

# Leaching of Mixtures of Biochar and Fly Ash

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## INTRODUCTION

Increasing atmospheric levels of greenhouse gases, especially CO<sub>2</sub>, and their effects on global temperature have led to interest in the possibility of carbon storage in terrestrial environments.<sup>2, 7, 9</sup> Both the residual char from biomass pyrolysis<sup>10-12, 15</sup> (biochar) and fly ash from coal combustion<sup>1, 16, 17</sup> have the potential to significantly expand terrestrial sequestration options. Both biochar and fly ash also have potentially beneficial effects on soil properties. Fly ash has been shown to increase porosity, water-holding capacity, pH, conductivity, and dissolved SO<sub>4</sub><sup>2-</sup>, CO<sub>3</sub><sup>2-</sup>, Cl<sup>-</sup> and basic cations.<sup>13, 14, 19</sup> Adding biochar to soil generally raises pH, increases total nitrogen and total phosphorous, encourages greater root development, improves cation exchange capacity and decreases available aluminum.<sup>3, 20</sup> A combination of these benefits likely is responsible for observed increases in yields for crops such as corn and sugarcane.<sup>20</sup> In addition, it has been found that soils with added biochar emit lower amounts of other greenhouse gases (methane and nitrous oxide) than do unamended soils.<sup>11, 20</sup>

Biochar and fly ash amendments may be useful in promoting terrestrial carbon sequestration on currently underutilized and degraded lands. For example, about 1% of the US surface lands consist of previously mined lands or highway rights-of-way.<sup>21</sup> Poorly managed lands could count for another 15% of US area. Biochar and fly ash amendments could increase productivity of these lands and increase carbon storage in the soil.

Previous results showed minimal leaching of organic carbon and metals from a variety of fly ashes.<sup>18</sup> In the present study, we examined the properties of mixtures of biochar, fly ash, and soil and evaluated the leaching of organic carbon and metals from these mixtures.

## MATERIALS AND METHODS

### *Sources of biochar, fly ash and soil.*

Two samples of biochar were obtained that differ in the process and temperature used to produce them. Biochar HW (courtesy of Stefan Czernik) was prepared by the National Renewable Energy Laboratory, Golden, CO, using the thermochemical

process development unit (TCPDU). It is a gasification char from hardwood; the highest treatment temperature was 600 °C. Biochar OKEB (courtesy of Danny Day) was prepared by Eprida, Corp. of Athens, GA. It is a slow-pyrolysis char from oak; the highest treatment temperature was about 475 °C. Fly ash and soil were collected at the Tennessee Valley Authority site in Paradise, KY.

#### *Carbon-nitrogen analysis.*

In the combustion method, 0.5-0.6 g of soil were weighed in a ceramic sample boat. The sample was inserted into the combustion chamber in a LECO® CN-2000 element analyzer (LECO Corporation, St. Joseph, MI) which heated samples to 1350 °C in the presence of oxygen. The combustion gases were analyzed for CO<sub>2</sub> (infrared spectroscopy) and N<sub>2</sub> (thermal conductivity detector). The elemental analyzer was calibrated with standards traceable to the National Institute of Standards and Technology (Gaithersburg, MA).

#### *pH measurements.*

In order to measure the pH of the biochar, fly ash and soil, mixtures of 2 parts water, 1 part sample and 2 parts 5mM CaCl<sub>2</sub> were prepared. The mixtures were mixed in a low speed shaker at room temperature for 2 hours and centrifuged at 2,000 rpm for 10 minutes in a 50 ml tube swinging-bucket rotor at room temperature. The pH was measured in the supernatant.

