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Soil Chemistry Still Affected 23 Years After Large Application Of Fluidized Bed Combustion Ash

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SOIL CHEMISTRY STILL AFFECTED 23 YEARS AFTER LARGE APPLICATION OF FLUIDIZED BED COMBUSTION ASH

ABSTRACT

This experiment was a followed-up on a study conducted by Korcak (1988) in which large quantity of Fluidized Bed Combustion Ash (FBCA) was applied to an established apple orchard to determine yield and nutrient content of leaves and fruits. This study was conducted to 1) assess the movement of macro and micro elements in an apple (*Malus domestica* Borkh.) orchard soil that received a one time application of 36 kg $m^{-2}$of fluidized bed combustion ash (FBCA) 23 years earlier and 2) determine the effects of these changes on soybean and alfalfa growth. Fifteen composite samples were collected from the area at three depths 0-10, 10-20 and 20-30 cm. Samples were also collected from similar depths in an adjacent non-orchard field with the same soil type as a control. The FBCA increased soil pH values from 4.9 to 7.7 in the sub-surface. Mehlich-3 extractable Al, Mn and Zn concentrations did not increase with application of FBCA; however, Cu, Ca, P and Mg did. For the 0-10 cm depth, Ca concentration increased from 0.39 to 22.7g kg^{-1}. Total combustible mercury concentrations for the FBCA treatment were similar to those of the control soil. Soybean and alfalfa growth did not change significantly with FBCA application. Results from this study demonstrated that 23 years after FBCA application, some sub-soil chemical properties remained high but did not reach toxic levels for soybean and alfalfa growth.

INTRODUCTION

Large quantities of coal byproducts such as fly ash, bottom ash, boiler slag, flue gas desulfurization (FGD) gypsum, wet and dry scrubber materials and fluidized bed combustion ash are produced annually in the United States (MacDonald, 2008). He stated that of the 125 million tons of coal combustion byproduct produced in the United States in 2006; only 43 percent were being used beneficially. Presently, a large portion of these coal byproducts are being stored on site or placed in land fills (Ramme and Jacobsmeyer, 2008). With the increase cost and regulations for land fills, land applications of byproducts are becoming more economically feasible (Norton et al. 1998). Alternative uses such as agricultural have been investigated (Kurama and Kaya, 2008, Codling et al., 2002; Codling and Wright, 1998; McCarty et al., 1994; Korcak, 1988). Small applications of coal byproducts to agricultural land have improved soil fertility and water infiltration (USDA, 1997; Codling et al., 2002; Codling and Wright, 1998; Stehouwer et al., 1998).

Fluidized Bed Combustion Ash (FBCA) is a dry high calcium, alkaline residue produced during the removal of gaseous emissions of sulfur from coal (USDA, 1997). Limestone is added to coal during the combustion process in order to reduce sulfur emission to the environment (Chang et al., 1991; Korcak, 1988). Generally, FBCA has been applied based on the lime requirement of a soil. However, this material is sometimes applied at higher rates because of the need to dispose of large amounts of ash (Wright et al., 1998). In a pot study, Korcak (1980) observed reduction in apple seedling growth when FBCA was applied at rates eight times the lime requirement of the soil. However, in a field experiment Korcak (1988) observed no adverse effects on apple trees when larger quantities of FBCA were applied to established apple trees. He concluded that there is a potential for application of large quantities of FBCA to agricultural land.

There are concerns, however, of long-term effects of these materials on soil properties and potential heavy metal accumulation in soil when these materials are applied at disposal rates to agricultural lands. Although, coal byproducts may contain low levels of heavy metals, application of large amounts may increase heavy metal concentrations in the soil and adversely impact soil properties and fertility over time (Jegadeesan et al., 2008).

To evaluate the nutrient availability of the FBCA amended soil alfalfa (*Medicago sativa* L.) and soybean [*Glycine max* (L.) Merr.] were selected for this experiment as test crops due to their high calcium and phosphorus requirement (Hanson and Barnes, 1973; Smiciklas et al., 1989).

This experiment was a followed-up on a study conducted by Korcak (1988) in which a large quantity of Fluidized Bed Combustion Ash (FBCA) was applied to an established apple orchard to determine yield and nutrient content of leaves and fruits 23 years earlier.

The objective of our study was to assess the long-term effects of disposing of high volume of FBCA on change in soil pH, leaching of macro and micro nutrients through the sandy soil profile and the availability of nutrients for soybean and alfalfa growth.

