Potential for Metal Leaching and Toxicity from Fly Ash Applied for Increasing Carbon Sequestration in Soil

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ABSTRACT

Previous work with leaching of metals from several fly ashes (both class F and class C) indicated minimal potential of leaching of toxic levels of metals from most fly ashes tested. Also, mixing fly ash with soil and other amendments (phosphate fertilizer) significantly decreases Cr, Li, Pb, and Cd in the leachate. One concern is that the characteristics of fly ash may be changed by the addition of NOx removal equipment that potentially results in higher levels of ammonia in the fly ash. We are concerned with fly ash since our laboratory and field studies show that addition of fly ash may increase carbon sequestration in reclaimed mine soils. However, the use of such amendments must overcome public concerns about the possible release of toxic metals before the practice is generally accepted. We have recently been testing fly ash with a wide range of pH (3.7-12.4) originating from systems with SCR systems for NOx removal equipment. Three types of leaching experiments were done on these samples and soils from near a power plant. Batch and column leaching experiments were done using dilute CaCl solutions. In addition samples were leached using a nitric acid method. All three methods indicated that the potential for leaching heave metals was greatest in the highest ammonia sample tested. However, toxicity testing with the Microtox© system has indicated little potential toxicity in leachates from the fly ash sources except for the fly ash at the highest pH (12.4) and no measured toxicity in the highest ammonia sample. When the leachate from the high pH fly ash was neutralized, toxicity was eliminated. Additional data on ammonia and metal concentrations in high ammonia and high pH fly ash leachates should enable greater generalizeability of the results.

INTRODUCTION

The rise in atmospheric carbon dioxide (CO_2) levels coupled with implications for global climate change have led to interest in the potential to store or sequester carbon in terrestrial environments.[7,13,19] This may create an opportunity to utilize fly ash in the reclamation of mine soils and to offset CO_2 emissions by increasing carbon content of soils. However, concerns associated with the use of fly ash must be addressed.

Fly ash amendments may be useful in promoting terrestrial carbon sequestration on currently underutilized and degraded lands. Nearly 2×10^9 ha of land are considered to be degraded worldwide.[18] In the United States alone, approximately 4×10^6 ha consist of degraded lands previously used for mining operations.[28] Based upon the 1.4×10^8 ha of poorly managed lands estimated for the United States and estimates of carbon sequestration within degraded lands (i.e., 1.5 Mg C yr^{-1} ha^{-1}), there is a potential for degraded lands in the United States to sequester approximately 11 Pg of carbon over the next 50 years.[2,21] Because these lands are degraded, improvements in the soil through applications of soil amendments may promote more rapid carbon sequestration.

The potential for beneficial use of fly ash as a soil amendment is well documented. Ash additions to easily clodded, clay loam soil increased aggregation, while decreasing bulk density and the modulus of rupture.[26] Fly ash has been shown to increase porosity, water-holding capacity, pH, conductivity, and dissolved SO_4^{2-}, CO_3^{2-}, HCO_3^-, Cl^- and basic cations, although some effects are notably decreased in high-clay soils.[20,24] Preliminary results from field and laboratory experiments indicate fly ash may promote sequestration of CO_2 in soil.[4,23]

The primary concern with use of fly ash as a soil amendment is the potential leaching of hazardous metals, especially when applying high rates of ash.[1,8,14] Further, new technologies may influence leaching of metals from fly ash. In 1990 the Clean Air Act Amendments were passed in an effort to better control post-combustion generation of NOx, an ozone precursor. The processes of selective non-catalytic reduction (SNCR) and selective catalytic reduction (SCR) were born as methods of decreasing NOx, and can result in NOx reductions of upwards of 50%.[25] Both processes involve injecting ammonia (or related compounds) into flue gas.

Difficulties may arise with these NOx-reduction strategies when the catalysts for the reaction become less efficient.[25] Over time increasing amounts of ammonia, in the form of ammonium salt, are present in the flue gas following the SCR or SNCR unit processing, a trend known as "ammonia slip." [6,17,25] This free ammonia then adsorbs onto the fly ash, and is later released as ammonia gas when fly ash-augmented concrete becomes alkaline as it is hydrated for pouring.[6,17]

The purpose of our research is to address the concerns related to application of fly ash to soil, the leaching of materials from fly ash and in particular metals and toxicity. The research reported here addresses the differences in leaching likely to be seen with the use of high ammonia fly ash when compared to low ammonia ash for soil amendment.