#### *Carbon sorption experiments.*

Carbon sorption experiments were performed in batch by mixing 0.5 g of biochar samples with a series of humic acid concentrations (0-100 mg C/L) dissolved in 5 mM CaCl<sub>2</sub> in 30 ml final volume. However, the biochar was very light and was difficult to resuspend as it usually floated on the liquid solution. After shaking the mixtures for 48 hours, the mixtures were centrifuged for 15 minutes at 2,000 rpm in a 50 ml tube swinging-bucket rotor at room temperature. TOC and pH was measured in the supernatants.

#### *Leaching experiment design.*

The leaching experiments were run in duplicate using columns with different amounts of biochar, fly ash, and soil (Table 1). Columns made of 50 ml syringes 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. CaCl<sub>2</sub> (100 ml of a 5mM solution) was slowly dripped into the column. A short tube connected to a syringe was mounted at the bottom end of the column, allowing the sample to be pulled through the column. Effluent was collected, filtered and analyzed for chemical composition and toxicity measurements.

In the batch experiment, 10 g of biochar was mixed with 100 ml of 5mM CaCl<sub>2</sub>. After shaking the mixtures for 48 hours, the mixtures were centrifuged for 15 minutes at 2,000 rpm in a 50 ml tube swinging-bucket rotor at room temperature. Then the supernatant was filtered and analyzed for chemical composition and toxicity measurements.

Preparing the column with the biochar sample was more manageable and the biochar sat in place between the other components of the column (Table 1).

**Table 1: Composition of columns for leaching experiments**

Column layers	Column 1: S	Column 2: FA	Column 3: B-HW/S	Column 4 B-HW/S/FA	Column 5 B-OKEB/S	Column 6 B-OKEB/S/FA	
Lower	Soil (10g)	Fly Ash (10g)	Biochar HW (1g)	Biochar HW (1g)	Biochar OKEB (1g)	Biochar OKEB (1g)	
Middle			Soil (9g)	Soil (8g)		Soil (9g)	Soil (8g)
Upper				Fly Ash (1g)			Fly Ash (1g)

#### *Element analysis.*

Filtered leachate samples were analyzed on a Perkin Elmer 9000 Elan ICP-MS following the manufacturer's instructions. Blanks were run and subtracted from the sample analysis. If a negative number resulted from the subtraction, the sample value was reported as zero.

#### *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.<sup>3, 6</sup> The method uses the luminescent bacteria *Vibrio fischeri* NRRL-11177. The luminescent bacteria were added to the leachates and 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

