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ORIGINAL PAPER

Leaching of Selected Trace Elements from Plant Growth Media Composed of Coal Fly Ash (FA), and of FA amended with Sphagnum Peat Moss and Soil. Part 1: Leaching of trace Elements from Group 1: Cesium (Cs) and Lithium (Li), and from Group 2: Beryllium (Be), Strontium (Sr), and Barium (Ba).

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ABSTRACT
This study investigated the leaching of selected trace elements (Cs, Li, Be, Sr, and Ba) from plant growth media made of two coal fly ashes (one from semi-bituminous coal and one from lignite), and from these ashes combined with the soil and with the soil and sphagnum peat moss. Leachate fractions will be 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 leachate has been determined using inductively coupled plasma (ICP) emission spectrophotometry. The presence of sphagnum peat moss and soil in coal ash based plant growth media expressed ameliorative role reducing the presence of trace elements in the leachate. Elevated concentrations of Li, Sr and Ba in the leachate may cause some en environmental health concerns and require further investigations.

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INTRODUCTION

The potential for environmental contamination by major coal combustion residue, fly ash (FA) is one of the main areas of concern regarding proper disposal of these coal combustion by-products [1, 2, 3].
Fly ash contains several toxic elements, such as Arsenic (As), cadmium (Cd), cobalt (Co), mercury (Hg) lead (Pb), zinc (Zn), and other heavy metals, which can leach out and contaminate soils as well as surface water and groundwater [4]. When fly ash is not properly disposed, and if leached, these elements cause the severe contamination of subsurface water. Consequently, these elements may become a hazard to the environment because of their contribution to the formation of toxic compounds. This contamination could lead to health, environmental and land-use problems [5].
On the other hand, the utilization as a soil amendment in agriculture represents a potentially large market for FA [6]. There are significant benefits that result from the application of fly ash 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 in the soil [3, 6].
The pozzolanic nature of coal FA causes plant growth media to harden, especially in high concentration, thereby making it difficult to grow crops [7]. Sphagnum peat moss (SPM) shows a potential to ameliorate coal FA based plant media by improving the texture of such media, making media less harder, decreasing high pH of the media, and potentially binding heavy metals present in FA [8].
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 fly ash applied to agricultural soils is largely free of health and environmental risks and EPA does not regulate its agricultural use [9].
Specific Aim of our leaching experiments is to determine the environmental safety of different growth media composed of FA and soil. In this study we investigated the leaching of selected elements belonging to Group 1 (Cs and Li) and from Group 2 (Be, Sr, and Ba) from the soil control and plant growth substrate composed of coal fly ashes from two sources, and ashes mixed with soil and with the soil and sphagnum peat moss (SPM).

MATERIALS AND METHODS

Plexiglas columns (30.4 -cm long, 5-cm inner diameter) have been be employed to study the transport and leaching of cations and heavy metals from a FA amended soil. A Fargo-Ryan soil (pH=6.1-8; organic matter=8%) has be 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 will be placed at the bottom of the soil column. Fly ash from at least 3 different local North Dakota sources, after thorough examination of its chemical composition, will be used in this study (with emphasis on finding a minimum one FA with a very high concentration of heavy metals, B and Se.

Experimental treatments will consisted of 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% sphagnum peat moss (*weight based*)(50FAND+50SPM)
4. 30 FAND + 30% sphagnum peat moss + 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% sphagnum peat moss (50FAVC+50SPM)
7. 30% FAVC + 30% sphagnum peat moss + 30% soil (30FAVC+30SPM+30S)

The quantities of FA, as required by the treatment have been mixed uniformly with top 10-cm depth soil in the column. The experiment has been conducted in three replications. Whatman No. 42 filter paper will be also placed at the top of the soil column. The packed soil and growth substrates have been saturated and excess water have been 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 have been collected at each ½ pore volume (pore volume = to be determined) for a total of five pore volumes. Concentrations of Cs, Li, Be, Sr, and Ba in the leachate have been determined using inductively coupled plasma (ICP) emission spectrophotometry. After leaching of five pore volumes of water, soil from each column have been divided into 0-10, 10-20, and 20-28-cm sections. The soil and all growth substrates have been air-dried and mixed to obtain a uniform subsample from each depth sample. Concentrations of Cs, Li, Be, Sr, and Ba have been measured in Mehlich3 (M3; 0.02 M glacial acetic acid + 0.25 M NO_3 + 0.015M NH_4 F + 0.013 M HNO_3 + 0.001 M EDTA) (10). 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

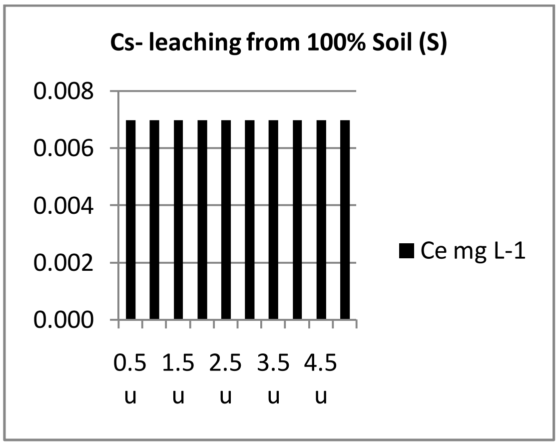
Table 1. Concentrations of selected trace elements from Group1 (Cs and Li) and from Group 2 (Be, Sr, and Ba) in plant growth media used in leaching studies.

