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Transport of Heavy Metals and Cations in a Fly Ash Amended Soil

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The potential for heavy metal contamination of groundwater in and around coal combustion residue disposal sites is one of the main areas of concern regarding proper disposal of these by-products. The use of fly ash as an amendment to agricultural soils has been investigated to explore its effects on crop growth and production. Precautions must be taken to prevent possible water contamination as a result of fly ash usage in agricultural soils (Dreesden *et al.* 1977; Menon *et al.* 1990; Riekerk 1983). Dreesden *et al.* (1977) showed positive correlations between the concentrations of either water or acid extractable B, F, Mo, and Se or acid extractable As in fly ash and those of the similar elements in effluent waters near a fly ash landfill. Solubility of fly ash in water is an important factor which determines the extent of water pollution from fly ash (Rohrman 1971).

Most soils in citrus production areas in Central Florida are high in sand content with little organic matter. Attention must be given to leachability of constituents from any of the soil applied amendments while managing these soils. An investigation on the possibility of application of fly ash to these sandy soils for citrus production must be preceded by an evaluation of leachability of various metals following the application of fly ash. The objective of this study was to investigate the transport of heavy metals and cations in a sandy soil amended with various rates of fly ash.

MATERIALS AND METHODS

Plexiglass columns (30-cm long, 7-cm inner diameter) were employed to study the transport and leaching of cations and heavy metals from a fly ash amended soil. A Candler fine sand (uncoated, hyperthermic Typic Quartzipsamments; pH = 5.5, sand = 96.7%, organic matter = 1.3%) was sampled from a citrus grove near Lake Alfred, Polk County, FL. The soil was air-dried, ground to pass a 2-mm sieve, and packed in the above columns to a height of 28-cm (bulk density of 1.5 g/cm^3). A Whatman

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No. 42 filter paper was placed at the bottom of the soil column. Fly ash from Tampa Electric Company (TECO, Tampa, FL) was used in this study which contained 6.62% Fe and 208, 115, 111, 82, 56, 48, and 20 mg/kg Zn, Cr, Mn, Pb, Ni, Cu, and Cd, respectively. The application rates were: 0, 10, 20, 30, 40, and 50% of the soil (by weight basis). The quantity of fly ash as required by the treatment was mixed uniformly with top 10-cm depth soil in the column. The experiment was conducted with three replications.

A Whatman No. 42 filter paper was also placed at the top of the soil column. The packed soil was saturated and excess water was allowed to drain overnight. Distilled water was applied to the top of each column at a constant flow rate of 1.0 $mL \cdot min^{-1}$ using a peristaltic pump. Leachate fractions were collected at each 1/2 pore volume (pore volume = 463 cm^3) for a total of five pore volumes. The electrical conductivity (EC) and pH of each leachate fraction were measured. Concentrations of Ca, Cu, Mn, Fe, Pb, Zn, Cr, and Se in the leachate were determined using inductively coupled plasma atomic emission spectroscopy (ICPAES; Plasma 40 unit, Perkin Elmer, Inc.).

After leaching of five pore volumes of water, soil from each column was divided into 0 to 10, 10 to 20, and 20 to 28-cm sections. The soil was air-dried and mixed to obtain a uniform subsample from each depth sample. Soil pH was measured in water at 1:2 ratio of soil:water (wt:vol). Concentrations of Ca, Cu, Mn, Fe, Pb, Zn, Cr, and Se were measured using ICPAES in Mehlich 3 (M3; 0.02 M glacial acetic acid + 0.25 M NH_4NO_3 + 0.015 M NH_4F + 0.013 M HNO_3 + 0.001 M EDTA) (Mehlich 1984) extraction using ICPAES.

RESULTS AND DISCUSSION

The total quantities of elements (including K, Ca, Na, Fe, Mn, Cu, Zn, Se, and Cr) recovered in five pore volumes of leachate were significantly influenced by fly ash rate and the number of leachate fraction (ANOVA table is not presented). The recovery of most elements (except Cu) in the leachate increased with an increase in the rate of fly ash application (Table 1). The recovery of Cu in the leachate, on the other hand, decreased with an increase in rate of fly ash.

The highest concentration of most elements were observed in the leachate corresponding to one and a half to two pore volumes (Table 2). Only Fe and Cu leached in maximum quantity within one pore volume. The recovery of all elements decreased considerably in leachate fractions beyond three pore volumes.