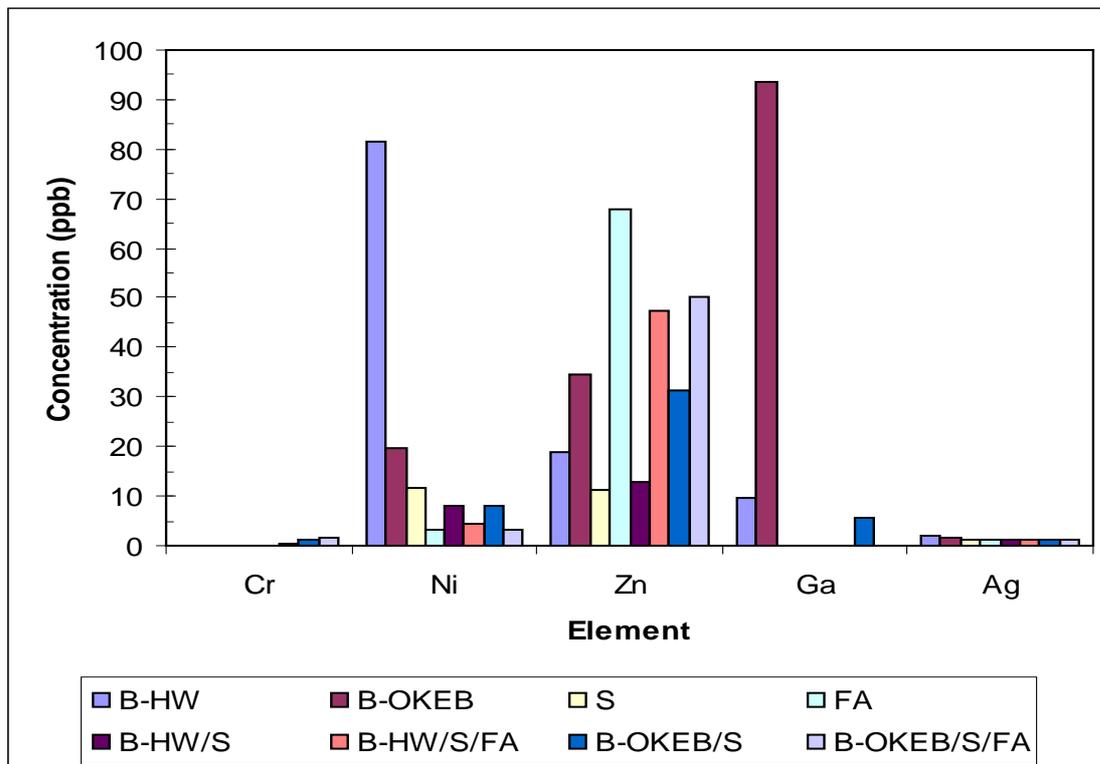
The carbon sorption experiments showed release of carbon from biochar rather than sorption except at the highest concentrations in the Biochar HW sample (Table 2). In previous work<sup>16</sup> we showed very high potential rates of sorption for fly ash. In contrast, the biochar showed a large release of carbon during the same type of experiments (Table 2). We previously observed typical Langmuir isotherms with the fly ash<sup>16</sup> but with the biochar the results were very scattered (Table 2) and for the Biochar OKEB sample we observed carbon release even at the highest amount of humic acid added (100 mg C/L) with a final concentration in the solution of 257 mg C/L. In contrast, the Biochar HW showed carbon release to high concentrations (approximately 40 mg C/L) of added humic carbon but at the highest concentrations there was some sorption. Similar results were obtained by Chang and Berner<sup>4, 5</sup> for oxidative leaching of bituminous coal, in which more C was released as dissolved C than was oxidized to CO<sub>2</sub> by oxygen in water.

We confirmed that both fly ash and two types of biochar (oak char [OKEB], and hardwood [HW] char) exhibited minimal leaching of heavy metals including Cr, Ni, Zn, Ga, and Ag (Figure 1) and no detectable leaching of Pb or Cd (data not shown) under the conditions tested. Biochar HW showed increased leaching of Ni and Biochar OKEB

showed increased leaching of Ga. In comparison, lower levels of Zn and Ni were reported previously using fly ash samples.<sup>18</sup> The Biochar HW had a slightly higher C/N ratio (334) and pH (7.7) than did the Biochar OKEB (284 and 6.5, Table 3).

**Table 2. Carbon sorption experiments using the biochar samples.**

Humic Acid Added mg C/L	Biochar HW Measured Concentration mg C/L	Biochar OKEB Measured Concentration mg C/L
0.485	192.5	46.890
2.588	114.8	71.88
5.592	181.600	55.40
7.377	171.5	164.9
11.96	177.2	130.9
21.56	119.7	179.8
31.02	148.4	267.4
40.96	43.41	59.16
52.42	53.73	251.8
62.19	65.7	179
81.35	79.32	194
102.00	97.45	257.1



**Figure 1. Heavy metals found in leaching samples. The values are the average of duplicate samples Abbreviations are as shown as in Table 1.**