Media	S	FAND	50FAND +50SPM	30FAND+ 30SPM+ 30S	FAVC	50FAVC+ 50SPM	30FAVC+ 30SPM+ 30S
Cesium (Cs) mg/kg	30.1	78.8	37.7	28.9	86.2	25.2	12.5
Lithium (Li) mg/kg	10.9	15.5	13.2	24.8	56.8	11.0	7.3
Beryllium (Be) mg/kg	0.52	2.18	1.63	0.91	2.50	1.90	0.55
Strontium (Sr) mg/kg	32.8	3972.6	2707.2	804.9	4100.0	3469.3	841.9
Barium (Ba) mg/kg	160.8	7805.3	1842.8	775.1	2910.5	2098.8	642.3

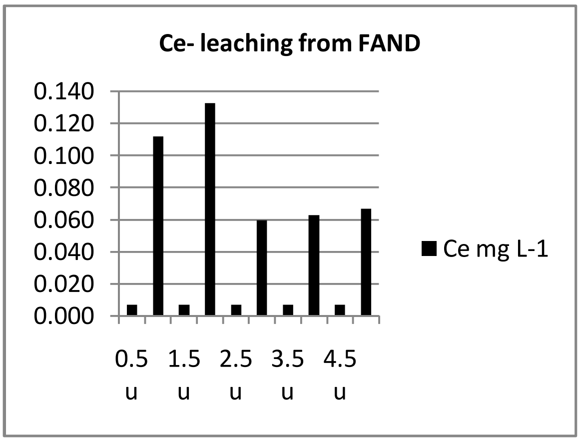
The concentration of all tested elements in the soil control were lower than in coal fly ashes. The addition of soil and sphagnum peat moss to the media had a decisive influence on the lowering the concentration of all tested elements in growth media.

Graphs 1-7. The concentration of cesium (Cs) in mg/l in the leachate, depending on growth media composition and pore volume of leachate (pore volumes on 0-X axis, from 0 to 5 pore volumes, collected at each 0.5 pore volumes, abbreviation "u" for pore volumes collected)

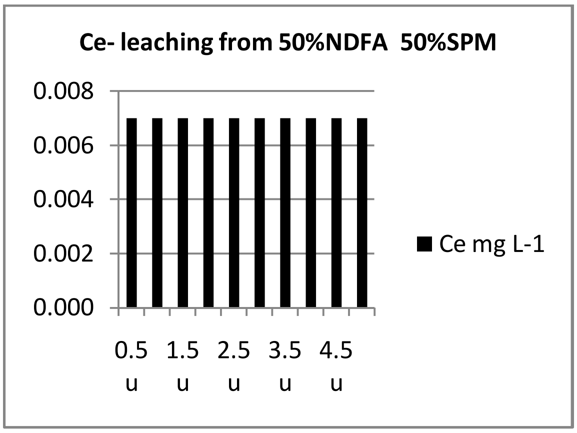
Graph 1



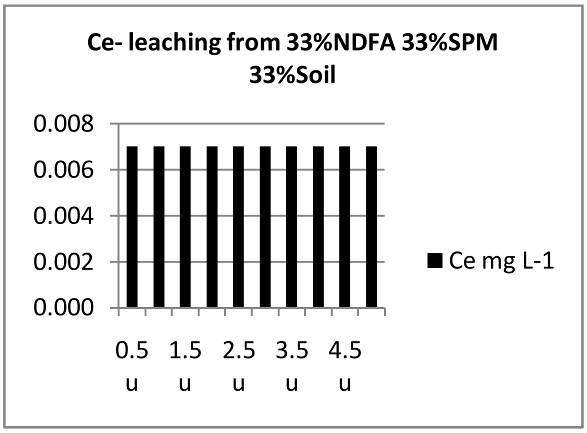
Graph 2



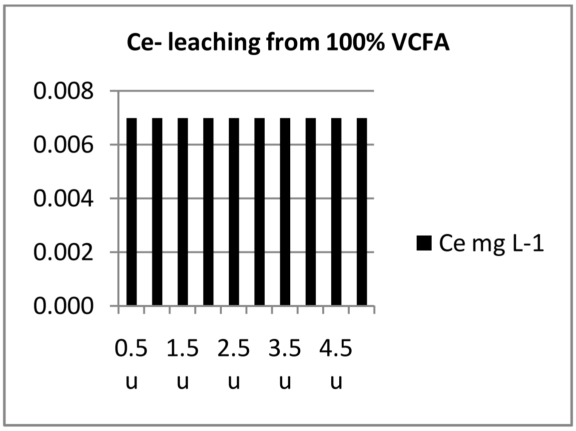
Graph 3



Graph 4



Graph 5



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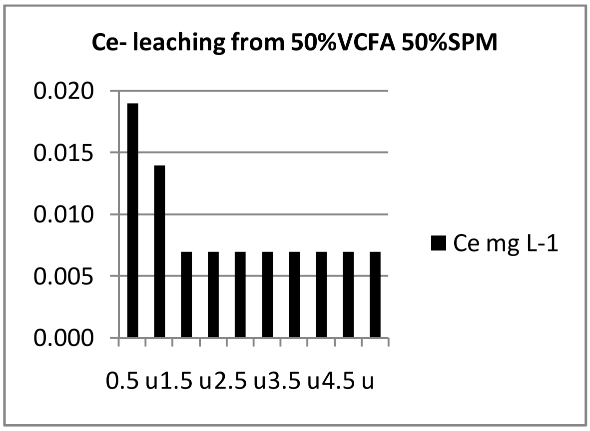

