

## ORIGINAL ARTICLE

# Aluminium in coal fly ash (FA), in plants grown on FA, and in the leachates from FA

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### ABSTRACT

Two coal fly ashes (FA), one from Montana semi-bituminous coal and another from North Dakota lignite alone or in combination with bottom ash (BA) from Montana semi-bituminous coal were tested as plant growth media for the following plant species: barley (*Hordeum vulgare*), oats (*Avena sativa*), rye (*Secale cereale*), wheat (*Triticum aestivum*), ryegee; a hybrid between wheatgrass (*Agropyron cristatum*) and winter wheat (*Triticum aestivum*), and triticale; a hybrid between wheat (*Triticum aestivum*) and rye (*Secale cereale*). The concentration of Al, in coal ashes and in plant seedlings was determined using Inducted Coupled Plasma Spectrophotometry (ICP). All tested plant species germinated and grow in FA and/or FA + BA containing media. These data demonstrate that tested plants can grow on media consisting of coal ash, and therefore these plants can be used to cover FA or BA residue piles. In summary, the presence of sphagnum peat moss and soil in coal ash based plant growth media expressed ameliorative role by reducing the presence of Al in plant growth media and in plant seedlings grown on these media, but it did not translate into the decrease of the presence of Al in the leachate from these media. Elevated concentrations of Al in the leachate may cause some environmental health concerns and require further investigations.

**KEY WORDS:** coal ash, aluminum, plant growth media, leaching

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### INTRODUCTION

The intensive use of coal in the United States for electrical power generation causes production of large amount of coal residue which needs to be safely disposed. Since coal residue contains a variety of potentially hazardous trace elements, improper disposal and management could have a considerable environmental impact. Coal residue is produced during the combustion of solid fuel and can be carried with the flue gas, which is called fly ash (FA), or deposited as a bottom ash (BA), having similar characteristics as a FA (1, 2). During an average coal combustion process, about 12% of the combusted fuel becomes ash (3). Fly ash contains several toxic elements; including aluminum (Al). There is increasing awareness and concern of the Al toxicity to human population and ecosystems due to acid rain (4). Although there are strong debates on Al effects on humans, so far no final conclusions have been made. Al might be degenerative to the neurological system causing dialysis encephalopathy, cognitive decline, and is known to play a role in Alzheimer's disease (5). Al present in coal ash which can leach out and contaminate soils as well as surface water and groundwater (6). When fly ash is not properly disposed, and if leached, it may cause the severe contamination of subsurface water. Consequently, it may become a hazard to the environment because of their contribution to the formation of toxic compounds. The contamination could lead to health, environmental and land-use problems (7). A vegetative cover is a remedial technique utilized on FA landfills for soil stabilization and for the physical and chemical immobilization of contaminants. There is a great concern, that plants planted or voluntarily growing over a media with excessive amounts of FA may absorb Al, Se and several trace elements in toxic amounts, which may result in toxicity to animals and humans if such plants are ingested (8, 9, 10, 11). The aim of this study was to determine the environmental safety oriented on Al concentration in different growth media composed of FA and soil. In this study we investigated the growth of plant seedlings on coal ash based plant growth media, and the leaching of Al from these media. We also traced the leaching of Al from the 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). We compared the level of leaching of Al from soil control to the leaching from FA, and also tried to determine if the addition of sphagnum peat moss (SPM) to coal

based ash media decreases the level of Al leaching. We did also the comparison of the levels of Al obtained in our study to Al concentrations found in aqueous solutions, in groundwater, rivers, and other waters.

## MATERIALS AND METHODS

### Trial 1. Chemical analysis of coal fly ash (FA)

Seven different coal ashes (from lignite and semi-bituminous coal), collected from diverse locations in North Dakota, Minnesota and Montana have been tested for heavy metals concentration by using inductively coupled plasma (ICP) spectrophotometry.