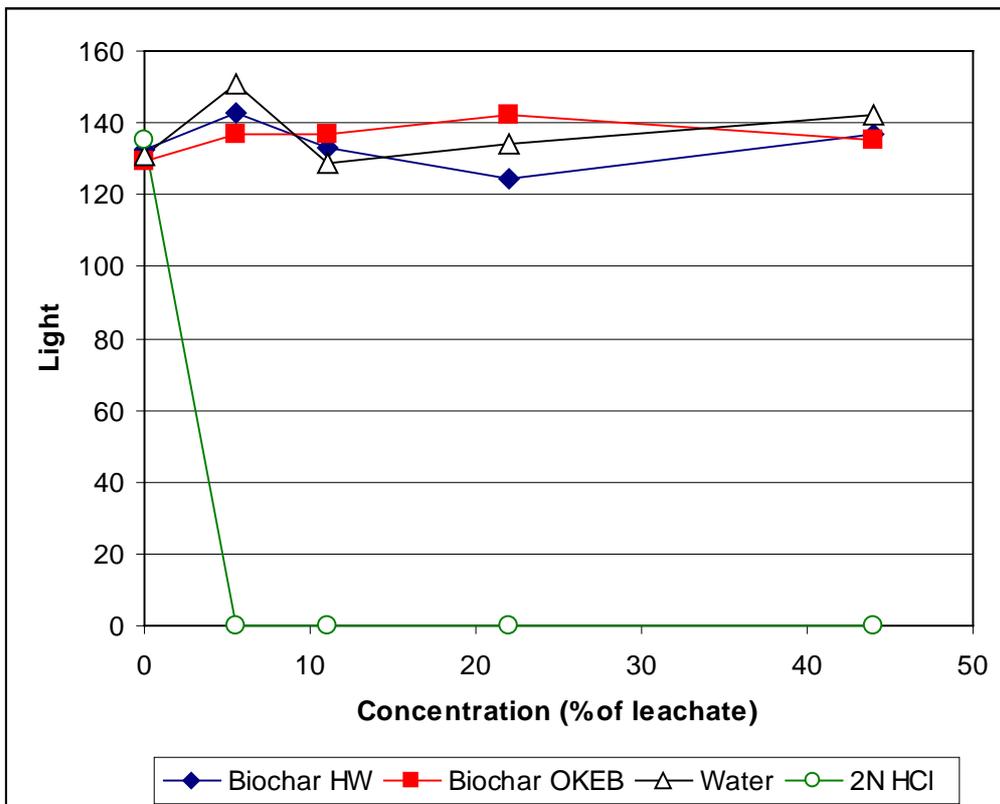
**Table 3. Characteristics of the two biochar samples.\***

Sample ID	Nitrogen %	Carbon %	C:N %	pH in Water	pH in 5mM CaCl <sub>2</sub>
Biochar HW	0.26	86.79	334	8.8	7.7
Biochar OKEB	0.24	68.12	284	6.0	6.5

\* The values are the average of duplicate samples.

There was no toxicity exhibited by the fly ash (not shown) or biochar leachates (Figure 2) as measured by the Microtox® assay under the conditions tested. In previous results no toxicity was reported in testing the fly ash samples except one high pH sample.<sup>18</sup> The pH of the biochar samples fell at mid-range (pH 7.7 and 6.5, Table 3).

The most notable leachate component from both types of biochar, but not the fly ash, was organic carbon with the HW biochar leaching less organic carbon than the OKEB biochar (5.71 ppm vs. 59.3 ppm). Alone (in batch sorption experiments), or in mixtures of 90% soil and 10% biochar (column studies), we noted significant loss of carbon from the biochar into soluble components. However, when we added fly ash to the column experiments (80% soil, 10% fly ash, and 10% biochar) we observed significant decreases in the amounts of C leached (20% for HW, and 47% for OKEB).



**Figure 2: Microtox results for biochar samples. No toxicity was found using the biochar samples. Water and 2 N HCl were used as controls. The values are the average of duplicate samples.**

The results indicate that applying a combination of fly ash and biochar may result in maximizing the amount of carbon sequestration in soil while also increasing beneficial soil properties and fertility. The lower amount of carbon leached from the HW biochar compared to the OKEB biochar is likely due to the more recalcitrant form of the carbon in the HW char, due to its preparation at a higher temperature (600 °C) than the OKEB biochar (450 °C). High heat treatment temperatures during biochar preparation increase both the total carbon content of the biochar and the proportion of the carbon that is present in fused aromatic rings resistant to chemical and physical degradation.<sup>8</sup> Additional leaching tests with biochar samples covering a range of heat treatment temperatures and feedstocks would help to confirm our hypothesis.

