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ORIGINAL ARTICLE

Leaching of Selected Trace Elements from Plant Growth Media composed of Coal Fly Ash (FA) Sphagnum Peat Moss and/or Soil. Part 2: Leaching of trace elements from Group IV: titanium (Ti) and zirconium (Zr), from Group V: Vanadium (V), and from Group VI: Chromium (Cr) and Molybdenum (Mo).

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ABSTRACT
This study investigated the leaching of selected trace elements (Ti, Zr, V, Cr, and Mo) from plant growth media composed of two coal fly ashes (FA), one from semi-bituminous coal, and another from lignite), with or without soil or sphagnum peat moss (SPM). Leachate fractions have been collected at each ½ pore volume for a total of five pore volumes. Concentrations of mentioned above trace elements in plant growth media and in leachates have been determined using inductively coupled plasma (ICP) emission spectrophotometry. Addition of soil and SPM coal FA based plant growth media reduced concentration of trace elements in plant growth media, but it did not alter concentration of these elements in the leachate from these media. Elevated concentrations of Vanadium in the leachate may cause some environmental health concerns and warrants further investigations.

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INTRODUCTION

Major coal combustion residue, FA carries the potential for environmental contamination during the disposal of these coal combustion by-products [1, 2, 3, 4]. Because FA contains multiple toxic elements, predominantly heavy metals, the disposal of FA may lead to leaching out of these elements and contaminate soils as well as surface water and groundwater [5]. This contamination could lead to the health, environmental, and land-use problems [6].On the other hand, the utilization of FA as a soil amendment in agriculture represents a potentially large application for FA [7, 8]. There are significant benefits that result from the application of FA as a soil amendment. These benefits include improved soil texture, increased soil nutrient holding capacity, increased concentration of extractable K, Ca, Mg, Cu, Fe, and Mn [7]. However, the pozzolanic nature of coal FA causes plant growth media to harden, especially in high concentration, thereby making it difficult to grow crops [9]. Thus, it has been demonstrated that SPM may improve the texture of such media, making media less harder, decreasing high pH of the media, and potentially binding heavy metals present in FA (10). The major limiting factor to use FA in agriculture is the environmental concern that persists even through the U.S. Environmental Protection Agency (EPA) has determined that power plant FA applied to agricultural soils is largely free of health and environmental risks, and EPA does not regulate its agricultural use [4]. The specific aim of this experiment was to determine the environmental safety of different growth media composed of FA, soil and SPM. The leaching of selected elements belonging to Group 4 (Ti and Zr), Group 5 (V)and group 6 (Cr and Mo), and also from the soil (control) and plant growth media composed of coal FA from two sources, and FA mixed with soil and/or SPM.

MATERIALS AND METHODS

Plexiglas columns (30.4 cm long, 5 cm inner diameter) were used to study the transport and leaching of cations and heavy metals from growth media. A Fargo-Ryan soil (pH=6.1-8; organic matter=8%) was sampled and used as a control treatment. The soil has been air-dried, ground to pass a 2-mm sieve, and packed in the above columns to a height of 30 cm (bulk density of 1.5 g/cm). A Whatman No. 42 filter