METHODS

Sources of fly ash and soil

Fly ash was obtained from various power companies from systems and plants (Table 1) using SCR scrubbers. These samples were selected for the potentially high concentrations of ammonia in the fly ash. The fly ash samples were obtained within weeks of the start of the leaching experiments. In addition 3 soil samples from near a power plant were used for comparison in some of the leaching experiments as indicated below (Table 1).

Table 1. Fly ash and soil used in the three types of leaching experiments.

Material	Class	pH	NH_4	Notes	Experiments[1]
B	F	3.98	0.70	SCR Scrubber	Ba, Co, Acid
C	C	3.66	95.6	SCR scrubbers, Cyclone, course grind	Ba, Co, Acid
H	C	12.4	0.50	Line sprayer dryer & SCR scrubber	Ba, Co, Acid
S1	C	4.06	4.45	SCR Scrubber	Ba, Co, Acid
S2	C	4.13	1.85	SCR Scrubber	Ba, Co, Acid
Soil16	NA				Ba, Acid
Soil 44	NA				Ba, Acid
Soil 49	NA				Acid

[1] The three types of leaching experiments are indicated as: Ba = Batch, Co = column, Acid = Nitric Acid

Fly Ash Characterization

Ammonia was extracted by adding 2 M KCl to 12 g of fly ash and extracting on a shaker for 2 hours. The samples were removed from the shaker and then placed in a refrigerator where they were allowed to settle for 1 week. The samples were removed from the refrigerator and the clear supernatant was decanted. Ammonia analysis was run using two methods. Samples taken at the time of the experiment for ammonia analyses were placed into a freezer until the technician was able to run the samples on a Bran Luebbe AAIII autoanalyzer. The samples were stored in the freezer for approximately a month prior to analysis. Due to reproducibility problems with these samples, fresh extracts were made from the original fly ash several months (February 2005) after the initial analysis. These samples were analyzed with Hach spectrophmetric technique immediately after extraction. The pH of the fly ash was measured in a mixture of 2 parts water to 1 part fly ash. The moisture content of the fly ash was measured by assessing loss of weight of 10 grams of sample upon drying in a 40°C oven for 24 hours.

Experimental Design

Three sets of leaching experiments were run with the fly ash samples. A set of samples (SCR fly ash and 3 soils) was extracted using a nitric acid procedure (below). In the acid extraction experiment two replicate samples were analyzed. Batch (saturated) leaching experiments (see below) were run with both the SCR fly ash samples and two soil samples (Table 1). Column (unsaturated) experiments were only run with the fly ash samples. For the column and batch experiments three replicates of each sample were leached and analyzed.

Nitric acid extraction followed EPA SW-846 Method 3050B (Acid Digestion of Sediments, Sludges, and Soils). A 1.5 g (wet weight) sample of each fly ash was extracted with 70% HNO_3 at 95°C.

For the column experiments a series of 50 ml volume columns were set up on ring stands. The bottom of the column was lined with glass wool to prevent the solid fractions from flowing through the column. A total of 10 g of fly ash was placed into the column and 100 ml of 5mM $CaCl_2$ was slowly added and allowed to flow through the column. A small rubber hose and a syringe were mounted at the bottom end of the column, allowing the sample to be pulled through the column. Collected effluent was filtered and analyzed as described below.

In the batch experiments a total of 10 g of fly ash was mixed with 100 ml of 5mM $CaCl_2$. The mixture was then placed on a low speed shaker for 48 hours. The mixture was then removed from the shaker and placed on a centrifuge at 2000 rpm for 15 minutes. The clear supernatant was extracted, filtered, and analyzed as described below.

Elemental Analysis

In all cases the collected effluents were filtered through a 0.2 um acrodisc filter. The filtered leachates were placed in vials for later analysis. The analysis was run on a Perkin Elmer 9000 Elan ICP-MS using procedures as described by the manufacturer. Blanks were run and subtracted from sample analysis. If a negative number resulted from the subtraction, the sample value was reported as zero.

