



Original Article

Agro-Toxicological Aspects of Coal Fly Ash (FA) Phytoremediation by Cereal Crops: Effects on Plant Germination, Growth and Trace Elements Accumulation

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ABSTRACT

A vegetative cover is a remedial technique utilized on coal fly ash (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 on media with high content of FA may absorb toxic amounts of Se and/or heavy metals. If such plants are ingested, it may result in toxicity to animals or humans. Despite these objections, the utilization of FA as a growth medium for plants is an attractive alternative for disposal of FA in landfills. We hypothesized that selected plants will grow in media containing FA and/or bottom ash (BA) from several sources.

*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 tested as plant growth media for the following plant species: barley (*Hordeum vulgare*), oats (*Avena sativa*), rye (*Secale cereale*), wheat (*Triticum aestivum*), regreen; 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, As, B, Ba, Be, Co, Cd, Cr, Cu, Mo, Pb, Sr, Ti, Tl, and V in growth media and in young plants was determined using Inducted Coupled Plasma Spectrophotometry (ICP).*

All tested plant species germinated and grown in FA and/or FA + BA containing media. However, germination and/or growth of the majority of tested plants were decreased by the presence of FA and/or BA in growth media. Concentration of all analyzed elements was greater in growth media containing FA and/or BA than in soil control, and also was greater in plants grown on medium containing FA and/or BA than in soil. 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.

Key words: coal ash, plant growth media, heavy metals accumulation

INTRODUCTION

Coal remains the primary fuel used to generate electricity worldwide; coal combustion generates 39% of the world's electricity and 70% of US electricity [1,2]. 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 heavy metals, 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 [3, 4]. During an average coal combustion process, about 12% of the combusted fuel becomes ash [5].

A vegetative cover is a remedial technique utilized on FA landfills for soil stabilization and for the physical and chemical immobilization of contaminants [6, 7, 8, 9]. Many herbaceous plants, primarily grasses, which exhibit rapid growth, are moderately resistant to environmental stress, and are therefore often used as cover crops in environmental restoration and remediation projects [7].

There is a great concern, that plants planted or voluntarily growing over a media with excessive amounts of FA may absorb Se and several heavy metals in toxic amounts, which may result in toxicity to animals and humans if such plants are ingested [10, 11]. Deep-rooted plants grown over capped FA landfills might absorb heavy metals directly from the FA below the soil cover. Shallow rooted plants can also absorb heavy metals by contacting FA moved upward into the soil cap by

earthworm activity or by absorption of such elements as dissolved ions moved upward by capillary movement.

Despite mentioned above objections, the utilization of FA as a growth medium for plants is an attractive alternative to disposal of FA in landfills [9, 12, 13, 14, 15].

We hypothesized that soil containing FA and/or BA can be used as a growth media for several plant species including barley (*Hordeumvulgare*), oats (*Avena sativa*), rye (*Secalecereale*), wheat (*Triticumaestivum*), regreen; a hybrid between wheatgrass (*Agropyroncristatum*) and winter wheat (*Triticumaestivum*), and triticale; a hybrid between wheat (*Triticumaestivum*) and rye (*Secalecereale*). Therefore, the aim of this study was to determine the rate of germination and growth of listed above plants in growth media containing FA and/or BA and to determine concentration of several elements including Al, As, B, Ba, Be, Co, Cd, Cr, Cu, Mo, Pb, Sr, Ti, Tl, and V in growth media and growing plants.

MATERIAL AND METHODS

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 (*Hordeumvulgare*), Jerry oats (*Avena sativa*), rye (*Secalecereale*), wheat (*Triticumaestivum*), perennial ryegrass (*Loliummultiflorum*), and ReGreen (wheat x wheatgrass hybrid (*Triticumaestivum* x *Thinopyrumintermedium*)).

The rationale for choosing listed above plant species was: 1) the diversity of its nutritional requirements, 2) resistance to unfavorable environmental conditions, and 3) these plants belong to popular cereal crops.

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 3 replications.

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, As, B, Ba, Be, Cd, Co, Cr, Cu, Mo, Pb, Sr, Ti, Tl, and V in growth media and digested young plants was determined. Before digestion plant samples were washed in order to remove possible adhering FA particles, oven dried at 60° C to constant weight, and grounded to pass a 0.841 screen. Plant samples were wet-digested in a nitric-perchloric acid mixture prior to analysis of elements [13]

Chemical analysis was performed using inductively coupled plasma (ICP) emission spectrophotometry [15]. The data were analyzed statistically using ANOVA and Statistical Analysis System [16].

RESULTS

All tested plants germinated (Fig. 1) and were able to grow (Fig. 2) in media with FA and /or BA. Germination of tested plants was decreased in media containing FA and/or BA 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 was less ($P < 0.05$) in media consisting of FA2 or FA2+BA; triticale was less ($P < 0.05$) in media consisting of FA1, FA2, BA or FA2+BA; barley and Jerry winter wheat germination was less ($P < 0.05$) in media consisting of FA2, BA or FA2+BA; and Jerry oats was less in media consisting of BA or FA2+BA (Fig. 1).

Weight of plants was affected ($P < 0.05$) by media consisting of FA and/or BA (Fig. 2).

Tables 1-10 present concentration of several elements including Al, As, B, Ba, Be, Co, Cd, Cr, Cu, Mo, Pb, Sr, Ti, Tl, and V in growth media and in young plants.

The concentration of Al in all media consisting of coal ash 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 1).

