freshly collected and weathered for a long period of time in an ash landfill) and extraction time (i.e., 2 and 6 h) on mean concentrations of arsenic (As) and selenium (Se). For a given element, different letters atop bars denote significant differences at the 0.05 level.

Arsenic concentration in the fresh ash 2 h extraction are greater than the USEPA's Maximum Contaminant Level (0.010 ppm) (USEPA, 2013). Additionally, all measured concentrations of Se are greater than the MCL (0.050 ppm) (USEPA, 2014b). However, these are measurements of total element concentrations, and not speciation, which plays a large role in toxicity. The choice of extractant has also elevated results above those of a previous study with the same material (Cantrell, 2014).

The lack of a significant difference between extraction times for weathered ash, as well as a decline with greater extraction time from the fresh ash, indicate that some process is serving to create non-reactive or insoluble forms of As and Se over both extraction and storage times. As weathered ash was exposed to environmental weathering for years prior to the study, it is possible that the mechanism that caused an observed reduction in concentration with extraction time in fresh ash is also involved in the lower extractable concentrations in weathered ash.

Analysis in a prior study (Cantrell, 2014) indicated that calcium selenite (CaSeO_3) and hydrated complexes of calcium and aluminum oxides served as a sink for Se. It takes a period of several months to stabilize these compounds under environmental conditions, such as those to which the weathered ash was exposed, during which time selenite (Se^{+4}) can oxidize to selenate (Se^{+6}), a far more mobile form that can easily leach (Cantrell, 2014). This indicates that acid extraction in the fresh ash may have followed a chemical process similar to the formation of CaSeO_3 to render a larger fraction of the Se insoluble, giving a similar result to that of the weathered ash.

The dominant form of As in coal wastes is the less soluble arsenate (As^{5+}). Arsenic undergoes similar reactions as Se to form precipitates, but is unlikely to reduce to more mobile forms (Cantrell, 2014). The overall lower level of initial soluble trace elements contributed to the lower observed concentrations, and it is probable that a similar chemical process explains the observed decline in As between fresh ash extractions. Speciation of As and Se was not performed in this study, which would have determined what forms the As and Se existed in, but further research into the chemistry of these trace element species would be helpful.

Results of this study both support and negate the initial hypotheses. The forms of trace elements within the weathered ash are likely dominated by insoluble forms, due to transformations, such as the weathering process of Se discussed above, and leaching of mobile forms to soil and ultimately groundwater over years of infiltration. If the results of the weathered ash are indicative of how fresh ash would behave environmentally, then this fly ash would be suitable for disposal via land application. However, the actual chemical speciation and reactivity of the trace ele-

ments are still largely unknown. The wide temporal and spatial variability of soil properties leaves open the possibility that insoluble forms deemed safe could dissolve under conditions not currently understood and eventually pose a health risk. However, concerns about the concentration of P displacing trace elements seem unlikely given the results of this study. Observed P concentrations increased with extraction time, but As and Se were both lower in weathered ash, which has been exposed to environmental conditions similar to those land-applied fly ash might experience. This indicates that processes controlling P are different from those controlling As and Se. Currently, the best usage of fly ash for land application as it is currently understood is to base maximum application rates on total trace element concentration, until such time that the speciation of the stable forms are better understood.

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