### Trial 2. Plant seedlings growth on coal ash based media

As a plant growth media, soil control (Fargo clay), and two coal FA, one from Montana semi-bituminous coal and another from North Dakota lignite alone or in combination with BA from Montana semi-bituminous coal were used.

Experimental treatments consisted of following growth media:

1. Soil (Fargo Clay) as a control
2. FA from North Dakota lignite coal (FA1)
3. FA from semi-bituminous coal from Montana (FA2)
4. BA from the same semi-bituminous coal from Montana
5. FA/BA (1:1 weight based) from semi-bituminous coal from Montana

Six plant species have been tested including barley (*Hordeum vulgare*), Jerry oats (*Avena sativa*), rye (*Secale cereale*), wheat (*Triticum aestivum*), perennial ryegrass (*Lolium multiflorum*), and ReGreen (wheat x wheatgrass hybrid (*Triticum aestivum* x *Thinopyrum intermedium*)).

For each plant, 30 seeds were planted and covered with thin layer of growth media in 10 cm Petri dish, and watered to approximate field capacity of growth media.

Plants were grown for 14-21 days (depending on the time of seedlings germination and growth), harvested, dried, and weighed. Experiments have been replicated three times. The concentration of Al in growth media and digested young plants was determined.

Chemical analysis was performed using inductively coupled plasma (ICP) emission spectrophotometry (10). The data were analyzed statistically using ANOVA and Statistical Analysis System (12).

### Trial 3. Leaching study

Plexiglas columns (30.4 -cm long, 5-cm inner diameter) have been employed to study the transport and leaching of Al from a FA amended soil. A Fargo-Ryan soil (pH=6.1-8; organic matter=8%) has been 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).

Experimental treatments 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. Concentration of Al have been measured in Mehlich3 (M3; 0.02 M glacial acetic acid + 0.25 M NO<sub>3</sub> + 0.015M NH<sub>4</sub> F + 0.013 M HNO<sub>3</sub> + 0.001 M EDTA) (13) extractions using inductively coupled plasma (ICP) emission spectrophotometry 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

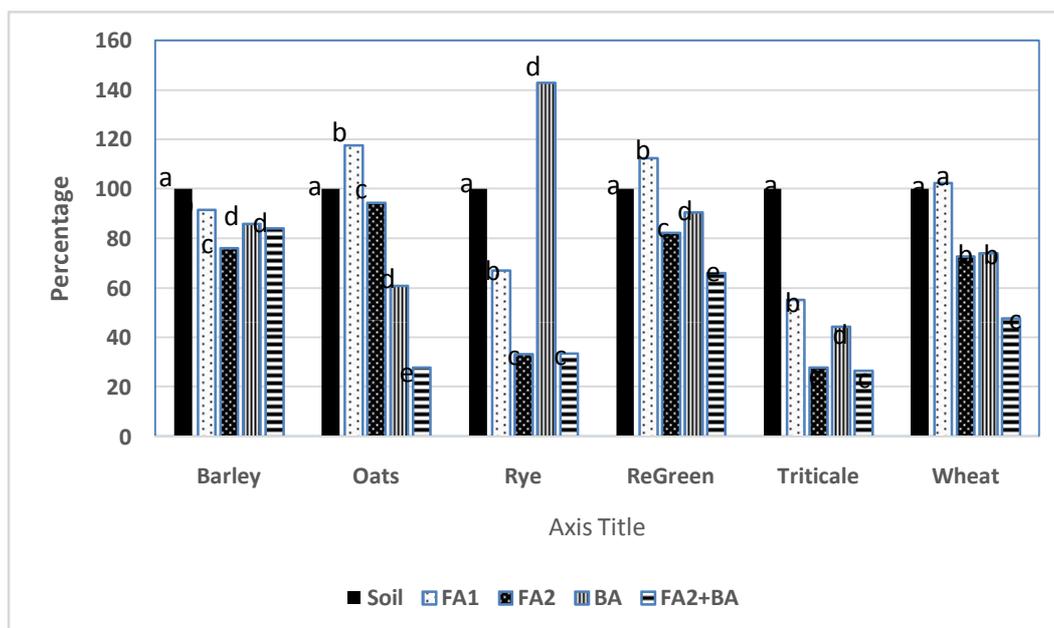
**Table 1. The concentration of Al in different coal fly ashes (in %), depending on ash source.**