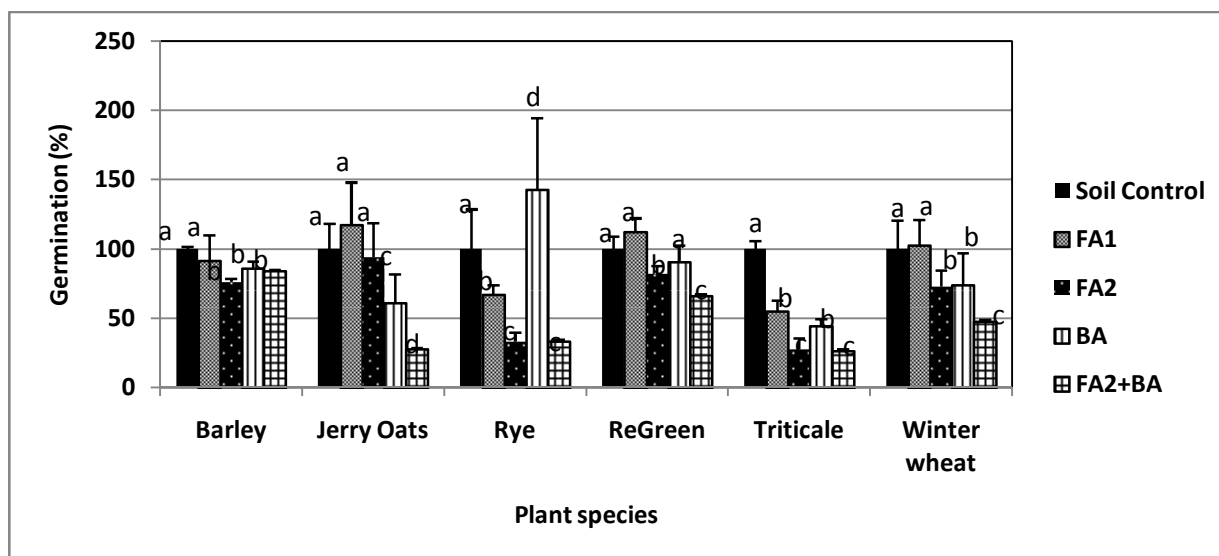


Fig. 1. Germination of plants (%; expressed as percentage of control soil) grown in media consisting of soil control, FA and/or BA (mean \pm SEM); a,b,c,d $P < 0.05$ values with different superscripts differ within a species.

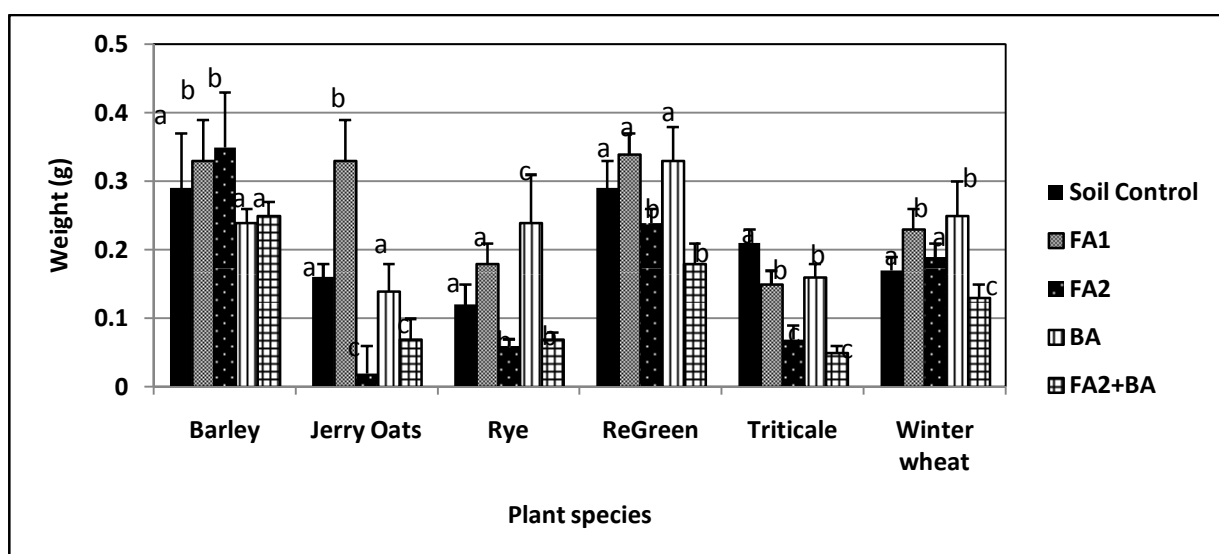


Fig. 2. Weight (g) of plants grown on media consisting of soil control, FA and/or BA harvested on day 14-21 (mean \pm SEM); a,b,c,d $P < 0.05$ values differ within a species.

Table 1. 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⁻¹). 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 \pm 0.07 ^a | 159 \pm 17 ^a | 171 \pm 21 ^a | 418 \pm 54 ^a | 134 \pm 22 ^a | 382 \pm 59 ^a | 172 \pm 20 ^a |
| FA1 | 7.11 \pm 0.32 ^b | 1052 \pm 92 ^b | 2119 \pm 141 ^b | 2097 \pm 249 ^b | 882 \pm 79 ^b | 1825 \pm 205 ^b | 1159 \pm 201 ^b |
| FA2 | 6.28 \pm 0.36 ^c | 501 \pm 40 ^c | 1991 \pm 212 ^b | 1096 \pm 197 ^c | 880 \pm 84 ^b | 1664 \pm 190 ^b | 1161 \pm 179 ^b |
| BA | 4.06 \pm 0.24 ^d | 319 \pm 30 ^d | 323 \pm 40 ^c | 910 \pm 114 ^c | 343 \pm 29 ^d | 464 \pm 75 ^a | 516 \pm 42 ^c |
| FA2+BA | 4.47 \pm 0.29 ^d | 470 \pm 39 ^c | 319 \pm 29 ^c | 1026 \pm 209 ^c | 484 \pm 31 ^c | 797 \pm 80 ^c | 880 \pm 97 ^d |

The concentration of B in all media consisting of coal ash was ~28-65-fold greater ($P<0.05$) than in soil control, and was greater in media consisting of FA1 and FA2 than BA or FA2+BA. The concentration of B was greater ($P<0.05$) in plants grown in media consisting of coal ash than in soil control (Table 2).