MATERIAL AND METHODS

Soil for this study [Rumford loamy sand (coarse-loamy, siliceous, mesic Typic hapludult)] with pH of 5.8 and calcium of 440 mg kg^{-1} was collected from an old apple [*Malus domestica* Borkh.] orchard on which a one time application of FBCA was made 23 years earlier (Korcak, 1988).

The characteristics of the FBCA are presented in Table 1. The FBCA was surface applied at a rate of 36 kg m^{-2} to determine the effects of high volume of FBCA applications on soil chemical properties, yield and nutrient concentration in apple leaves and fruit (Korcak, 1988).

Apple trees were removed two years prior to this study but the soil was not plowed or mixed. Presently grass, tall fescue (*Festuca arundinacea* Schreb.) is being grown on the area which is mowed three times per year. No additional fertilizer was applied to this area after the previous experiment was terminated. Each soil sample was a composite of five soil samples taken with a 15 mm diameter stainless soil probe. Each soil core was divided into increments of 0-10, 10-20 and 20-30 cm depth. The exposed surface of each soil core was scraped to prevent possible contamination of the subsurface soil by the surface soil during the removal of the soil probe. For the control, five soil samples of the same soil type were collected from an adjacent field that did not receive FBCA application. Although, in most cases the 0-10 cm depth was mostly un-reacted FBCA, tall fescue growth on this area was similar to that of the study area. Soil samples were air dried, crushed with a stainless steel rolling pin and sieved through a 2 mm screen. Soil pH was determined with a1:1 soil de-ionized water slurry, after 1 hr equilibrium. Calcium, Mg, P, Al, Cu, Mn and Zn were determined using a Mehlich-3 extraction (Mehlich, 1984). Soil samples from 0-10 and 10-20 cm depths were analyzed in duplicate with a blank after every 20 samples. Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) was used with scandium as an internal standard to determine Ca, Mg, P, Al, Cu, Mn and Zn concentrations in the Mehlich-3 extracting solution. Total mercury was determined with a DMA-80 direct mercury analyzer (Milestone Inc Shelton, CT). Total carbon was determined with a LECO analyzer (St. Joseph, MI).

Bulk soil was collected from the previously sampled FBCA and control sites at three depths (0-15, 15-30 and 30-45 cm) for a greenhouse study. Soil from each depth was sieved to < 3 mm and 1.7 kg was placed into a plastic pot 15 cm in diameter with three replicates, making a total of 36 pots.18 pots were planted with soybean and 18 with alfalfa. Pots were placed randomly on a greenhouse bench. Greenhouse conditions were 16 hour light and 8 hour darkness. One week after planting plants thinned to 4 and 20 soybean and alfalfa respectively per pot. Plants were harvested five weeks after planting and dry weight was determined. Statistical Analysis System was used to determine the significance of the soil amendment treatment and growth (SAS Institute, 2003). Separation of means was determined using Duncan's multiple range tests at $p < 0.05$ (Steel and Torrie, 1980).

Table 1: Selected properties of Fluidized Bed Combustion Ash

Elements	FBCA
pH	12.5
Cu mgkg^{-1}	36
Mn mg kg^{-1}	25
Zn mg kg^{-1}	80
Al g kg^{-1}	19.2
Fe g kg^{-1}	10.2
P_2O_5 g kg^{-1}	0.2
MgO g kg^{-1}	8.0
CaO g kg^{-1}	330
$CaSO_3$ g kg^{-1}	60
$CaSO_4$ g kg^{-1}	520

Source: Korcak, 1988

RESULTS AND DISCUSSIONS

Soil pH

Fluidized bed combustion ash (FBCA) significantly increased soil pH at all depths compared to the control soil (Table 2). For example, pH value at the lowest depth sampled (20-30 cm) increased from 4.94, for the control to 7.65 for the FBCA treatment. The increase in soil pH may have resulted from the leaching of calcium carbonate from the FBCA through the soil profile over time. The higher pH at the lower depth may improve soil fertility by reducing metal activities and making essential nutrients more available for crop uptake. Foy (1992) found that liming acidic subsoil reduces aluminum solubility and increased essential nutrient solubility which improved crop production. Organic carbon (OC) in the FBCA amended soil was higher than the control; for example, in the 0-10 cm depth OC levels were 1.93 and 27 g kg^{-1} for the and control and FBCA amended soils respectively.