Statistical Methods

Statistical analysis was performed on the leachate data using SAS software (SAS, Cary, NC). Principal component analysis was performed on the leachate composition data from the nitric acid extractions of the fly ash sources and soil. The leachate composition from the column and batch experiments was examined using a two-way analysis of variance (ANOVA) with fly ash source and leaching type (batch or column) as factors.

Toxicity Measurements

Toxicity of the column leachates was assessed using a Microtox 500 analyzer. The Microtox system is a standard biosensor-based measurement technique for toxicity testing of water and soil.[9,12] The method uses the luminescent bacteria *Vibrio fischeri* NRRL-11177. The luminescent bacteria were added to the leachates and the toxicity was measured by the decreased luminescence compared to a negative control. A positive control was run using a multi-element standard (Perkin Elmer, Shelton, CT) containing Al, As, Ba, Be, Bi, Cd, Co, Cr, Cs, Cu, Fe, Ga, Li, Ni, Pb, Rb, Se, Ag, Si, Ti, V, and Zn .

RESULTS AND DISCUSSION

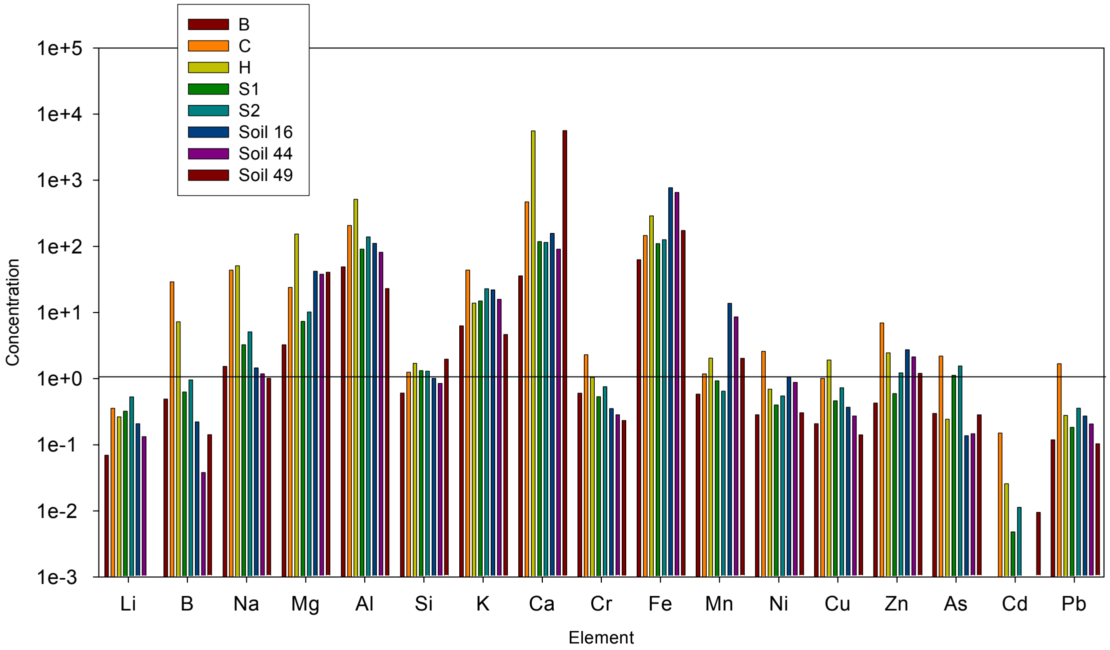
Fly Ash Characterization

The fly ash ammonia content was highest (in the 2nd set of ammonia measurements) in the C fly ash sample (Table 1). At the time of this measurement (about 4 months after the leaching experiments), none of the other samples exhibited the extreme ammonia concentration noted in this sample. We had run ammonia measurements at the time of the leaching experiment using a different technique with different results. Some of these samples exhibited high ammonia (data not shown). However, there were significant problems of reproducibility and standardization with those measurements and we have no confidence in those results. In the next set of experiments, ammonia concentration will be assayed with the new technique on fresh leachates. In general, although all these samples were obtained from plants with SCR units, there appeared to be significant differences in ammonia content from the different sources.