Table 2. The concentration of B in growth media and in plants ($\text{mg} \times \text{kg}^{-1}$) grown on media consisting of soil control, FA1, FA2, BA or FA2+BA.

| Media | Growth medium | Barley | Jerry oats | Rye | Regreen | Triticale | Winter wheat |
|--------|------------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| Soil | 19± 4 ^a | 7± 1.3 ^a | 9± 1.3 ^a | 9± 1.1 ^a | 7± 0.8 ^a | 22± 3.1 ^a | 18± 3.3 ^a |
| FA1 | 966± 104 ^b | 362± 29 ^c | 760± 52 ^b | 700± 89 ^c | 421± 44 ^c | 665± 70 ^c | 625± 59 ^c |
| FA2 | 1230± 133 ^b | 207± 24 ^b | 468± 55 ^b | 370± 44 ^d | 286± 31 ^b | 441± 51 ^b | 351± 40 ^b |
| BA | 540± 47 ^c | 94± 11 ^d | 226± 27 ^c | 132± 12 ^b | 115± 17 ^d | 230± 28 ^d | 210± 26 ^d |
| FA2+BA | 659± 57 ^d | 142± 17 ^e | 275± 29 ^d | 133± 17 ^b | 276± 33 ^b | 313± 21 ^e | 312± 47 ^b |

The concentration of Ba in all media consisting of coal ash was ~0.5-2-fold greater ($P<0.05$) than in soil control, and was greater in media consisting of FA1 and FA2 than BA or FA2+BA. The concentration of Ba was greater ($P<0.05$) in plants grown in media consisting of coal ash than in soil control except winter wheat grown on media consisting of Ba (Table 3).

Table 3. The concentration of Ba (in %) in growth media and in plants ($\text{mg} \times \text{kg}^{-1}$) grown on media consisting of soil control, FA1, FA2, BA or FA2+BA

| Media | Growth medium | Barley | Jerry oats | Rye | Regreen | Triticale | Winter wheat |
|--------|------------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| Soil | 0.19±0.03 ^a | 4±0.65 ^a | 8±1.9 ^a | 25±6 ^a | 8±1.7 ^a | 16±3.3 ^a | 26±4 ^a |
| FA1 | 0.36±0.05 ^b | 171±22 ^b | 153±17 ^b | 234±34 ^b | 109±12 ^b | 108±12 ^b | 142±19 ^b |
| FA2 | 0.35±0.03 ^b | 179±29 ^b | 221±30 ^c | 117±21 ^c | 64±7 ^c | 107±14 ^b | 118±16 ^c |
| BA | 0.26±0.02 ^c | 18±4 ^c | 19±4 ^d | 43±11 ^d | 26±4 ^d | 41±5 ^c | 27±5 ^d |
| FA2+BA | 0.29±0.04 ^c | 31±3 ^d | 47±8 ^e | 49±9 ^d | 30±4 ^d | 116±10 ^b | 57±11 ^e |

The concentration of Co in all media consisting of coal ash was ~0.5-2-fold greater ($P<0.05$) than in soil control. The concentration of Co was greater ($P<0.05$) in plants grown in media consisting of coal ash than in soil control except for triticale grown on media consisting of BA (Table 4).

Table 4. The concentration of Co in growth media and in plants ($\text{mg} \times \text{kg}^{-1}$) grown on media consisting of soil control, FA1, FA2, BA or FA2+BA.

| Media | Growth medium | Barley | Jerry oats | Rye | Regreen | Triticale | Winter wheat |
|--------|-------------------------|-------------------------|-------------------------|-------------------------|------------------------|-----------------------|------------------------|
| Soil | 6.81±1.42 ^a | 0.05±0.001 ^a | 0.03±0.007 ^a | 0.01±0.002 ^a | 0.08±0.01 ^a | 0.36±0.4 ^a | 0.54±0.8 ^a |
| FA1 | 12.29±2.22 ^b | 0.26±0.04 ^b | 1.08±0.18 ^b | 0.91±0.04 ^b | 1.05±0.07 ^b | 0.57±0.4 ^b | 1.19±0.7 ^b |
| FA2 | 14.95±2.91 ^b | 0.90±0.16 ^c | 1.28±0.26 ^b | 1.99±0.03 ^c | 0.92±0.05 ^b | 0.77±0.9 ^c | 1.58±0.13 ^c |
| BA | 9.86±2.20 ^b | 0.47±0.09 ^d | 0.19±0.03 ^c | 1.08±0.11 ^b | 0.32±0.03 ^c | 0.38±0.3 ^a | 0.88±0.11 ^d |
| FA2+BA | 11.25±2.17 ^b | 0.10±0.02 ^e | 0.3±0.007 ^d | 0.24±0.03 ^d | 0.29±0.04 ^c | 0.86±0.7 ^c | 0.73±0.9 ^d |

The concentration of Cr in all media consisting of FA1, FA2 or FA2+BA but not BA alone was ~0.5-4-fold greater ($P<0.05$) than in soil control, and was greater in media consisting of FA1 than FA2 or FA2+BA. The concentration of Cr was greater ($P<0.05$) in plants grown in media consisting of coal ash than in soil control except barley, rye, regreen and winter wheat grown on media consisting of BA and regreen and winter wheat grown on media consisting of FA2+BA (Table 5).