Mehlich-3 Extraction

The FBCA application significantly increased magnesium (Mg) concentrations in the 0-10 cm depth compared to the control (Table 2). However, there were no significant difference in Mg concentrations between the control and FBCA treatments at the 10-20 and 20-30 cm depths. The higher Mg in the surface FBCA treated soil may have resulted from Mg (dolomitic) limestone that is sometimes used during coal combustion (USDA, 1997).

Table 2: Effects of FBCA application on soil pH and Mehlich-3 extractable soil nutrients after 23 years.

Treatments	Depth	pH	Mg	P	Ca
	cm		------------mg kg^{-1}-----------		----g kg^{-1}----
Control	0-10	4.92c†	72b	6.85b	0.39d
Control	10-20	4.98c	44c	1.53c	0.20d
Control	20-30	4.94c	65bc	0.15c	0.23d
FBCA	0-10	7.88ab	302a	10.9b	22.75a
FBCA	10-20	8.03a	76b	18.5a	4.22b
FBCA	20-30	7.66b	61bc	8.38b	1.52c

† Means within columns with the same letters are not significantly different at $p<0.05$.

Phosphorus (P) concentrations were higher for FBCA treatment compared to the control (Table 2). The highest P concentration for the FBCA was at the 10-20 cm depth and was twelve times as high as the control at this depth. For example, at the 10-20 cm depth P concentrations for the control were 1.53 compared to18.5 mg kg^{-1} for the FBCA treatment. The higher P at the 10-20 cm depth shows that soluble P did moved from the 0-10 cm where there was less soil to FBCA ratio and accumulates in the lower depth where there was a higher soil to FBCA ratio. Calcium concentrations were significantly higher when FBCA was applied compared to the control (Table 2). Calcium concentrations for the 0-10 cm depth increased from 0.39 for the control to 22.7 g kg^{-1} for the FBCA. Calcium concentrations decreased significantly with increasing depth for the FBCA treatment but not for the control. Even though, Ca moved through the soil profile Ca concentrations at the 0-10 cm depth were 14 times as high as for the 20-30 cm depth. The application of the high lime (calcium carbonate) FBCA significantly increased Ca concentration in this soil over time.

There were no significant difference in mercury concentrations between the control and FBCA amended soil (Table 3). Copper concentrations in the FBCA amended soil were significantly higher than those of the control (Table 3). For example, at the 0-10 cm depth Cu concentrations were 2.24 mg kg^{-1} for the FBCA compared to 1.28 mg kg^{-1} for the control. For the control, Cu concentrations decreased with depth but there were no significant differences between the 10-20 and 20-30 cm depths. Only for the 20-30 cm depth of the FBCA treatment was the Cu concentration significantly different. Even though, Cu concentrations were significantly higher for the FBCA than for the control, Cu levels were much lower than levels found in other agricultural soils.

Table 3: Effects of FBCA application on Mehlich-3 extractable soil metals after 23 years.

Treatments	Depth	Hg	Cu	Zn	Mn	Fe	Al
		--------------mg kg^{-1}--------------					
Control	0-10	0.108a†	1.28c	5.31a	55.0 a	408a	1010ab
Control	10-20	0.065b	0.64d	3.17b	35.9 b	189b	1029a
Control	20-30	0.064b	0.40d	2.85b	17.6c	149c	1049a
FBCA	0-10	0.103a	2.43a	4.51a	7.47d	132 c	909bc
FBCA	10-20	0.048b	2.64a	3.15b	24.4c	165bc	420d
FBCA	20-30	0.050b	1.80b	2.93b	16.2c	168bc	809bc

† Means within columns with the same letters are not significantly different at $p<0.05$.

There were no significant differences in zinc concentrations when FBCA was added compared to the control (Table 3). For both the control and the FBCA treatment, Zn concentration decreased with depth, but there were no significant differences between Zn levels at the two lower depths.

In all cases, manganese (Mn) concentrations were significantly higher in the control soil than in the FBCA treated soil (Table 3). Manganese concentrations in the control decreased with depth while the Mn concentrations for the FBCA treated soil increased with depth.

Iron concentrations were significantly higher in the control soil compared to the FBCA treatments and decreased with depth (Table 3). Iron concentration in the FBCA treatment increased slightly with depths. The lower iron in the FBCA soil may have resulted from the increased in pH from the FBCA application.

Aluminum (Al) concentrations were significantly higher for the control soil compared to the FBCA amended soil and did not change significantly with depth (Table 3). The lower Al may have resulted from the higher pH of the FBCA (Table

2). Aluminum concentrations for the FBCA amended soil at 0-10 and 20-30 cm depth were twice as high as the concentration at10-20 cm depth although there was little change in pH values. For example, Al concentrations for the 0-10 and 20-30 cm depths of the FBCA amended soil were 909 and 809 mg kg $^{-1}$ with a pH of 7.88 and 7.66 respectively, compared to 420 mg kg^{-1} for the 10-20 cm depth with a pH of 8.03.