paper was placed at the bottom of the soil column. Fly ashes from two local Midwest sources (one from North Dakota's lignite coal, and one from Montana's semi-bituminous coal), after thorough examination of its chemical composition, were used.
Experimental treatments consisted of the following plant growth substrates:
1. Soil (Fargo clay) as a control (S)
2. Fly ash from semi-bituminous coal from Montana collected from North Dakota State University power plant (FAND)
3. 50% FAND + 50% SPM (weight based; 50FAND+50SPM)
4. 30 FAND + 30% SPM + 30% soil (30FAND+30SPM+30S)
5. Fly ash from North Dakota lignite coal collected from Valley City State University power plant (FAVC)
6. 50% FAVC + 50% SPM (50FAVC+50SPM)
7. 30% FAVC + 30% SPM + 30% soil (30FAVC+30SPM+30S)
The quantities of FA, as required by the treatment, was mixed uniformly with top 10-cm depth soil in the column. The experiment has been conducted in three replications. The packed soil and growth substrates have been saturated and excess water was allowed to drain overnight. To facilitate leaching, distilled water has been gradually applied to the top of each column to deliver one pore volume of water per 24 hours. Leachate fractions were collected at each ½ pore volume for a total of five pore volumes**.** After leaching of five pore volumes of water, soil from each column was divided into 0-10, 10-20, and 20-28-cm sections. The soil and all growth substrates were air-dried and mixed to obtain a uniform subsample from each depth sample. Concentrations of Ti, Zr, V, Cr, and Mo have been measured in Mehlich3 (M3; 0.02 M glacial acetic acid + 0.25 M NO_3 + 0.015M NH_4F + 0.013 M HNO_3 + 0.001 M EDTA) (11). extractions using inductively coupled plasma (ICP) emission spectrophotometry. The differences between the results due to various FA sources, rates, and sample depth have been evaluated using statistical analysis.

RESULTS

The concentrations of Ti, Zr, V, and Mo in the soil were lower than in coal FA. The addition of soil and SPM to the growth media decreased the concentrations of tested elements in growth media (Table 1). The greatest decrease of these elements was detected in FAVC mixed with SPM or with SPM and soil, as compared to FAND used as a component of the same mixtures (Table 1).

Table 1. Concentrations of selected trace elements from Group 4 (Ti and Zr), Group 5 (V), and group 6 (Cr and Mo) in plant growth media used in leaching studies. ^{a,b,c,d,e,f,g} $P<0.05$ values with different superscripts differ within each element, depending on plant growth media.

Media	S	FAND	50FAND +50SPM	30FAND+ 30SPM+30S	FAVC	50FAVC+ 50SPM	30FAVC+ 30SPM+30S
Titanium (Ti) mg/kg	40.7^a	1442.1^b	770.3^c	449.4^d	1444.3^b	965.9^c	224.5^e
Zirconium (Zr) mg/kg	19.8^a	95.9^b	76.9^c	50.8^c	110.6^b	77.9^c	23.0^a
Vanadium (V) mg/kg	21.1^a	35.5^b	29.6^b	26.5^b	31.7^b	22.5^a	12.3^c
Chromium (Cr) mg/kg	14.1^a	14.8^a	11.9^b	15.5^a	16.8^c	12.5^b	8.4^d
Molybdenum (Mo) mg/kg	0.52^a	3.7^b	2.68^c	1.35^d	6.24^e	5.06^e	1.6^d

The concentrationsof all tested elements in the leachate fractions was measured as a function of the type of media and of leachate fractions. The concentrations of Ti, Zr, V, Cr, and Mo in the leachates were correlated to the type of media, and the levels of these elements in leachate were measured to determine if they correspond to the levels presented in the media. These concentrations were not dependent on the pore volume of the leachate (lack of statistically significant differences), regardless of media used. Because of this, our data in Table 2 represent averages for all pore volumes of the leachate collected.
The presence of soil and SPM in the media in most cases did not reduce the efflux of mentioned above heavy metals from these media. This is really a remarkable observation, which might be explained by the fact of similar concentration of tested elements in the SPM, and sometimes in the soil as the concentration of the same elements in coal FA.

Table 2. Concentrations of selected trace elements from Group 4 (Ti and Zr), Group 5 (V), and group 6 (Cr and Mo) in the leachates obtained from different plant growth media used in leaching studies. [a,b,c,d,e,f,g] P<0.05 values with different superscripts differ within each element

Media	S	FAND	50FAND +50SPM	30FAND+ 30SPM+ 30S	FAVC	50FAVC+ 50SPM	30FAVC+ 30SPM+30S
Titanium (Ti) μg/liter	13^{a}	36^{b}	28^{b}	15^{a}	29^{c}	27^{c}	22^{d}
Zirconium (Zr) μg/liter	$<3^{a}$	$<3^{a}$	$<3^{a}$	$<3^{a}$	8^{b}	2^{c}	$<3^{a}$
Vanadium (V) μg/liter	48^{a}	13^{b}	4^{c}	4^{c}	57^{d}	58^{d}	72^{e}
Chromium (Cr) μg/liter	$<3^{a}$	5^{b}	11^{c}	24^{d}	4^{b}	7^{e}	6^{e}
Molybdenum (Mo) μg/liter	7^{a}	7^{a}	16^{b}	18^{b}	39^{c}	62^{d}	37^{c}