Table 5. The concentration of Cr in growth media and in plants ($\text{mg} \times \text{kg}^{-1}$) grown on media consisting of soil control, FA1, FA2, BA or FA2+BA media consisting of soil control, FA1, FA2, BA or FA2+BA.

| Media | Growth medium | Barley | Jerry oats | Rye | Regreen | Triticale | Winter wheat |
|--------|-----------------------|------------------------|------------------------|-------------------------|------------------------|------------------------|-------------------------|
| Soil | 17.3±2.1 ^a | 2.35±0.43 ^a | 1.89±0.28 ^a | 2.99±0.17 ^a | 1.84±0.22 ^a | 2.37±0.3 ^a | 2.62±0.37 ^a |
| FA1 | 73.0±5.5 ^b | 25.23±3.4 ^b | 43.24±5.2 ^b | 23.36±3.11 ^b | 13.6±2.1 ^b | 33.27±2.9 ^b | 36.26±4.21 ^b |
| FA2 | 39.6±3.7 ^c | 4.36±0.56 ^c | 3.81±0.5 ^c | 4.41±0.57 ^c | 3.22±0.41 ^c | 3.45±0.18 ^c | 4.40±0.59 ^c |
| BA | 13.8±2.1 ^d | 1.96±0.32 ^a | 4.16±0.4 ^d | 2.68±0.33 ^a | 1.41±0.24 ^a | 3.31±0.4 ^d | 1.24±0.17 ^d |
| FA2+BA | 25.1±3.7 ^e | 4.30±0.45 ^c | 2.68±0.22 ^e | 3.53±0.45 ^d | 1.62±0.35 ^a | 4.31±0.26 ^e | 1.59±0.13 ^e |

The concentration of Cu in all media consisting of coal ash was ~1.5-4-fold greater ($P<0.05$) than in soil control, and was greater in media consisting of FA2 than FA1, BA or FA2+BA. However, concentration of Cu was affected ($P<0.05$) by growth media only in selected plants. The concentration of Cu was greater in jerry oats grown in media consisting of FA1, FA2 or FA2+BA; in rye grown in media consisting of FA1 or FA2+BA; in triticale grown in FA1 and FA2+BA, and in winter wheat grown in FA2 or FA2+BA (Table 6). Concentration of Cu in barley and regreen was not affected by growth media.

Table 6. The concentration of Cu in growth media and in plants ($\text{mg} \times \text{kg}^{-1}$) grown on media consisting of soil control, FA1, FA2, BA or FA2+BA.

| Media | | Barley | Jerry oats | Rye | Regreen | Triticale | Winter wheat |
|--------|-------------------------------|------------------------------|------------------------------|------------------------------|-------------------------------|------------------------------|------------------------------|
| Soil | 15.79 \pm 2.09 ^a | 7.34 \pm 0.88 ^a | 3.47 \pm 0.44 ^a | 6.23 \pm 0.86 ^a | 12.47 \pm 1.33 ^a | 7.29 \pm 0.47 ^a | 6.17 \pm 0.72 ^a |
| FA1 | 32.95 \pm 4.09 ^b | 7.71 \pm 0.6 ^a | 6.88 \pm 0.73 ^b | 8.00 \pm 0.9 ^a | 11.75 \pm 1.45 ^a | 9.84 \pm 0.87 ^b | 6.49 \pm 0.55 ^a |
| FA2 | 61.75 \pm 7.27 ^c | 6.62 \pm 0.92 ^a | 8.77 \pm 1.05 ^c | 7.29 \pm 0.81 ^a | 12.13 \pm 0.97 ^a | 7.35 \pm 0.68 ^a | 7.42 \pm 0.81 ^b |
| BA | 26.95 \pm 3.03 ^d | 6.59 \pm 0.71 ^a | 3.06 \pm 0.29 ^a | 6.73 \pm 0.92 ^a | 10.76 \pm 1.12 ^a | 7.74 \pm 0.86 ^a | 6.04 \pm 0.66 ^a |
| FA2+BA | 47.52 \pm 3.95 ^e | 5.77 \pm 0.72 ^b | 7.35 \pm 0.91 ^b | 8.14 \pm 0.77 ^a | 11.42 \pm 1.28 ^a | 8.65 \pm 0.71 ^c | 7.24 \pm 0.71 ^b |

The concentration of Mo in all media consisting of coal ash was ~2-3.5-fold greater ($P<0.05$) than in soil control, and was greater in media consisting of FA1 or FA2 than BA or FA2+BA. The concentration of Mo was greater ($P<0.05$) in plants grown in media consisting of coal ash than in soil control except regreen grown on media consisting of BA (Table 7).

Table 7. The concentration of Mo in growth media and in plants ($\text{mg} \times \text{kg}^{-1}$) grown on media consisting of soil control, FA1, FA2, BA or FA2+BA.

| Media | | Barley | Jerry oats | Rye | Regreen | Triticale | Winter wheat |
|---------|-------------------------------|------------------------------|------------------------------|------------------------------|-------------------------------|------------------------------|------------------------------|
| Soil | 2.90 \pm 0.33 ^a | 1.54 \pm 0.18 ^a | 2.18 \pm 0.31 ^a | 0.61 \pm 0.04 ^a | 0.87 \pm 0.9 ^a | 1.69 \pm 0.2 ^a | 1.65 \pm 0.19 ^a |
| FA 1 | 10.35 \pm 1.08 ^b | 45.2 \pm 3.32 ^b | 70.9 \pm 6.67 ^b | 46.3 \pm 4.32 ^b | 28.56 \pm 3.07 ^b | 46.27 \pm 4.1 ^b | 50.61 \pm 6.2 ^b |
| FA 2 | 9.10 \pm 0.72 ^b | 4.44 \pm 0.71 ^c | 7.32 \pm 0.68 ^c | 4.76 \pm 0.45 ^c | 4.36 \pm 0.51 ^c | 4.72 \pm 0.37 ^c | 7.72 \pm 0.95 ^c |
| BA | 6.67 \pm 0.59 ^c | 3.82 \pm 0.4 ^c | 5.52 \pm 0.72 ^d | 2.76 \pm 0.3 ^d | 1.49 \pm 0.17 ^d | 3.91 \pm 0.4 ^d | 3.74 \pm 0.4 ^d |
| BA +FA2 | 7.60 \pm 0.88 ^d | 3.89 \pm 0.33 ^c | 4.71 \pm 0.5 ^d | 3.65 \pm 0.41 ^e | 3.21 \pm 0.44 ^e | 5.62 \pm 0.62 ^e | 5.17 \pm 0.63 ^e |