FA source	1. AVS-FA	2.CCS-FA	3.CM-FA	4.CM-BA	5.HLP-FA	6.SS-FA	7.WS-FA
Al (%)	4.62	3.26	7.11	6.28	10.77	8.84	4.06

Fly ash (FA) source: 1. Antelope Valley Station (Bismarck) - fly ash-lignite (AVS-FA); 2. Coal Creek Station (Headwaters Resources) - fly ash-lignite (CCS-FA); 3. Coalstrip Montana (Rosebud Mine; from NDSU) -fly ash-semi-bituminous (CM-FA); 4. Coalstrip Montana (Rosebud Mine; from NDSU) - bottom ash-semi-bituminous (CM-BA); 5. Hoot Lake Plant (Otter Tail Power Company-Fergus Falls) - fly ash - semi-bituminous (HLP-FA); 6. Stanton Station (Great River Energy) - fly ash-lignite (SS-FA); 7. Washburn Station (from Valley City) - fly ash-lignite (WS-FA).

The concentration of Al in our soil used as control was 1.24%, and Al concentration in all tested coal ashes (Table 1) was significantly higher than in soil, ranging from 3.26% up to 10.77%.

All tested plants germinated (Fig. 1) and were able to grow in media with FA and /or BA.



**Fig. 1. Germination of plants (%; expressed as percentage of control soil) grown in media consisting of soil control, FA and/or BA (mean±SEM); a,b,c,d P<0.05 values with different superscripts differ within a species.**

Germination of tested plants was decreased in media containing FA and/or BA as compared to soil control (Fig. 1). Compared to soil control, germination of rye was lower ( $P<0.05$ ) in media consisting of FA1, FA2 or FA2+BA, but higher in media consisting of BA, ReGreen germination was lower ( $P<0.05$ ) in media consisting of FA2 or FA2+BA, triticale was lower ( $P<0.05$ ) in media consisting of FA1, FA2, BA or FA2+BA, barley and jerry winter wheat germination was lower ( $P<0.05$ ) in media consisting of FA2, BA or FA2+BA, and jerry oats was lower in media consisting of BA or FA2+BA (Fig. 1).

The concentration of Al in all media consisting of coal ash (Table 2) was ~3-5-fold greater ( $P<0.05$ ) than in soil control, and was greater in media consisting of FA1 and FA2 than BA or FA2+BA. Concentration of Al was greater ( $P<0.05$ ) in plants grown in media consisting of coal ash than in soil control, except for triticale grown in media consisting of BA (Table 2). Rye and Triticale seedlings were able to accumulate the highest concentrations of aluminum.

**Table 2. The concentration of Al (in %) in growth media and in plants grown in media consisting of soil control, FA1, FA2, BA or FA2+BA (in mg/kg<sup>-1</sup>). a,b,c,d P<0.05 values with different superscripts differ within a column.**

Media	Growth media	Barley	Jerry oats	Rye	Regreen	Triticale	Winter wheat
Soil	1.43±0.07 <sup>a</sup>	159±17 <sup>a</sup>	171±21 <sup>a</sup>	418±54 <sup>a</sup>	134±22 <sup>a</sup>	382±59 <sup>a</sup>	172±20 <sup>a</sup>
FA1	7.11±0.32 <sup>b</sup>	1052±92 <sup>b</sup>	2119±141 <sup>b</sup>	2097±249 <sup>b</sup>	882±79 <sup>b</sup>	1825±205 <sup>b</sup>	1159±201 <sup>b</sup>
FA2	6.28±0.36 <sup>c</sup>	501±40 <sup>c</sup>	1991±212 <sup>b</sup>	1096±197 <sup>c</sup>	880±84 <sup>b</sup>	1664±190 <sup>b</sup>	1161±179 <sup>b</sup>
BA	4.06±0.24 <sup>d</sup>	319±30 <sup>d</sup>	323±40 <sup>c</sup>	910±114 <sup>c</sup>	343±29 <sup>d</sup>	464±75 <sup>a</sup>	516±42 <sup>c</sup>
FA2+BA	4.47±0.29 <sup>d</sup>	470±39 <sup>c</sup>	319±29 <sup>c</sup>	1026±209 <sup>c</sup>	484±31 <sup>c</sup>	797±80 <sup>c</sup>	880±97 <sup>d</sup>