Metal Leaching

Differences in leaching potential between the different sources of fly ash are even more evident in the nitric acid leachates. There were many instances of detection of heavy metals in the nitric acid leachates (Figure 1). There is known to be a distinct inverse relationship between pH of the leachate and the concentration of metals in the leachate.[15] However, with the nitric acid leaching we often were able to detect heavy metals in the soils. Boron was predominately found in the fly ash samples and at much lower concentration in the soils samples (Figure 1). The soils appeared to have appreciable iron when compared to the fly ash.

Figure 1. Elements in leachates from nitric acid leaching experiments.

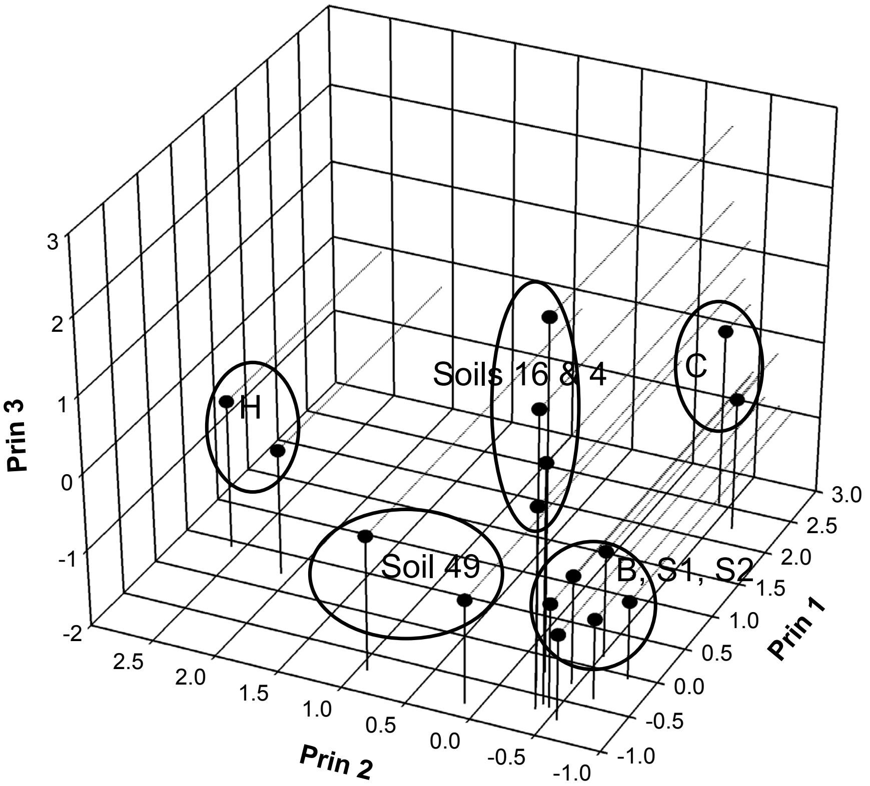


A principal component analysis of the data from the nitric acid leaching indicated that there were differences in leaching characteristics among the different fly ash samples (Figure 3). The three principal components accounted for 84% of the variation in the leaching of metals from the samples, with a high percentage of that accounted for by the first principle component (50%). Smaller amounts were accounted for by the next two principal components (19% and 15%).

The separation of the different types of samples in the principal component analysis indicated the differences in leaching characteristics among the samples. The replicate samples tended to group together indicating similar leaching characteristics (Figure 3). The C (high ammonia) and H (high pH) samples clearly separated from the other samples and each other. Two of the soil samples (16 and 44) grouped together and were separated from the other soil sample (49). Finally the low pH fly ash samples (B, S1, and S2) all tended to group together. This group included two C type fly ash samples (S1 and S2) and one type F sample (B). The groupings indicated that the pH and ammonia tended to have more influence in the leaching of these samples than the type of fly ash.

The elements that load highly positive on the first principle component are the heavy metals (Table 2) except for Cu. Thus, the C (high ammonia) sample stood apart in its leaching of heavy metals from the other samples (Figure 2). The 2nd principle component separated the H (highest pH fly ash) from the others. Included on the factors that loaded heavily on this 2nd component were Cu, Ca, and Mg.

Figure 2. Plot of 3 principal components for nitric acid leachates. Solid drop lines indicate position on the P1 x P2 plane and dotted lines indicate position on P2 x P3 plane.