The concentration of Sr in all media consisting of coal ash was ~10-17-fold greater ($P<0.05$) than in soil control, and was greater in media consisting of FA2 than FA1, BA or FA2+BA. The concentration of Sr was greater ($P<0.05$) in plants grown in media consisting of coal ash than in soil control (Table 8).

Table 8. The concentration of Sr in growth media (in %) and in plants ($\text{mg} \times \text{kg}^{-1}$) grown on media consisting of soil control, FA1, FA2, BA or FA2+BA.

| Media | | Barley | Jerry oats | Rye | Regreen | Triticale | Winter wheat |
|---------|--------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| Soil | 0.025 \pm 0.004 ^a | 10.3 \pm 1.12 ^a | 18.3 \pm 2.0 ^a | 25.2 \pm 3.1 ^a | 15.0 \pm 1.57 ^a | 21.4 \pm 22.2 ^a | 22.1 \pm 2.52 ^a |
| FA 1 | 0.24 \pm 0.03 ^b | 81.1 \pm 9.2 ^b | 149.6 \pm 16.2 ^b | 202.8 \pm 23.2 ^b | 98.6 \pm 10.2 ^b | 141.2 \pm 15.4 ^b | 163.7 \pm 17.7 ^b |
| FA 2 | 0.43 \pm 0.05 ^c | 432.6 \pm 38.1 ^c | 494.8 \pm 52.7 ^c | 500.0 \pm 47.0 ^c | 305.1 \pm 34.6 ^c | 382.4 \pm 39.0 ^c | 391.5 \pm 40.2 ^c |
| BA | 0.28 \pm 0.03 ^d | 80.8 \pm 7.9 ^b | 128.6 \pm 14.4 ^d | 105.4 \pm 11.2 ^d | 61.1 \pm 55.2 ^d | 107.0 \pm 11.3 ^d | 113.4 \pm 12.8 ^d |
| BA +FA2 | 0.34 \pm 0.04 ^e | 413.0 \pm 47.5 ^c | 524.3 \pm 49.1 ^c | 302.7 \pm 34.9 ^e | 232.4 \pm 27.4 ^e | 272.9 \pm 23.4 ^e | 347.8 \pm 33.0 ^e |

The concentration of Ti in all media consisting of coal ash was ~3-9-fold greater ($P<0.05$) than in soil control, and was greater in media consisting of FA2 than FA1, BA or FA2+BA. The concentration of Ti was greater ($P<0.05$) in plants grown in media consisting of coal ash than in soil control except barley grown in media consisting of FA2+BA, jerry oats grown in FA1 rye grown in FA1 or BA, regreen grown in FA1, FA2, or BA, triticale grown in FA1 or BA, and winter wheat grown in FA1 or BA (Table 9).

Table 9. The concentration of Ti in growth media (in %) and in plants (mg x kg⁻¹) grown on media consisting of soil control, FA1, FA2, BA or FA2+BA.

| Media | | Barley | Jerry oats | Rye | Regreen | Triticale | Winter wheat |
|--------|--------------------------|------------------------|------------------------|-------------------------|------------------------|------------------------|------------------------|
| Soil | 0.049±0.002 ^a | 6.3±0.7 ^a | 10.2±1.12 ^a | 46.3±5.2 ^a | 27.6±3.1 ^a | 21.8±2.2 ^a | 42.6±3.34 ^a |
| FA1 | 0.14±0.03 ^b | 16.3±1.8 ^b | 9.0±1.1 ^a | 36.7±3.31 ^b | 24.7±2.8 ^b | 26.5±2.32 ^b | 19.3±1.82 ^b |
| FA2 | 0.43±0.05 ^c | 32.7±2.98 ^c | 64.9±7.2 ^b | 135.5±14.6 ^c | 28.4±2.77 ^a | 62.2±6.7 ^c | 67.2±7.11 ^c |
| BA | 0.15±0.02 ^b | 17.9±1.85 ^b | 15.1±1.47 ^c | 24.9±2.28 ^d | 9.2±0.83 ^c | 21.7±0.28 ^a | 19.2±1.46 ^b |
| FA2+BA | 0.27±0.04 ^d | 2.8±0.23 ^d | 64.6±7.0 ^b | 58.7±6.0 ^e | 37.5±3.21 ^d | 60.3±5.25 ^d | 57.6±4.94 ^d |

The concentration of V in all media consisting of coal ash was ~1.5-4-fold greater ($P < 0.05$) than in soil control, and was greater in media consisting of FA1 or FA1 than BA or FA2+BA. Concentration of V was affected ($P < 0.05$) by growth media for selected plants only. Concentration of V in barley was not detectable in plants grown in soil control or BA. Compared to soil control, concentration of V in jerry oats was greater ($P < 0.05$) in plants grown in FA1, FA2 or FA2+BA, in rye was greater in plant grown in FA1, in triticale was greater in plants grown in FA1 (Table 10).