**Table 3. Concentrations of Al in the leachates (mg/l).**

Media	S	FAND	50FAND +50SPM	30FAND+ 30SPM+30S	FAVC	50FAVC+50SPM	30FAVC+ 30SPM+ 30S
Aluminum (Al) mg/kg	0.24	7.11	4.37	3.23	10.68	4.59	2.33

The concentration of Al in the leachates from soil control were very significantly lower than from coal fly ashes. The addition of soil and sphagnum peat moss to the media had a decisive influence on the lowering the concentration of aluminum in growth media.

## DISCUSSION

The results of our study demonstrated that cereal crop plants can germinate and grow in media consisting of coal ash, indicating a possibility to use these plants as a cover of piles of coal ash in order to prevent air and water erosion of FA from coal ash piles, and to keep coal ash confined to original disposal sites. Furthermore, since plants were able to grow in media consisting of coal ash only, coal ash can be used also as a soil supplement. However, precaution against water contamination should be undertaken. (1, 14, 15).

The highest concentration of Al in tested by us fly ashes reached 10.76%. Such concentration only slightly exceeds Al levels spotted in US soils. Al occurs naturally in the United States soils at the levels of 7-100 g/kg (16, 17). Despite this, the concentrations of Al in plant tissues in our experiments were high, in winter wheat reaching 1161 mg/kg and in barley 1052 mg/kg. On the other hand, such concentrations were approximately three times lower than the highest concentrations of Al found in plant tissues in other studies: 3410 mg/kg in grasses and 3410 mg/kg in clovers (5, 18). In addition, the main toxic effect of Al is the inhibition of plant root growth, and such effect has not been expressed in our experiments.

The concentration of Al in the United States drinking water ranges from 0.001-1 mg/l (ECA 2011). The Al concentration in drinking water of the USA is mainly below 0.1 mg/l, and the US EPA accepted a broad level for Al in drinking water at the range of 0.05-0.20 mg/l. There are concerns regarding the Al toxicity in freshwater systems. The toxicity of Al to fish in acidic waters, especially of lakes and rivers, has been well documented (19). Respiratory problems in fish occur in fish due to Al toxicity, when the disturbance of ion regulatory is resulting in imbalances in ions, especially sodium and chloride. High concentrations of water Ca may decrease Al toxicity to fish. In our leaching study Al concentration, even in the leachates from soil control, exceed the concentrations allowed for drinking water. The concentrations of Al in the leachates were in our experiments lower, when coal ash was ameliorated with sphagnum peat moss or soil. Despite this, Al concentration in the leachates from coal ash based plant growth media were relatively high, reaching levels spotted in aquatic systems surrounding metal industry installations (5).

In summary, the presence of sphagnum peat moss and soil in coal ash based plant growth media expressed ameliorative role reducing the presence of aluminum elements in plant growth media, but it did not translate into the decrease of the presence of Al in the leachate from these media. Elevated concentrations of Al in the leachate may cause some environmental health concerns and require further investigations.

Large scale implementation of plant cover over coal ash landfills will be required to fully test possible application of cereal plant species. Plant species should be grown till reaching maturity and only results of such experiments will provide data for large-scale application of "green technology" to establish the growth of selected plant species on coal ash.

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