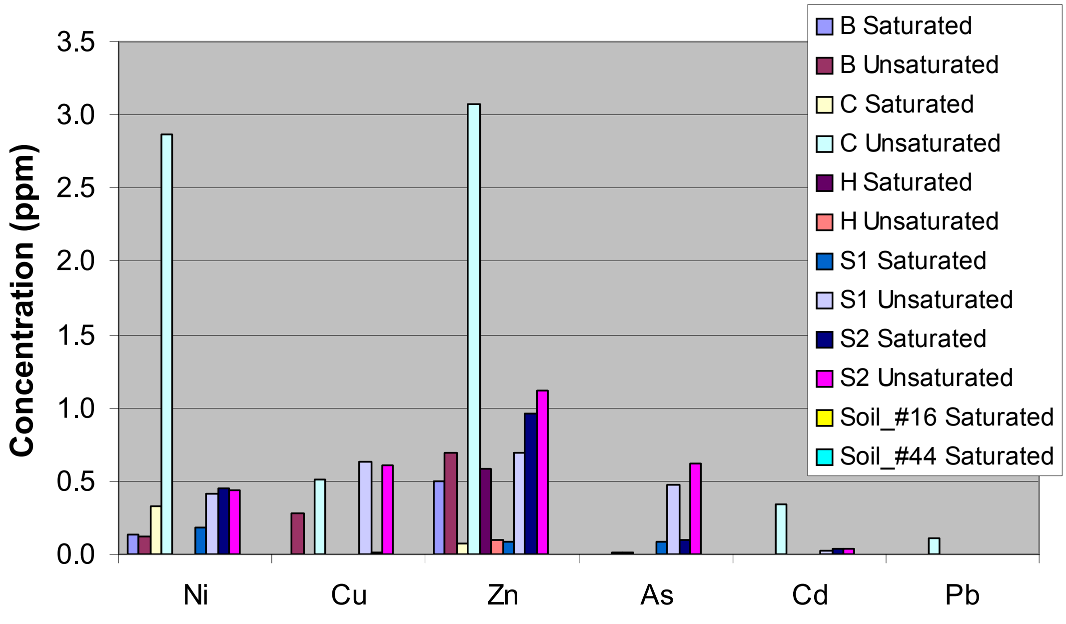


Examination of the leaching data from the batch and column experiments indicated that heavy metal leaching potential was greatest in the C sample (Figure 3). In general the S2 sample had the next highest content of heavy metals in the leachate. Ni, Zn, and Cu concentrations in the leachates were generally higher than As, Cd, and Pb. Lead was only detectable in the C sample. The differences that occurred between saturated and unsaturated (batch vs. column) leaching indicated that the concentrations in the unsaturated leachates tended to be greater than in the unsaturated leachates (Figure 3). In previous experiments with low ammonia fly ash, we have found that the leaching of metals such as As, Cd, and Pb were reduced in leachates when fly ash was mixed with soil.[22] There may also be a kinetic limitation on leaching as in previous experiments we found that two weeks of exposure of fly ash to water in columns increased leaching of B, As, and Cd.[22]

Table 2. Loading of elements on the 3 principal components. The elements loading most heavily on the components are indicated by bold type.

Element	Prin1	Prin2	Prin3
As	0.2706	-0.2377	-0.2360
B	**0.3415**	0.0040	-0.0137
Ca	-0.0243	**0.5075**	-0.1020
Cd	**0.3391**	-0.0353	-0.0238
Cr	**0.3428**	0.0120	-0.0809
Cu	0.1953	**0.4029**	-0.0769
Fe	-0.0467	0.0510	**0.6211**
K	0.3157	-0.1469	0.1912
Li	0.1942	-0.0947	-0.0745
Mg	0.0388	**0.5505**	0.1102
Mn	-0.0877	-0.0414	**0.6026**
Na	0.2718	0.3451	-0.0490
Ni	**0.3142**	-0.0707	0.2536
Pb	**0.3402**	-0.1035	0.0403
Si	0.0508	0.2225	0.0905
Zn	**0.3151**	-0.0033	0.2026

Figure 3. Heavy metals in leachates from column (unsaturated) and batch (saturated) leaching experiments.