Table 10. The concentration of V in growth media and in plants (mg x kg⁻¹) grown on media consisting of soil control, FA1, FA2, BA or FA2+BA.

| Media | | Barley | Jerry oats | Rye | Regreen | Triticale | Winter wheat |
|--------|------------------------|-----------------------|-----------------------|------------------------|------------------------|------------------------|------------------------|
| Soil | 27.3±3.0 ^a | 0.0 | 0.4±0.05 ^a | 3.23±0.44 ^a | 2.61±0.34 ^a | 3.78±0.5 ^a | 3.01±0.4 ^a |
| FA1 | 98.9±9.7 ^b | 2.0±0.22 ^a | 3.7±0.4 ^b | 7.48±0.82 ^b | 2.88±0.31 ^a | 5.42±0.42 ^b | 2.54±0.26 ^b |
| FA2 | 83.8±7.22 ^b | 1.1±0.14 ^b | 2.3±0.19 ^c | 3.95±0.4 ^c | 1.63±0.2 ^b | 1.26±0.13 ^c | 2.96±0.37 ^c |
| BA | 40.1±3.76 ^c | 0.0 | 0.0 | 0.29±0.04 ^d | 2.16±0.27 ^c | 0.88±0.07 ^d | 0.94±0.07 ^d |
| FA2+BA | 58.2±4.9 ^d | 0.6±0.04 ^c | 2.2±0.24 ^c | 1.93±0.25 ^e | 1.46±0.37 ^b | 2.08±0.26 ^e | 2.96±0.39 ^c |

The concentration of As, Be, Cd, Pb, and Tl in growth media or plants were below ICP detection limits.

DISCUSSION

The results of present 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 coal ash to be confined to selected site. 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 since small proportion (~4%) is water soluble [6, 13, 17, 18, 19, 20, 21].

Other studies have also demonstrated that plants were able to grow in media consisting of 100% FA or in soil supplemented with 5% of FA [22, 23].

However, in this study we terminated plant growth after 14-21 days. Therefore, additional studies should be undertaken to determine if these plants would grow on tested growth media till full maturity.

In the present study, for the majority of analyzed elements including Al, As, B, Ba, Be, Co, Cd, Cr, Cu, Mo, Pb, Sr, Ti, Tl, and V in growth media and in young plants concentration in coal ashes was greater compared to soil control.

The concentration of aluminum (Al) in all plant growth media didn't exceed the concentrations found in some American soils [24, 25]. Concentration in soil varies widely ranging from below 7 to over 100 g/kg. The concentration of Al in all our tested plant growth media didn't exceed this value. Despite this, the concentrations of Al in plant tissues in our experiments were very high, exceeding even 2000 mg/kg in the case of rye seedlings grown on FA 1 medium. Similar studies with grasses grown on a landfill containing coal combustion waste showed several times lower concentration of aluminum in plant tissues [26].

The concentration of arsenic (As) in plants was below the detection limits, despite relatively high concentration of As in fly ashes used as growth media (up to 64 mg/kg). Such concentration meets the standards for considering plant growth media as phytotoxic [27].

The concentration of boron (B) in all growth media containing coal ashes reached 1230 mg/kg in coal ash from lignite coal and exceeded several times values expected to be present in the soil

(usually up to 26- 33 mg/kg) [25]. Coal ash media in our experiments contained significantly higher amounts of boron, than noted in literature [28]. Coal FA could be an effective source of plant-available B, since the B in FA is easily available to plants [15]. The adequate supply of B for plants occurs when boron tissue concentration is in the range of 5- 30 mg B/kg. The range between adequate supply and toxicity is quite narrow for B [27]. In our case we did have the problem with boron toxicity for plants. The level of boron concentration in plant tissues reached 665 mg/kg in triticale seedlings, 700 mg/kg in rye seedlings, and 760 mg/kg in oats seedlings. In addition, plants expressed the most common symptom of excessive B accumulation. This symptom was the necrosis along leaf margins and at the growing points, reflecting the buildup of B following the transpiration stream [28]. It would indicate that our seedlings, except for those grown on the soil, suffer from boron toxicity.

Barium is found in most soils at concentrations ranging from about 15 to 3,500 mg/kg and mean values ranging between 265 and 835 mg/kg, depending on soil type (29). Barium in our control treatment (soil) reached the level of 1900 mg/kg, and was within acceptable limits for soils. Barium in our fly ashes only slightly exceeded acceptable limits for soils. The concentration of Ba in plant seedlings, although strongly related to the concentration in growth media, remained within toxicologically acceptable limits (even if plants in our experiment would be fed to animals).

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 but one coal ash based plant growth media Cr concentration remained within these limits. Cr concentration in FA 2 reached 73 mg/kg, but even such concentration didn't exceed the level considered to be phytotoxic (100 mg/kg) [27].

The average concentration of cobalt (Co) in soil in the United States is 7.2 mg/kg, with a range of 1- 40 mg/kg (30). The concentration of Co in the soil used in our experiments was close to listed above average, but in media composed of ashes significantly exceeded the amount found in the soil. Despite elevated amounts of Co in our growth media, there is little evidence of cobalt toxicity to plants due to elevated concentrations in soil or other growth media [31].

Although plant growth media composed of coal ash contained elevated amounts of copper, as compared to the soil, it didn't result in elevated presence of Cu in plant tissues and the concentration of Cu remained almost unchanged and within average values for Cu concentration in plants [32].

High concentration of molybdenum is generally associated with alkaline soils. Some pastures have exceptionally high concentrations of molybdenum and may give rise to symptoms of molybdenum toxicity in sheep and cattle. Guideline values of up to 50 mg/kg dry weight have been fixed for molybdenum concentrations in agricultural soils [33].