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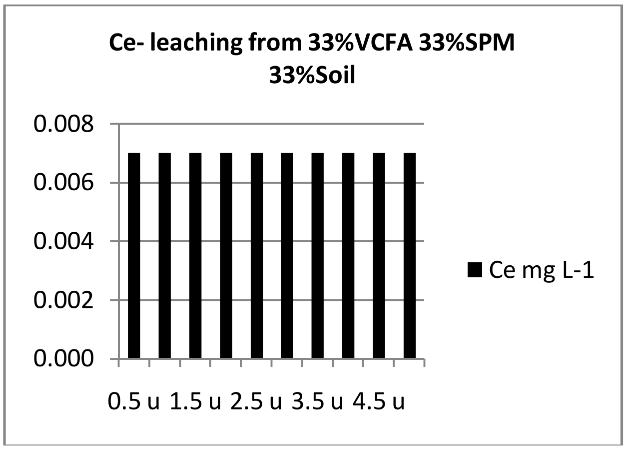
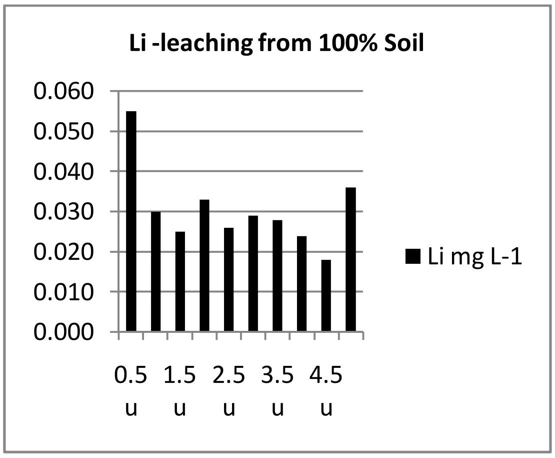


The concentration of cesium (Cs) in the leachate was almost uniform through all experimental treatments, and didn't change due to the fraction of the leachate, except for the FAND growth media and in the substrate consisting of 50% of fly ash from VCSU power plant and 50% of sphagnum peat moss.. In this substrate, the leaching of cesium was the strongest in first pore volumes of the leachate, and then stabilized at a relatively low level.

Graphs 8-14. The concentration of Lithium (Li) in mg/l in the leachate, depending on growth media composition and pore volume of leachate (pore volumes on 0-X axis, from 0 to 5 pore volumes, collected at each 0.5 pore volumes, abbreviation "u" for pore volumes collected).

Graph 8



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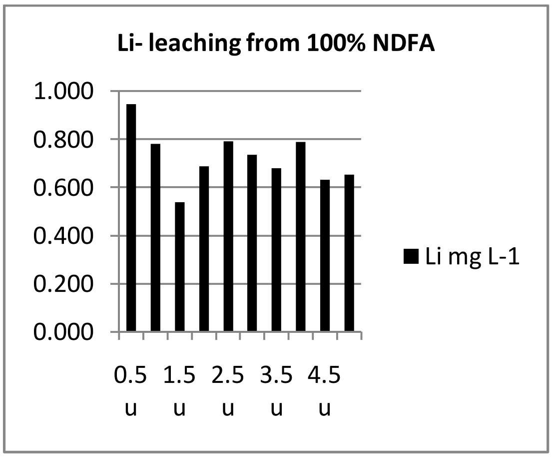

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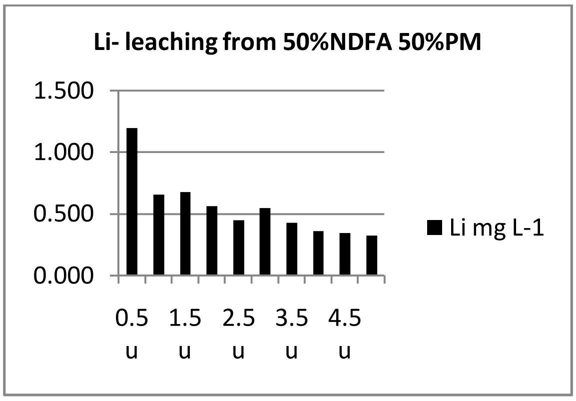

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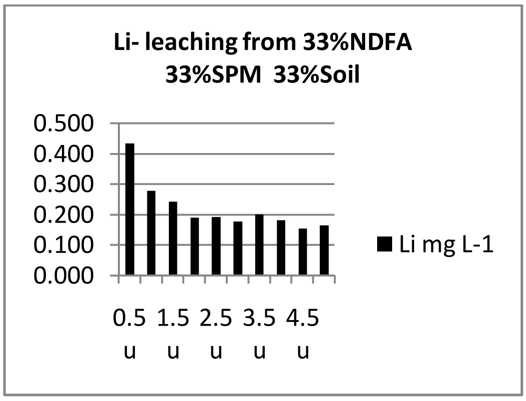

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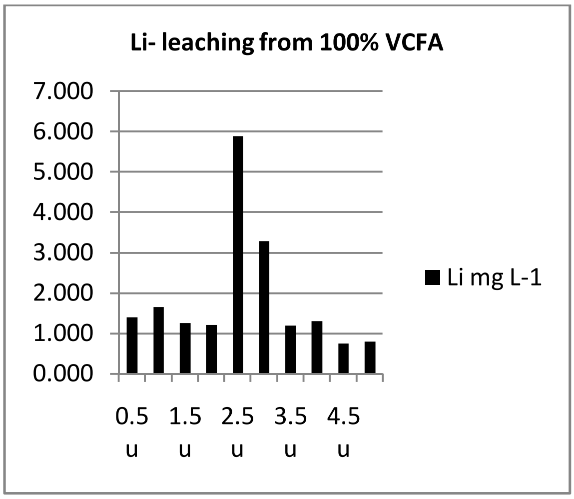