DISCUSSION

Heavy clay soils, like the soil used in our experiment (Fargo Clay) contain more titanium (Ti) than sandy soils [12, 13, 14], and the average Ti concentration in soil appears to be below 5 g/kg. Soil used in this study contained only a fraction (less than 0.5%) of this amount, and even our coal ash also didn't contain more than 1.5g Ti per kg. The concentration of Ti in the leachates in our experiment ranged from 13 μg/l in the leachate from soil control to 36 μg/l in the leachate from VCFA. Such levels remain within the Ti concentration in stream waters, as reported by Reimann and Caritat [15]. Ti presence in stream waters varies from 12 to 926 μg/l, being the highest in India, and the lowest in Nova Scotia, Canada. Contents of Zr in soils vary within the range of 30-250 mg/kg, being the lowest in peat soils and the highest in sandy soils [15, 16]. The lowest concentration of Zr in our experiment was present in the soil control – 19.8 mg/kg. The highest concentration of Zr in our experiment -110.6 mg/kg, obtained in coalFA, remains well below the highest concentrations found in the soil, not even mention any solid waste materials. Due to the limited solubility of most compounds and minerals of Zr, its concentration in waters is relatively low [17]. Different values of Zr concentration in waters are presented in literature [12], but it usually ranges from 20 to 200 μg/l [15]. Our leachates contained Zr in the range from below 3 up to 8 μg/l, and such values remain within naturally occurring in the environment. Vanadium contents of soils are related to those of the parent rocks from which they are formed [18, 19]. Average contents of V in soils vary from 10 mg/kg in sandy soils to 500 mg/kg in calcerous soils. The soils in the USA contain V in the range of 36-150 mg/kg [20]. The concentration of Vin all our growth media, including a coalFA alone, didn't exceed 50 mg/kg, and should be considered as very low. The concentration of V in the leachates in our experiment ranged from 4 to72 μg/l. Such values are within the values obtained from some US rivers, where V concentration reaches 70 μg/l [13]. It should be noted, though, that 70 μg/l of V has been found only in rivers in the area of the uranium ores in the US [13]. Waters of rivers polluted by industrial effluents contain V in the range of 4-19 μg/l [21], and in fact these values are lower than the V concentration in the leachate from our soil control (48μg/l). In most soils, chromium (Cr) occurs in low concentrations (2 - 60 mg/kg) and in our studies not only Cr concentration in the soil, but also in all coal FA based plant growth media Cr concentration remained within these limits [22]. Such concentration didn't exceed the level considered to be phytotoxic; phytotoxicity starts at100 mg/kg) [23]. Cr concentration in the leachates in our study ranges from less than 3 to 24 μg/l. The median Cr content in world river waters is given as 0.7 μg/, with the range of 0.04-1.3 μg/l, reaching the concentration of 46.8 μg/l, in industrially polluted waters [13]. Molybdenum occurrence in soils ranges from 0.1 to above 7 mg/kg (24), and any of all coal FA based growth media in our study didn't contain more Mo than naturally occurring in the soils. Concentrations of Mo in river and lake waters are highly variable, and range from < 0.2 to 60 μg/l (23). Health based limit value for Mo in drinking water is 70 μg/l [25], and Mo concentration in all leachates (up to 62 μg/l) in our study meets the standards for drinking water.

In summary, the presence of SPM and soil in coal FA based plant growth media expressed ameliorative by role by reducing the concentration of trace elements in plant growth media, but it did not translate into the decrease of the presence of these elements in the leachates from these media. Elevated concentrations of V in the leachates may cause some environmental health concerns and requires further investigations.

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