Although soil pH in our experiments were alkaline (pH 8.3-8.5), we didn't notice elevated amounts of Mo in soil used in our study. Concentration of Mo in FA media was a few times higher than in the soil, but didn't reach mentioned above extreme values. Despite this, plants grown on media with elevated concentration of Mo showed significantly elevated accumulation of Mo, as compared to plants grown on the soil. Concentrations of Mo in plant leaves may range from 0.1 to 1.5 ppm on a dry matter basis, and in our studies plants grown on Mo rich media very significantly exceeded this concentration. Concentrations of Mo in plants above 10 mg/kg might be dangerous for animals fed with these plants [34], but in our studies plants grown on Mo rich media didn't exceed this concentration.

Strontium is found naturally in soil in amounts that vary over a wide range, but the typical concentration is 250 mg/kg. The disposal of coal ash, incinerator ash, and industrial wastes may increase the concentration of strontium in soil [35]. The concentration of Sr in coal ashes, on the other hand, may vary depending on ash source and be as low as < 1 mg/kg and as high as 3,900 mg/kg [36]. In our experiment, the concentration of Sr in the soil was 250 mg/kg, and also the concentration in coal ash was higher than typical concentration for fly ash, reaching 4300 mg/kg in FA 2. Plant accumulation of Sr was correlated to the high concentration in fly ash based media, and for all plants grown of 2 oscillated between 300 to 500 mg/kg. Despite such high accumulation if Sr in plants it does not seem to create any toxicological risk, because frequently Sr levels in forage crops reach even higher values than in our experiments [27].

Heavy clay soils, like the soil used in our experiment (Fargo clay) contain more titanium (Ti) than sandy soils (34, 37), and the average concentration in soil appears to be below 5 g/kg. Our soil contained only a fraction (about 10%) of this amount, and even our coal ash also didn't contain more than 5g Ti per kg. The concentration of Ti in plants was also within acceptable limits [38].

The vanadium contents of soils are related to those of the parent rocks from which they are formed [39]. Average contents of V in soils vary from 10 mg/kg in sandy soils to 500 mg/kg in calcareous soils. The soils in the USA contain V in the range of 36-150 mg/kg [40]. The concentration of vanadium in all our growth media didn't exceed 100 mg/kg, and as a consequence, concentrations in plant tissues remained low.

In summary, plant species tested in our experiments showed significant adaptability to the growth on FA and/or BA based media. There were noticeable differences in seedlings growth, depending on the type and source of coal ash used. It suggests the necessity to perform pre-plantation tests in case of planning to provide green cover over FA piles. The novel element of our studies was to test different types of coal ashes, and to combine FA with BA. 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. Our results, though, are encouraging, because they show that plants are able to grow in such adverse conditions, as on coal ash media. In addition, our results indicate, that the transfer of heavy metals present in FA and/or BA to plants does not indicate the possibility of heavy metals transmission if a food chain, which would be dangerous from environmental health perspective.

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REFERENCES

1. Energy Information Administration. (2002). North Dakota Profile. <http://www.eia.doe.gov/cneaf/coal/statepro/imagemap/nd.htm>
2. Twardowska, I. and Stefaniak, S. (2006). Coal and coal combustion products: prospects for future and environmental issues. In: "Coal Combustion Byproducts and Environmental Issues", Ed. K. Sajwan et al., Springer Inc., New York, NY, pp. 13-20.
3. Carlson, C.L., and Adriano, D.C. (1993). Environmental impact of coal combustion residues. *J. Environ. Qual.* 22:227-234.
4. Sajwan K.S., Punshon T., and Seaman J.C. (2006). Production of coal combustion products and their potential uses. In: "Coal Combustion Byproducts and Environmental Issues", Ed. K. Sajwan et al., Springer Inc., New York, NY, pp. 3-9.
5. Hecht, N.L., and Duvall, D.S. (1975). Characterization and utilization of municipal and utility sludges and ashes. Environ. Prot. Technol. Series, EPA-67012-75. U.S. Environmental Protection Agency.
6. Bilski, J., Alva A.K., Sajwan O.S. (1995). Agricultural uses of coal fly ash.. In *Environmental Aspects of Soil Amendments, Vol. 1: Inorganic Fertilizers*, Ed: Jack E. Rechcigl, Lewis Publishers, Boca Raton, Florida, pp. 255-291.
7. Koo, B.J, Barton, C, Adriano, D. (2006). Evaluation of bahiagrass (*Paspalum notatum*) as a vegetative cover for a landfill containing coal combustion waste. In "Coal Combustion Byproducts and Environmental Issues", Ed. K. Sajwan et al., Springer Inc., New York, NY, pp. 225-231.
8. Kramer, U. (2007). Phytoremediation-Novel Approaches to Cleaning Up Polluted Soils." *Current Opinion in Biotechnology*, pp. 133-141.
9. List, M.M. (2007). Phytoextraction of metals from contaminated soil: a review of plant/soil/metal interaction and assessment of pertinent agronomic issues." *J. Hazard. Substance Res.* 22, 4-5.
10. Furr, A.K., Parkinson, T.F., Elfving, D.C., Gutenmann, W.H., Pakkala, J.S., and Lisk, D. J. (1979). Elemental content of apple millet and vegetables grown in pots of neutral soil amended with fly ash. *J. Agric. Food Chem.* 27:135-139.
11. Gutenmann, W.H., Pakkala, J.S., Churey, D.J., Kelly, W.C., and Lisk, D.J. (1979). Arsenic, boron, molybdenum, and selenium in successive cuttings of forage crops field grown on fly ash amended soil. *J. Agric. Food Chem.* 27:1393-1398.