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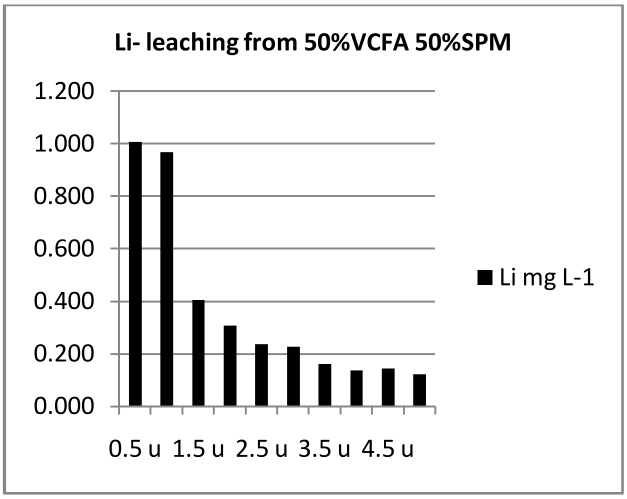

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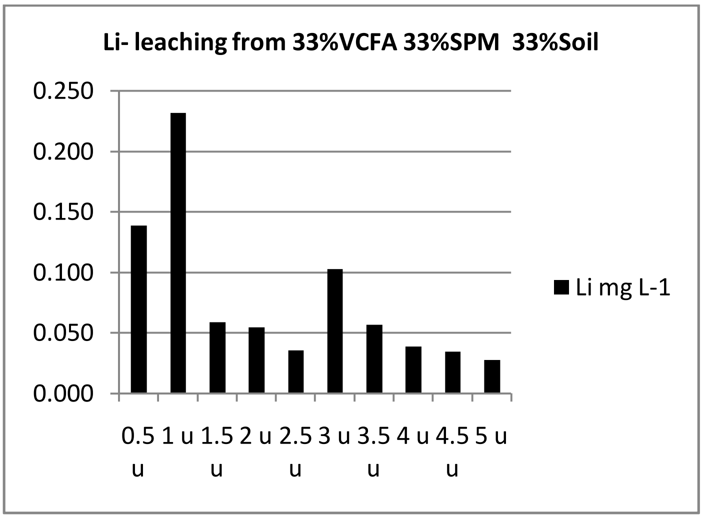
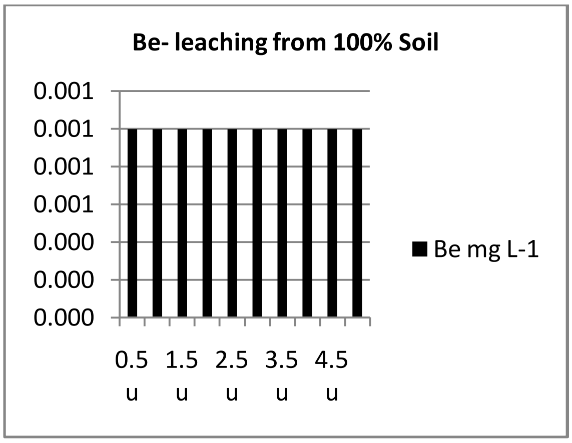


The leaching of lithium corresponded to the concentration of Li in the substrate. The highest concentration has been noted in VCFA substrate, and it resulted in the highest leaching of Li from this substrate. The highest levels of Li in the leachate have been obtained in 2.5 and 3 pore volume fractions in VCFA substrate. The addition of soil and sphagnum peat moss to both of coal fly ashes used in our study, showed the influence on the decrease of the level of Li in the leachates. In such cases, the highest levels of leaching have been noticed in first two pore volumes of the leachate, with the lowering levels of Li in higher fractions of the leachate, up to 5 pore volumes. The addition of the soil and sphagnum peat moss to the coal ash expressed strong lithium binding potential of lithium, resulting in significant reduction of the outflow of Li from the substrates having organic material added in the soil and/or in the sphagnum peat moss. The addition of sphagnum peat moss and soil to the fly ash showed a stronger Li binding ability that the addition of soil alone. As a result of it, there were the highest reductions of Li concentration in the leachates from the substrates composed of 33% of coal ash, 33% of soil and 33% of sphagnum peat moss.

Graphs 15-21. The concentration of beryllium (Be) in mg/l in the leachate, depending on growth media composition and pore volume of leachate (pore volumes on 0-X axis, from 0 to 5 pore volumes, collected at each 0.5 pore volumes, abbreviation “u” for pore volumes collected)

Graph 15



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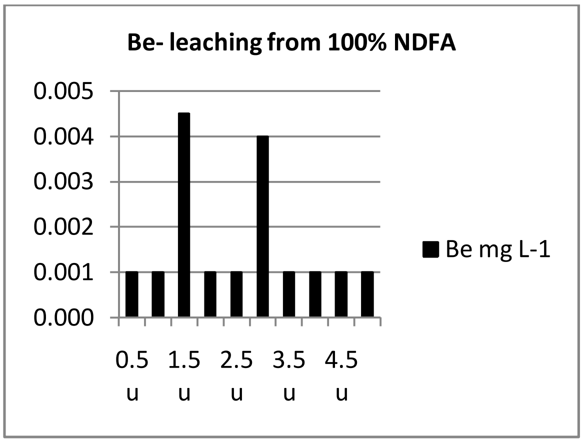

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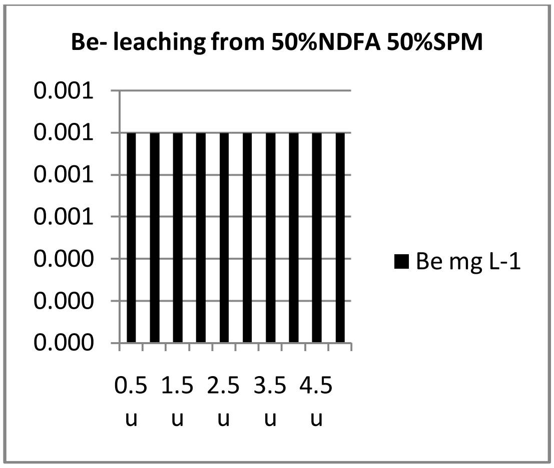