Crop Dry Weight

Soybean dry weight for the control at the 0-15 cm depth was not significantly different from that of the FBCA treatment (Figure 1). Dry weight decreased with increasing depth for both the control and the FBCA treatment. The dry weight of the crops grown on the FBCA treatment, however, was lower than that for the control. One possible reason for the lower dry weight for the crops grown on the FBCA treatment may be resulted from lower amount of available nutrients, even though the pH and essential nutrients were higher at the lower depth compared to the control soil. Alfalfa dry weight for the FBCA treatment was greater or equal to that of the control for the three depths. Further tissue analysis is needed to determine the availability of the macro and microelement for plant uptake.

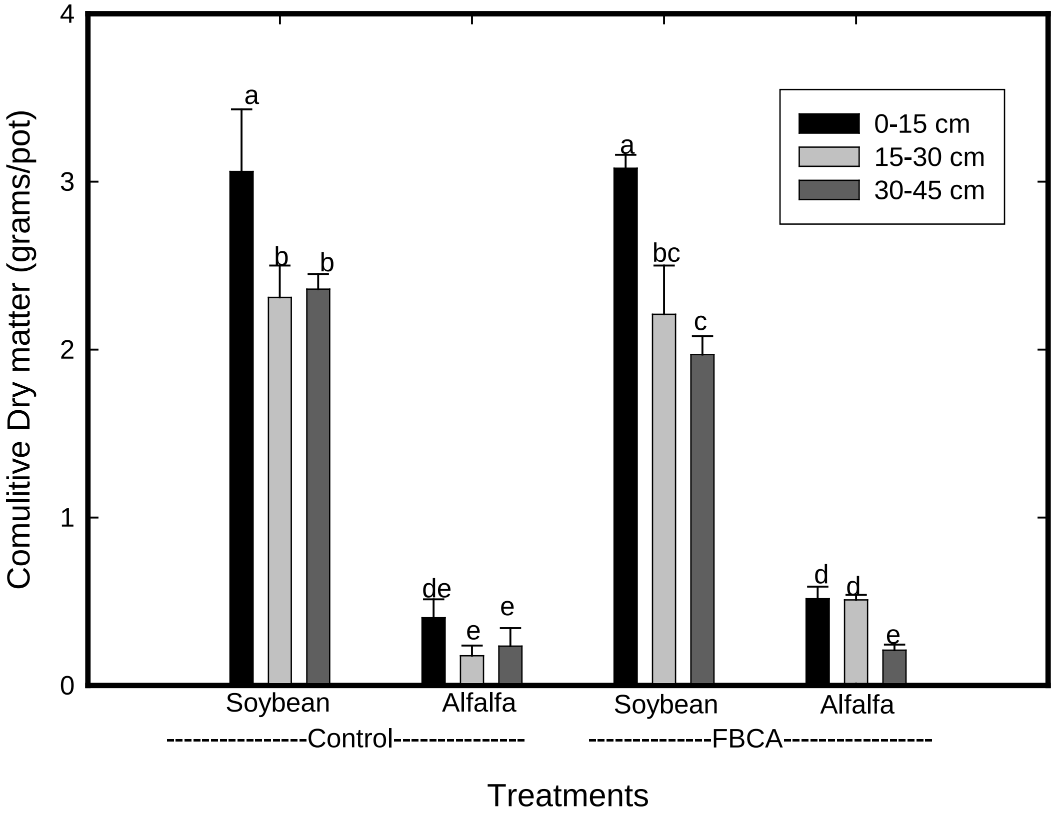

Figure1: Long-term effects of FBCA on soybean and alfalfa dry matter with increasing soil depth. Means plus standard deveation, n=3. Columns with the same letter are not significant $p<0.05$.

CONCULSIONS

Results from this study demonstrated that 23 years after an extremely high application (36 kg m^{-2}) of fluidized bed combustion ash, soil chemical properties have changed throughout the soil profile. The higher pH, calcium, magnesium, and phosphorus concentrations observed in the lower depths were not reflected in higher soybean and alfalfa dry weight. The small difference in alfalfa and soybean dry weight between the FBCA treated and control soil may have resulted from a low availability of plant nutrients for crop uptake.

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