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## REFERENCES

- [1] Amonette, J.E., Kim, J., Russell, C.K., Palumbo, A.V., and Daniels, W.L. International Ash Utilization Symposium, Lexington, KY 2004.
- [2] Bruce, J.P., Frome, M., Haites, E., Janzen, H., Lal, R., and Paustian, K. *Journal of Soil and Water Conservation* 1999, 54, pp. 382-389.
- [3] Chang, J.C., Taylor, P.B., and Leach, F.R. *Bull Environ Contam Toxicol*, 1981, 26, pp. 150-156.
- [4] Chang, S., and Berner, R.A. *Environ. Sci. Technol.*, 1998, 32, pp. 2883-2886.
- [5] Chang, S., and Berner, R.A. *Geochim. Cosmochim. Acta* 1999, 63, pp. 3301-3310.
- [6] Donnelly, K.C., Brown, K.W., Anderson, C.S., and Thomas, J.C. *Environmental Toxicology and Chemistry*, 1991, 10, pp. 1123-1131.
- [7] Eve, M.D., Sperow, M., Howerton, K., Paustian, K., and Follett, R.F. *Journal of Soil and Water Conservation*, 2002, 57, pp. 196-204.
- [8] Krull, E. In: *Characteristics of Biochar-Organo-Chemical Properties*, (Eds J. Lehmann and S. Joseph), Earthscan, London, 2009, Chpt. 4.
- [9] Lal, R., Follett, R.F., Kimble, J., and Cole, C.V. *Journal of Soil and Water Conservation* 1999, 54, pp. 374-381.

- [10] Lehmann, J. *Nature*, 2007, 447, pp. 143-144.
- [11] Lehmann, J., Gaunt, J., and Rondon, M. *Mitigation and Adaptation Strategies for Global Change*, 2006, 11, pp. 403-427.
- [12] Marris, E. *Nature*, 2006, 442, pp. 624-626.
- [13] Matsi, T., and Keramidas, V.Z. *Environ Pollut*, 1999, 104, pp. 107-112.
- [14] McCallister, D.L., Frank, K.D., Stevens, W.B., Hergert, G.W., Renken, R.R., and Marx, D.B. *Soil Sci*, 2002, 167, pp. 811-820.
- [15] Ogawa, M., Okimori, Y., and Takahashi, F. *Mitigation and Adaptation Strategies for Global Change*, 2006, 11, pp. 429-444.
- [16] Palumbo, A.V., Amonette, J.E., Tarver, J.R., Fagan, L.A., McNeilly, M.S., and Daniels, W.L. *World of Coal Ash*, Covington, KY 2007.
- [17] Palumbo, A.V., Daniels, W.L., Burger, J.A., McCarthy, J.F., Wullschleger, S., Amonette, J.E., and Fisher, L.S. *Advances in Environmental Research*, 2004, 8, pp. 425-438.
- [18] Palumbo, A.V., Tarver, J.R., Fagan, L.A., McNeilly, M.S., Ruther, R., Fisher, L.S., and Amonette, J.E. *Fuel*, 2007, 86, pp. 1623-1630.
- [19] Pathan, S.M., Aylmore, L.A., and Colmer, T.D. *J Environ Qual*, 2003, 32, pp. 687-693.
- [20] Renner, R. *Environ Sci Technol*, 2007, 41, pp. 5932-5933.
- [21] [USDA] U.S. Department of Agriculture, Soil Conservation Service, National Technical Information Service, SCS-TP-158, 1979.