The quantity of Se leached in five pore volumes increased by 56 μg in soil amended with 40% fly ash as compared to that from unamended soil (Table 1). The average concentration of Se in the 5 PV of leachate for the former treatment corresponded to 76.0 $\mu g\ L^{-1}$. This concentration is

Table 1. Effects of various rates of fly ash addition to a Candler fine sand on the quantities of various elements leached in a total of five pore volumes of leachate.

Fly ash rate (% of soil)	Total quantities of elements leached for 5 pore volumes								
	Ca	K	Na	Mn	Zn	Fe	Se	Cu	Cr
	-----------mg-----------			---------------------------------μg---------------------------------					
0	39	3.2	2.9	126	73	113	120	229	6.9
10	61	3.1	4.4	139	105	388	144	185	8.5
20	91	6.2	7.0	510	180	583	145	142	11.6
30	83	8.0	8.0	1171	242	698	144	164	13.9
40	140	8.0	12.0	883	387	494	176	159	15.4
50	231	16.8	21.4	1074	737	375	171	134	12.4
Regression analysis									
Intercept	22.75	1.52	0.97	105.17	-14.59	105.44	125.15	206.990	7.864
Slope	3.39	0.24	0.33	21.81	12.07	36.82 -0.64	0.99	-1.53	0.14
r^2	0.79	0.45	0.82	0.47	0.76	0.65	0.61	0.56	0.31
Significance	***	***	***	***	***	***	***	***	**

1 Pore volume = 463 ml.

, * = Regression is significant at $P < 0.05$ and $P < 0.01$, respectively.

Table 2. Elution pattern for various elements from a Candler fine sand amended with 50% fly ash (weight basis).

Fraction numbers	Pore volumes	Quantities of elements eluted									
		Ca	K	Na	Mn	Zn	Fe	Se	Cu	Pb	Cr
		----------	mg	----------	----------	----------	----------	µg	----------	----------	----------
1	½	2	0.2	0.1	13	14	195	10	27	5	2
2	1	7	0.5	0.4	13	25	154	15	25	10	2
3	1½	100	2.6	8.4	234	361	8	23	15	11	2
4	2	65	7.5	6.2	185	232	5	29	15	12	2
5	2½	24	2.0	2.1	151	79	4	22	12	11	2
6	3	11	1.6	2.0	169	26	3	19	11	14	1
7	3½	9	0.9	0.7	89	0	2	17	11	9	1
8	4	8	0.7	0.6	104	0	1	17	9	7	1
9	4½	3	0.4	0.4	58	0	2	10	9	6	0
10	5	3	0.4	0.4	58	0	1	8	0	5	0

Each fraction represents one-half of a pore volume (1 PV = 463 ml).

similar to that detected in subsurface drains, where the average Se concentration was 105 μg L^{-1} and the highest value exceeded 500 μg L^{-1} (Dept. of Water Resources of California 1986).

Leaching of Cr was low and its concentration in the leachate (Table 1) was below the critical lower limits set for drinking water (Rubenstein and Segal 1993). The amount of Cr leached in five pore volumes was 12.4 μg from soil amended with 50% fly ash. The average concentration of Cr in the 5 PV of leachate from the 40% fly ash treatment was 6.6 μg L^{-1}. Chromium is considered to have strong carcenogenic effect; therefore, minimizing its contamination into groundwater sources is of great importance (Rubenstein and Segal 1993).

The amounts of Zn leached in five pore volumes of leachate were 73 to 737 μg for unamended and soil amended with 50% of fly ash, respectively. The average concentration of Zn in the leachate from 50% fly ash amended soil was 318.3 μg L^{-1}. This value is within Zn concentration found in natural irrigation water (up to 5000 μg Zn L^{-1}; Zeng-Sang 1992) and also within that found in shallow groundwaters (Deverel *et al.* 1984).

The quantity of Pb in the leachate was the highest (14 μg) in the two and a half to three pore volume leachate fraction from the soil amended with 50% of fly ash (Table 2). This value corresponds Pb concentration of 60.31 μg L^{-1}, which would be unacceptable for drinking water quality (Rubenstein and Segal 1993).

The concentration of Cu in the leachate from soil amended with 50% fly ash was 57.9 μg Cu L^{-1}. This concentration does not exceed the mean concentration found in fresh water environment or that found in shallow groundwater (Deverel *et al.* 1984), and is within the critical upper limit set for drinking water (Rubenstein and Segal 1993).