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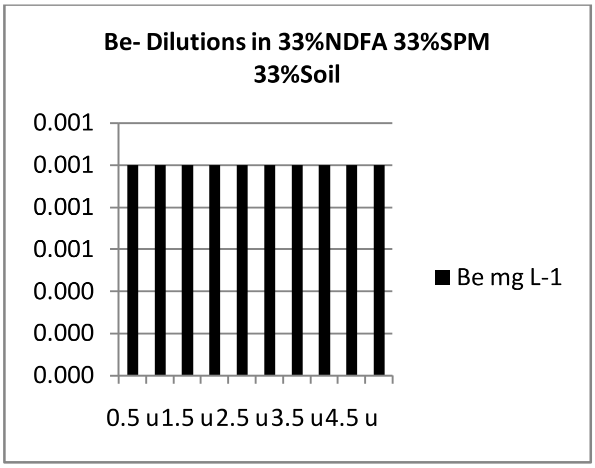

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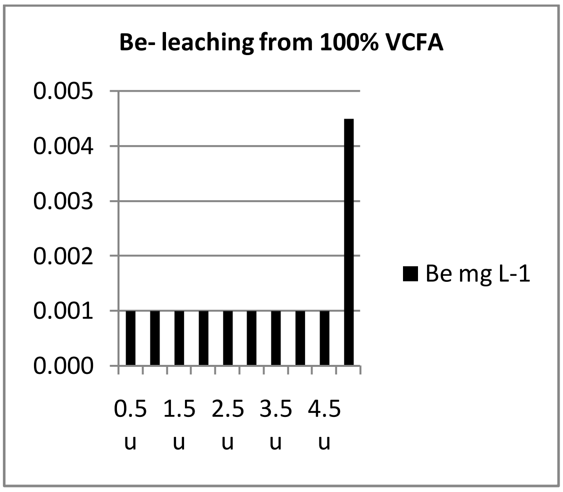

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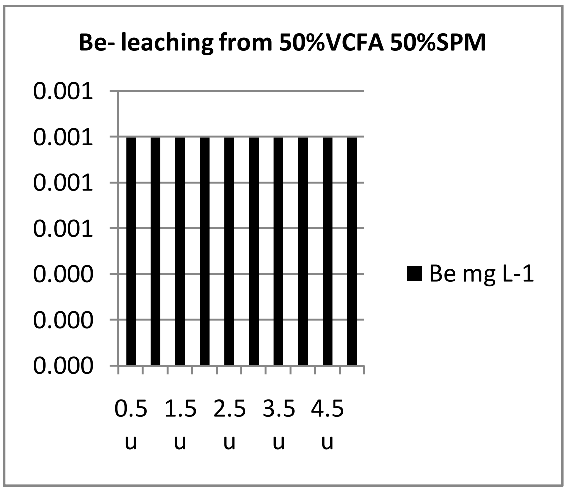

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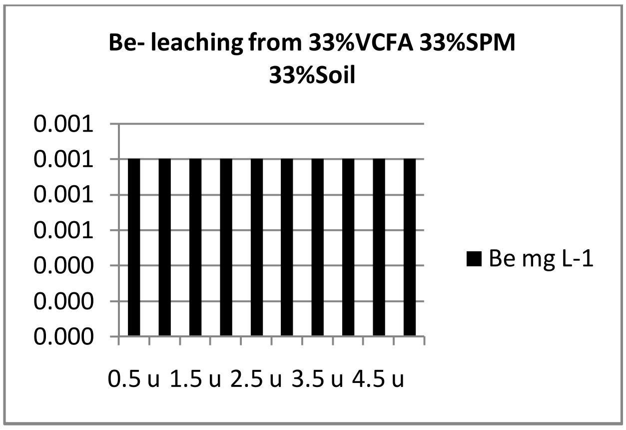
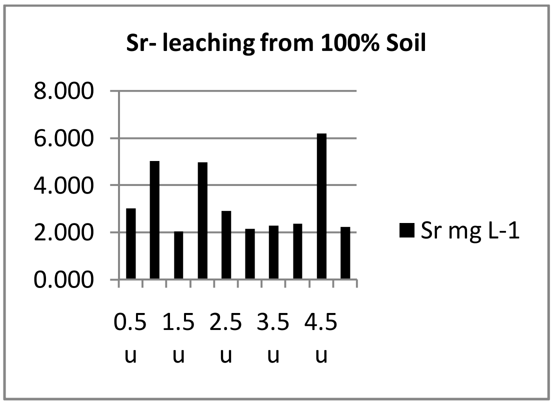
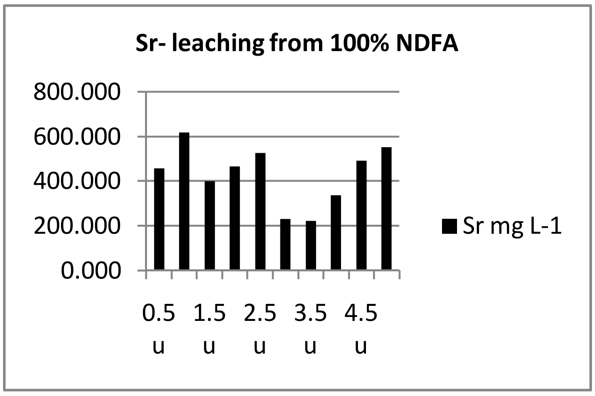


The concentration of beryllium in the leachate didn't show any dependence on the pore volumes in most cases, except for the levels in VCFA leachate where the highest levels of Be have been leached in the last pore volume collected, and in the case of NDFA substrate. In the lattest the highest levels of Be have been collected in 1.5 and 3 pore volumes.
The levels of Be in the leachate our study didn't show any dependence on the concentration in substrates, and the presence of sphagnum peat moss or soil didn't lead to the decrease in the leaching Be from the substrates.
Graphs 22-28. The concentration of strontium (Sr) in mg/l in the leachate, depending on growth media composition and pore volume of leachate (pore volumes on 0-X axis, from 0 to 5 pore volumes, collected at each 0.5 pore volumes, abbreviation "u" for pore volumes collected).