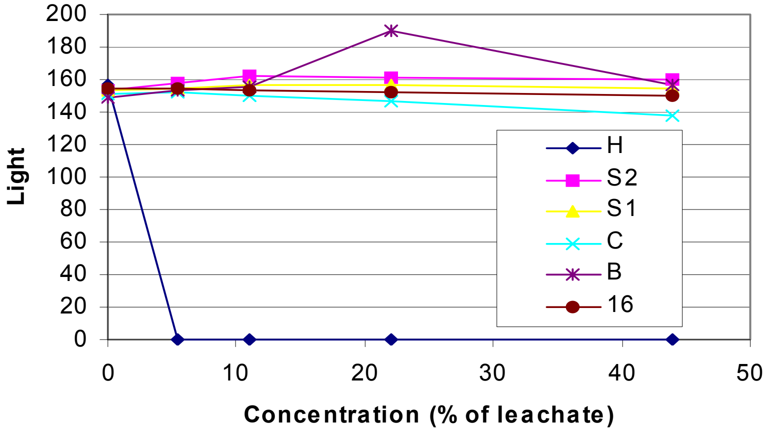
Toxicity

The results using the Microtox© system indicated that only the batch leachate from the H sample exhibited any toxicity (Figure 4). The pH of this leachate was 12.4 (Table 1) and when the leachate from this fly ash was neutralized, toxicity was eliminated (data not shown). Thus the effect may have been a pH effect or the neutralization of the leachate might have precipitated out toxic metals. We have run similar toxicity tests on other high pH fly ash samples and have not seen toxicity.[22] However, others have seen toxicity with coal ash samples extracted under harsh conditions (HCl or acetic acid extraction) at low pH 4.[16] It is important to consider the leaching method when assessing toxicity with the Microtox system as results are influenced by the method chosen.[11] Thus, additional data on ammonia and metal concentrations actually present in the fly ash, in neutralized leachate, and using mixtures of soil and fly ash with environmentally relevant leachates should help indicate potential sources of toxicity (if any) and variations among the fly ashes.

Implications

The decision on which amendments to use in promoting carbon sequestration in degraded lands will be influenced by many factors such as emissions of other greenhouse gases and potential for leaching of pollutants from the amendments. The leaching of metals from fly ash is one such factor that we continue to address. Experiments here and with other fly ash samples have indicated that under mild extraction conditions leaching of heavy metals is minimal.[22]

Figure 4. Microtox results for batch leached samples.



While low pH appears to be a major negative determinate in natural revegetation of many surface mine in the eastern USA, fly ash and other coal combustion residues can contribute Ca^{2+} and other basic cations to improve soil structure and increase the pH of acidic soils.[27] Also, soil depth and associate bulk water holding appears to be a positive factor in establishing white pine (*Pinus strobes*) on mine spoil.[5] Thus, fly ash incorporation within increased depths of soil, or the effective rooting zone, could be beneficial. The low pH and low ammonia fly ash samples here showed less potential for leaching of many metals than the higher pH and higher ammonia samples.

High ammonia fly ash appears to cause some problems with other uses of fly ash such as pozzolanic admixture in concrete.[3,6] The use of high ammonia fly ash for soil application should be examined further to see if potential leaching of metals seen in the harsh nitric acid experiments is reflected in more environmentally relevant leaching methods and in mixtures with soil.

CONCLUSIONS

There appeared to be significant differences in leaching characteristics with respect to heavy metals in the highest ammonia fly ash and the high pH fly ash. However, the toxicity of the high ammonia fly ash sample as measured by the Microtox method was still undetectable. The only toxicity was seen with the highest pH sample and neutralization of the leachate eliminated the toxicity. More studies of leaching of high ammonia fly ash under environmentally relevant conditions are needed.

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REFERENCES

[1] Adriano, D. C. and Weber, J. T. Journal of Environmental Quality, 2002, 30, p.596.

[2] Akala, V.A. and Lal, R. Land Degradation and Development, 2000, 11, pp. 289-297.

[3] American Coal Ash Association (ACAA). www.acaa-usa.org, 1999.

[4] Amonette, J. E., Kim, J., Russell, C. K., Palumbo, A. V., and Daniels, W. L. In Proceedings of the Second Annual Conference on Carbon Sequestration, Alexandria, Virginia, 2003.