The quantities of Fe and Mn leached from the soil amended with 50% fly ash increased substantially as compared to that from unamended soil. However, the concentration of Fe and Mn in the leachate did not exceed the maximum concentration found in shallow groundwaters (Deverel *et al.* 1984).

Concentrations of most elements (including Ca, K, Na, Mn, Zn, Fe, Se, Cu, and Cr) in the soil evaluated in this study were influenced by the rate of fly ash addition and the depth of soil profile (ANOVA table is not presented). Concentrations of Mehlich 3 extractable Ca, K, Na, Fe, Se, and Cr in the soil were lower at 10 to 20 and 20 to 28-cm depth than those at 0 to 10-cm depth (Table 3). Soil pH also was lower at the lower depth sample as compared to that of the surface soil. In 0 to 10-cm layer of soil, increasing the rate of fly ash application increased the soil pH and Mehlich 3 extractable elements with the exception of Na, Mn, Zn, and Cu (Table 3).

Table 3. Effects of various rates of fly ash additions to a Candler fine sand on soil pH and Mehlich 3 extractable cations and metals in the top 10-cm soil after leaching with five pore volumes of water.

Fly ash rates (% of soil)	Soil pH (0.01 M $CaCl_2$)	Mehlich 3 extractable cations and metals (mg/kg)									
		Ca	K	Na	Mn	Zn	Fe	Se	Cu	Pb	Cr
0	5.28	423	15	52	28	21	124	1.4	53	2.4	0.4
10	6.04	604	24	44	27	17	157	1.8	44	2.4	0.6
20	6.49	1046	31	27	28	17	204	2.3	44	3.2	0.9
30	6.82	1153	30	20	23	16	188	2.9	44	3.2	0.9
40	6.81	2206	49	43	25	16	261	3.8	41	4.0	1.4
50	7.37	3929	71	44	24	12	312	4.9	28	4.1	2.1
Regression analysis											
Intercept		-42.344	11.514	NS	28.284	19.529	119.454	1.124	51.568	2.806	0.286
Slope		64.11	1.01		-0.10	-0.13	3.53	0.07	-0.37	0.02	0.03
r^2		0.70	0.75		0.40	0.61	0.74	0.78	0.62	0.35	0.74
Significance		***	***		***	***	***	***	***	***	***

*** = Regression is significant at $P < 0.01$.

NS = Regression is non-significant.

The concentrations of Cr, Zn, Pb, Fe, Mn, and Cu in the surface 10-cm depth (data not presented), at the highest rate of fly ash addition (50% fly ash), did not increase to levels which could be considered as environmentally hazardous (Carlson and Adriano 1993; Dreesden *et al.* 1977; Logan and Traina 1993). Low concentrations of these metals despite application of high rate of fly ash could be due to moderate amounts of these elements present in the fly ash as compared to the concentrations found in other fly ash sources (Rai 1987). The increase in pH values in 0 to 10-cm soil layer with an increase in fly ash rate (Table 3) may also be responsible for decreasing the extractability of some heavy metals from the soil. This is in agreement with the conclusions of other investigators (Harmsen 1992; Logan and Traina 1993).

The concentration of Se in 0 to 10-cm depth soil with 50% fly ash amendment was 4.9 mg kg^{-1}, which is well above the concentrations reported to several soils which did not receive fly ash amendments; i.e., 0.4 mg Se kg^{-1} (Logan and Traina 1993). This could be in part due to an increase in soil pH as a result of fly ash application causing more favorable conditions for Se extraction (Carlson and Adriano 1993). Selenium concentration in the current study attained the values found in some polluted soils (Tokunaga *et al.* 1991); however, only five to 20% of Se in the soil is water soluble.

This study demonstrated that the addition of fly ash to the soil at relatively high levels up to 50% (by weight basis) did not result in leaching of heavy metals in amounts which could be considered hazardous to groundwater quality. The concentrations of heavy metals in the soil were also within the limits acceptable for agricultural soils. Among the various heavy metals examined in this study, only Se appears to be of some concern with regard to its accumulation in soil at high rates of fly ash application. The fly ash application rate should also be adjusted to avoid any substantial increase in soil pH which may result in a micronutrient deficiency problem. The fly ash used in this study contained relatively low concentration of most heavy metals. This explains the lack of either excessive accumulation of heavy metals in the soil or elevated concentrations in the leachate despite high rates of fly ash application.

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