Graph 22



Graph 23



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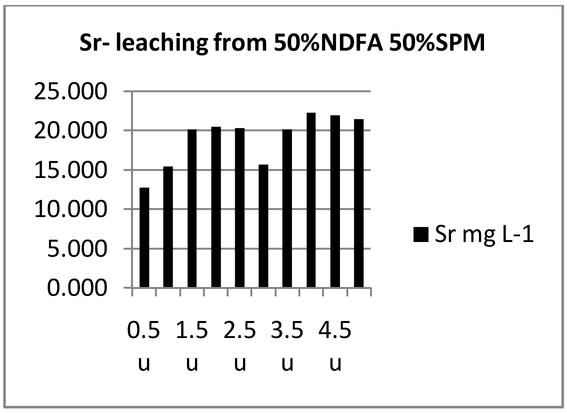

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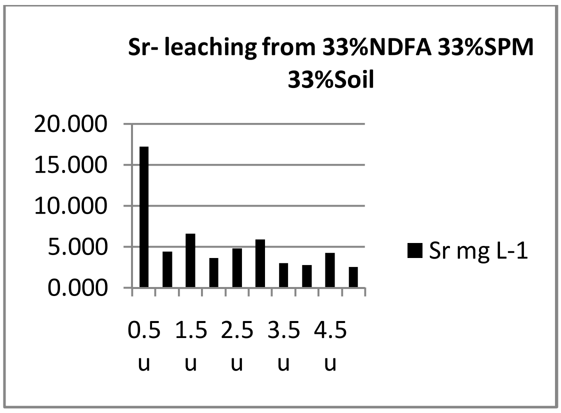

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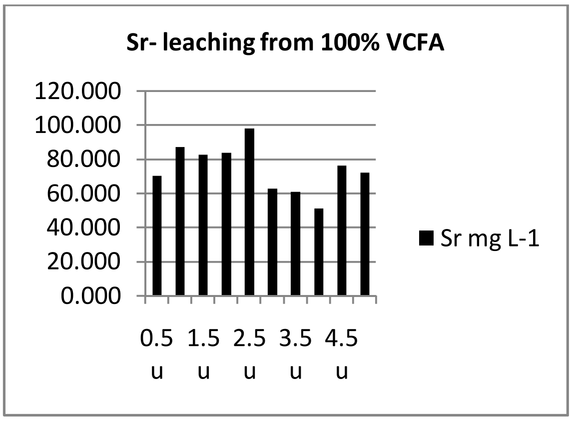

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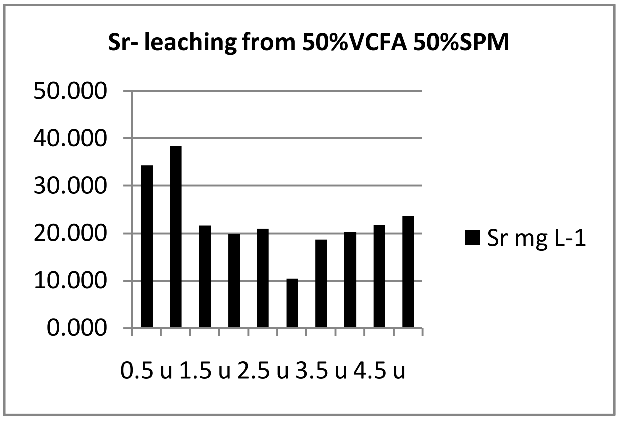

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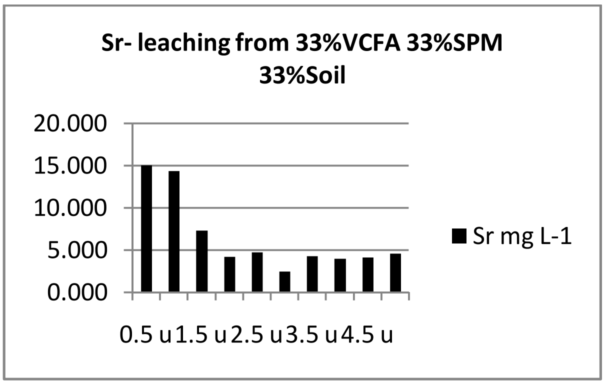
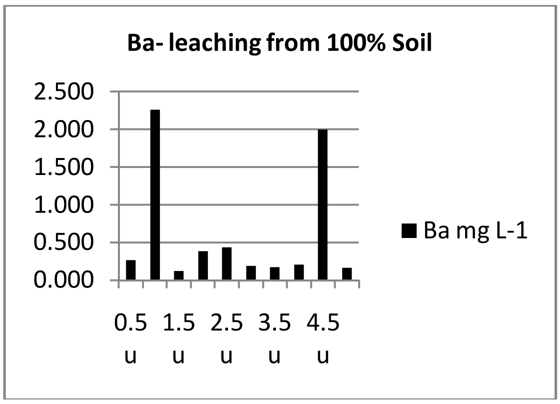


High concentrations of strontium in coal ashes in our study corresponded to high concentrations of Sr in the leachates. The levels of Sr have been in most cases maintained across all pore volume collections. Despite a similar concentration of Sr in the substrates composed of NDFA and VCFA, the leaching of strontium from NDFA was much higher than from VCFA