[5] Andrews, J.A., Johnson, J.E., Torbert, J.L., Burger, J.A., and Kelting, D.L. Journal of Environmental Quality, 1998, 27, p.192.

[6] Bittner, J., Gasiorowski, S., and Hrach, F. In Proceedings of the 2001 International Ash Utilization Symposium, Lexington, Kentucky, 2001.

[7] Bruce, J.P., Frome, M., Haites, E., Janzen, H., Lal, R., and Paustian, K. Journal of Soil and Water Conservation, 1999, 54, pp. 382-9.

[8] Carlson, C. L. and Adriano, D. C. Journal of Environmental Quality, 1993, 22, p.227.

[9] Chang, J. C., Taylor, P.B., and Leach, F.R. Use of the Microtox Assay System for Environmental-Samples Bulletin of Environmental Contamination and Toxicology, 1981, 26, pp. 150-6.

[10] Crews, J.T., Dick, W.A. Environmental Pollution, 1998, 103, p.55.

[11] Dombroski, E. C., Gaudet, I.D., Florence, L. Z, and Qureshi, A. A. A comparison of techniques used to extract solid samples prior to acute toxicity analysis using the microtox test Environmental Toxicology and Water Quality, 1996, 11, pp. 121-8.

[12] Donnelly, K. C., Brown, K.W., Anderson, C. S., and Thomas, J.C. Environmental Toxicology and Chemistry, 1991, 10, pp. 1123-1131.

[13] Eve, M.D., Howerton, S. K., Paustian, K., and Follett, R. F. Journal of Soil and Water Conservation, 2002, 57, pp. 196-204.

[14] Gangloff, W. J., Ghodrati, M., Sims, J. T., and Vasilas, B. L. Journal of Environmental Quality, 1997, 26, p.714.

[15] Kazonich, G., and Kim, A.G. Proceedings of the 1999 International Ash Utilization Symposium, Lexington, Kentucky, 1999

[16] Karuppiah, M., and G. Gupta. Journal of Hazardous Materials, 1997, 56, pp. 53-8.

[17] Külaots, I., Gao, Y., Hurt, R. H., and Suuberg, E. M. In Proceedings of the 2001 International Ash Utilization Symposium, Lexington, Kentucky, 2001.

[18] Lal, R., Kimble, J. M., Follett, R. F, and Cole, C. V. The Potential of U.S. Cropland to Sequester Carbon and Mitigate the Greenhouse Effect. Sleeping Bear Press, Ann Arbor, MI, 1998, 128pp.

[19] Lal, R., Follett, R. F., and Cole, C. V. Journal of Soil and Water Conservation, 1999, 54, pp. 374-381.

[20] Matsi, T., and Keramidas, V.Z. Environmental Pollution, 1999, 104, p.107.

[21] Oldeman, L.R., and Vanengelen, V.W.P. Geoderma, 1993, 60, pp. 309-325.

[22] Palumbo, A. V., Fisher, L.S., Tarver, J. R., Daniels, W. L., Yang, Z., Tiquia, S.M., Wu, L., Zhou, J., and Amonette, J. In: Proceedings of the 2nd Annual Conference on Carbon Sequestration. May 5-8, 2003. Alexandria, Va. http://www.carbonsq.com/proc.cfm?paper_id=5E

[23] Palumbo, A. V., Daniels, W. L., Burger, J. A., McCarthy, J. F., Wullschleger, S., Amonette, J., and Fisher, L.S. Advances in Environmental Research, 2004, 8, pp. 425-438.

[24] Pathan, S. M., Aylmore, L. A. G., and Colmer, T. D. Journal of Environmental Quality, 2003, 32, p.687.

[25] Rathbone, R. F., and Majors, R. K. In Proceedings of the 2003 International Ash Utilization Symposium, Lexington, Kentucky, 2003.

[26] Sale, L.Y., Chanasyk, D.S., and Naeth, M.A. Canadian Journal of Soil Science, 1997, 77, p.677.

[27] Skousen, J.G., Johnson, C.D., and Garbutt, K. Journal of Environmental Quality, 1994, 23, p.1224.

[28] [USDA] U.S. Department of Agriculture. Soil Conservation Service, National Technical Information Service, 1979, SCS-TP-158.