12. Scanlon, D.H., and Duggan, J.C. (1979). Growth and element uptake of woody plants on fly ash. *Environ. Sci. Technol.* 3:311-315.
13. Carlson, C.L., and Adriano, D.C. (1991). Growth and elemental content of two tree species growing on abandoned coal fly ash basins. *J. Environ. Qual.* 20:581-589.
14. Alva A.K., Bilski, J.J., Sajwan K.S., van Clief D. (2000). Leaching of metals from soils amended with fly ash and organic byproducts, in: *Biogeochemistry of Trace Elements in Coal and Coal Combustion*, Ed: K. Sajwan et al., Kluwer Academic, New York, pp. 193-207.
15. Bilski, J., Alva A.K. (1995). Transport of heavy metals and cations in a fly ash amended soil. *Bull. Environ. Contam. Toxicol.*, New York: Springer Verlag, 55:502-509,
16. SAS, (2005). Statistical Analysis System.
17. Rohrman, F.A. (1971). Analyzing the effect of fly ash on water pollution. *Environ. Manage.* August: 76-80.
18. Dreesen, D.R., Gladney, E.S. Owens, J.W, Perkins, B.L., Wienke, C.L., and Wangen, L.E. 1(977). Comparison of levels of trace elements extracted from fly ash and levels found in effluent waters from a coal-fired power plant. *Envir. Sci. Technol.* 11:1017-1031.
19. Riekerk, M. (1983). Coal-ash effects on fuel wood production and runoff water quality. *Southern J. Appl. Forest.* 2:99-103.
20. Menon, M.P., Sajwan, K.S., Ghuman, G.S., James, J., and Chandra, K. (1993a). Elements in coal and coal combustion residues and their potential for agricultural crops, in: *Trace Elements in Coal and Coal Combustion Residues*, Keefer, R.F. and Sajwan, K.S. (Eds.), Lewis Publishers, Chelsea, MI, pp. 116-137.
21. Ugurlu, A. (2004). Leaching characteristics of fly ash. *Environmental Geology*, 46:890-895.
22. Openshaw, S.C. (1992). Utilization of coal fly ash. Report # 92-3. Florida Center for Solid and Hazardous Waste Management, 40-41.
23. Menzies, N.W., and Aitken, R.L. (1996). Evaluation of fly ash as a component of potting substrates. *Scientia Horticulturae*, 67, 87-99.
24. Mirasol, J. (1920). Aluminum as a factor in soil acidity. *Soil Science*, X, 153- 207.
25. Agency for Toxic Substances and Disease Registry (ATSDR). (2006). Toxicological Profile for Aluminum, Atlanta, GA: U.S. Department of Health and Human Services, Public Health Services. <http://www.atsdr.cdc.gov/toxguides/toxguide-22.pdf?id=1129&tid=34>
26. Maharaj, S., Barton, C., Koo, B.J., and Newman, L. (2006). Phytoavailability of trace elements from a landfill containing coal combustion waste, in: *Coal combustion byproducts and environmental issues*, Springer., pp. 195-201.
27. Kabata-Pendias, A., and Adriano, D.C. (1995). Trace metals. In *Environmental Aspects of Soil Amendments*, Vol. 1: Inorganic Fertilizers, Ed: Jack E. Rechcigl, Lewis Publishers, Boca Raton, Florida, pp.139-167.
28. Mikkelsen, R.L., and Camberato, J.J. (1995). Potassium, sulphur, lime, and micronutrient fertilizers. . In *Environmental Aspects of Soil Amendments*, Vol. 1: Inorganic Fertilizers, Ed: Jack E. Rechcigl, Lewis Publishers, Boca Raton, Florida, pp. 109-137.
29. Agency for Toxic Substances and Disease Registry (ATSDR). (2007). Toxicological Profile for Barium, Atlanta, GA: U.S. Department of Health and Human Services, Public Health Services. <http://www.atsdr.cdc.gov/toxguides/toxguide-24.pdf?id=328&tid=57>
30. Smith IC, Carson BL (1981). *Trace metals in the environment*. Ann Arbor, MI, Ann Arbor Science Publishers.
31. USEPA, (2005). *Ecological soil screening levels for cobalt. Interim final report*. Washington, DC, United States Environmental Protection Agency, Office of Solid Waste and Emergency Response, 57 pp. (OSWER Directive 9285.7-67; http://www.epa.gov/ecotox/ecossl/pdf/eco-ssl_cobalt.pdf)
32. INCHEM,(1998). International programme on chemical safety. Environmental health criteria. Copper. <http://www.inchem.org/documents/ehc/ehc/ehc200.htm#SubSectionNumber:4.1.3>
33. Hornick, S. B., Baker, D. E. and Guss, S. B., Molybdenum in the Environment , (1977), 2, Marcel Dekker, New York.
34. Kabata-Pendias, A., and Mukherjee, A. 2010 Trace elements from soil to human, Springer Vetlag, Berlin., pp. 188.
35. Agency for Toxic Substances and Disease Registry (ATSDR). (2004). Toxicological Profile for Strontium, Atlanta, GA: U.S. Department of Health and Human Services, Public Health Services. <http://www.atsdr.cdc.gov/toxprofiles/phs159.html>
36. Mattigod, S.V., Dhanpat, R., and Amonette, J.E. (1999). Concentrations and distribution of major and selected trace elements in size-density fractioned fly ashes.in: *Biogeochemistry of Trace Elements in Coal and Coal Combustion Byproducts*, Kluwer Academic/Plenum Publishers, New York, pp. 115-131.
37. Monier- Williams, G.W. (1950) Titanium. In: *Trace elements in food*, New York, John Wiley, pp. 482-484.
38. Anke, M., Seifert, M. (2004). Titanium. In: Merian E, Anke M, Ihnat M, Stoeppler M (eds). *Elements and their compounds in the environment*. 2nd ed., Wiley-VCH, Weinheim, pp 1171-1191.
39. Waters, M.D.(1977).Toxicology of vanadium. *Adv. Mod.Toxicol.*,2:147-189.
40. Govindaraju, K. (1994). Compilation of working values and sample description for 383 geostandards. *Geostand Newsletters*, Special Issue 18: 1-158.

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