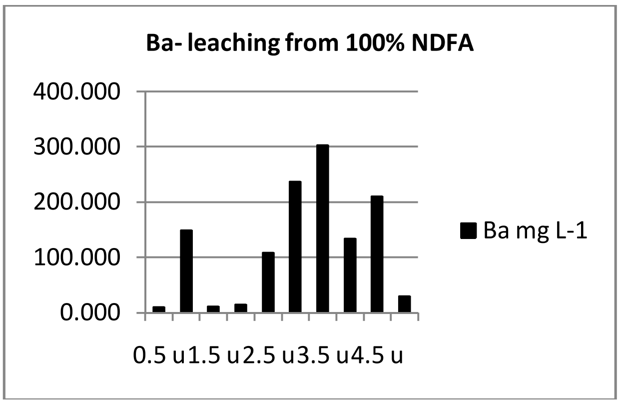
In case of strontium, there were very strong influences of the addition of organic material in a form of either a soil or a sphagnum peat moss to the media. The addition of a soil to coal ashes significantly decreased the leaching of strontium, but the most significant leaching restrictions have been achieved by the addition of the soil combined with sphagnum peat moss.

Graphs 29-35. The concentration of barium (Ba) in mg/l in the leachate, depending on growth media composition and pore volume of leachate (pore volumes on 0-X axis, from 0 to 5 pore volumes, collected at each 0.5 pore volumes, abbreviation "u" for pore volumes collected)

Graph 29



Graph 30



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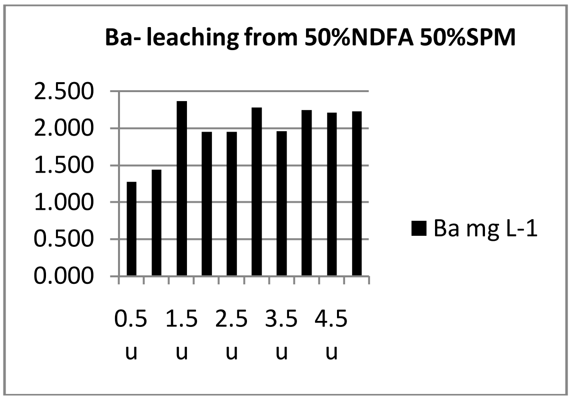

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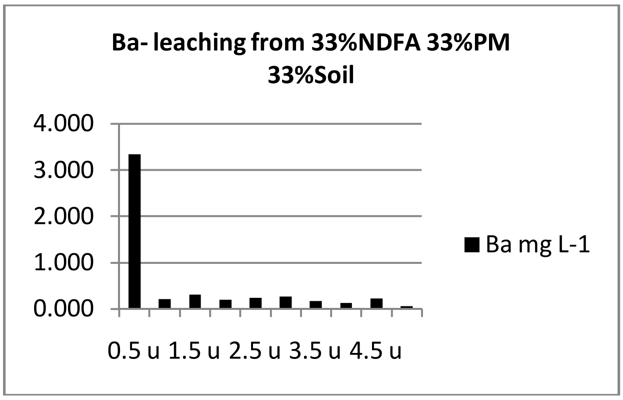

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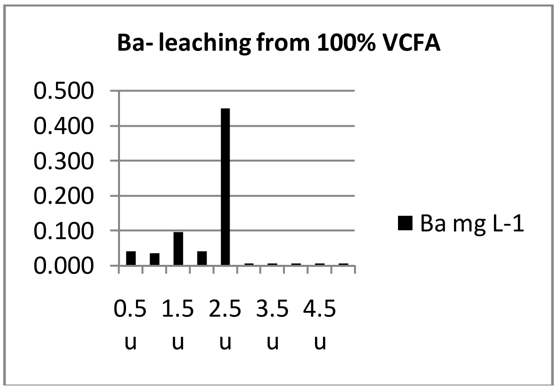

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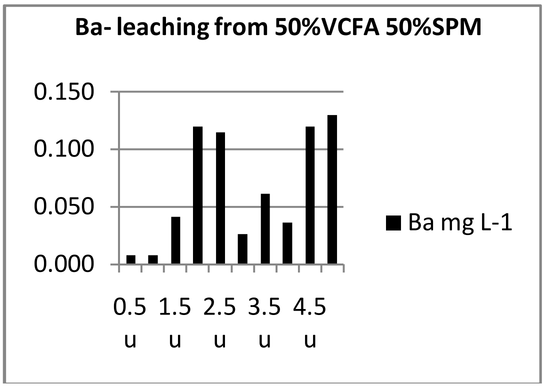

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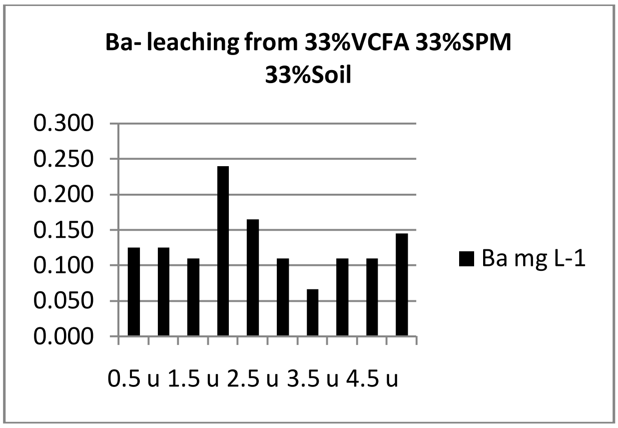

The level of barium in the leachates from VCFA substrate was much lower than from NDFA substrate, despite similar concentrations of Ba in these two substrates. The level of barium leaching from fly ash based substrates was highest between 2.5 and 4 pore volumes for NDFA and 2.5 pore volumes for VCFA. Any addition of organic material to a coal ash in the form of either a soil or sphagnum peat moss had a tremendous influence on the decrease of barium leaching from such substrates.

DISCUSSION

There is little information on the stable (not an isotope) cesium (Cs) status of soils. The common range for different soils can be estimated as from <1 mg/kg up to 30 mg/kg. [11]. Soil used in our study (Fargo clay) contained about 30 mg/kg of Cs, but coal ashes, especially VCFA exceeded this concentration up to 3 fold. It would be hard to speculate about possible toxicity to plants grown on such media, because the lack of data concerning proven established levels of Cs in plant growth media which would be detrimental to plant growth. The additions of the soil and sphagnum peat moss to fly ash based substrate were able to reduce the concentration of Cs. The concentrations of Cs in the effluent in our leaching experiment ranged between 0.007 mg/l to 0.13 mg/l. Such levels are much higher than the concentration reported in ground and drinking water [12]. Despite this, there is a little to worry from toxicological point of view, because Cesium cations in water are easily and rapidly transformed to CsOH and absorbed by suspended solids and sediments where it forms insoluble, immobile complexes [11].

The concentration lf lithium (Li) in the soils is highly correlated with the fine fraction contents (<0.002mm) and organic matter presence. The higher fine fraction concentration and higher organic matter contents, the higher Li presence might be expected [13]. Its average contents increase from 4.2mg/kg in light sandy soils to 14.8 mg/kg in heavy loamy soils [14], although there were report about natural occurring concentrations of Li of up to 45 mg/kg [15]. The concentration of Li in all substrates in our study didn't exceed range reported in soils, except for a slightly higher value (56.8mg/kg), obtained in VCFA.

In ground waters, Li varies from <0.05 to 150 µg/l [16], with lower levels found in the temperate zones, and some extreme values (up to 15000 µg/l) found in dry, hot regions. Although the average concentrations of Li in drinking water ranges from 4 to 60 µg/l [16], in waters used for irrigation Li contents in the range 5-100 µg/l can be harmful to crop plants [11].

The addition of soil and sphagnum peat moss to coal ashes reduced significantly the presence of Li in leachates, with the higher reduction in higher pore volumes (from 3 to 5 pore volumes.). What might be to some extend worrisome, are the levels of Li in all leachates, exceeding several times the limits considered to be harmful for plant irrigation. The highest Li content in our leachate reached almost 6 mg/l (i.e. 6.000 µg/l), which would exceed mentioned above values by 200 fold. It may raise the concern of possible groundwater contamination with excess of lithium leaching, but due to the availability of such data would require additional and thorough studies on Li leaching from plant growth media containing coal fly ashes.

The presence and distribution of beryllium (Be) in soils has not been investigated extensively. The mean natural Be contents for worldwide soils range from 0.48 to 3.52 mg/kg [12]. The concentration of B in our studies ranged from 0.52 mg/kg in the soil to 2.5 mg/kg in the plant growth substrate composed of fly ash from VCSU power plant. It indicates, that the concentrations of Be, even if coal ash substrate, were within the range common for soils. As a result of a low concentrations of Be in the substrates, concentrations of Be in the leachates also remained at a low level, and only slightly exceeded 4 µg/l for the highest level in the leachate from the substrate composed of fly ash from VCSU power plant. Such levels of Be in the water almost meet the EPA US standard for drinking water, which has been determined as 4 µg/l [17].

The concentration of strontium (Sr) in plant growth substrates in our study ranged from 32.8 mg/kg in the soil, up to 4100 mg/kg in coal fly ash. The concentration of Sr in our soil remains even on the low end of the spectrum of strontium presence in agricultural soils, which ranges from 32 mg/kg till more than 200 mg/kg [18, 19]. The values of Sr presence in both our coal ashes in our study exceed the highest Sr concentrations noticed in heavy loamy soils (up to 3100 mg/kg) and might be the issue of concern in further studies, because the concentration of Sr above 2000mg/kg in some phosphate fertilizers is considered as a source of soil contamination [15, 19].

Despite a very distinctive influence of the addition of soil and sphagnum peat moss to both fly ashes on the decrease of strontium leaching through the substrates in our study, the levels of Sr in our leachates remained high, and ranged from 8 to 600mg/l. Such values exceed several times concentrations found in river waters – 300µg/l [20] and the median concentration of 8 mg/kg present in seawater [21, 22], and should remain a matter of a great concern during future utilization of coal fly ashes as potential growth media for plants.

The reported range of Ba concentration range for soils is from 84 to 960 mg/kg, being the lowest in organic soils and the highest in loamy and clay soils [23, 24]. Barium concentration in the soil control in our experiments remained within mentioned above range, but barium presence in coal ashes, NDFA in particular, reached 7805 mg/kg. It exceeds about 8-fold the highest levels spotted in soils and should be a matter of concern and further studies.

The concentration of barium in soil solution shows considerable variation, from 43 µg/l in loamy soil to 307µg/l [25]. Unfortunately, the leachates in our study contained several times higher concentration of Ba, then spotted in soil solutions.

This problem should also be addressed in further studies and in any possible recommendations concerning the utilization of coal ash for plant fertilization purpose [26, 27].

Our study clearly indicated that before any attempt to utilize coal fly ash for plant fertilization, we should address not only the issue of trace elements concentration in coal ash based plant growth substrates, but also the study of leaching of trace elements from plant growth substrates. It looked very optimistic, that the additions of sphagnum peat moss and soil to coal ashes were able to reduce the concentration of potentially harmful trace elements in the leachate. Unfortunately, the presence of organic matter and increased sorption complex in the soil and sphagnum peat moss is not always able to neutralize negative influence of very high concentration of some trace elements, especially lithium (Li), strontium (Sr), and barium (Ba).

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