Environmental toxicology and coal fly ash chemical composition

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ABSTRACT
It is widely known that FA particles emitted from coal-fired plants contain several toxic trace metals (1). On the other hand, due to the availability of large quantity of FA and the presence of high concentrations of Ca and Mg in most FA sources, FA appears to be a suitable soil amendment for limiting purposes and to enhance Ca and Mg contents in the soil (2, 3). FA utilization as a soil amendment indicates the necessity to take precautions against the excessive accumulation of heavy metals by plants grown on a media with coal FA. The diversity of chemical properties among FA suggests that every use of FA as a soil amendment should follow its detailed chemical analysis because it has been established that leachate from places with high concentration of FA may affect water supply. Pollutants associated with FA include several elements (Al, As, Cd, Cr, Cu, Hg, Ni, Pb, and V) whose excessive presence in the environment may become toxic (1, 4, 5, 6). In this study we discuss environmental toxicology of listed above trace elements present in coal ash. Our work is based on the literature review and performed by our chemical analysis of coal FA to determine the concentration of mentioned above potentially toxic trace elements using inductively coupled plasma spectrometry (ICP). We compared the concentrations of these elements to the levels present in the soil, and diverse water sources. Based on these comparison, we speculated about the environmental safety of coal FA as a material to be utilized as plant growth media. Our own results of chemical analysis have been included into this short review as marked in bold.

KEY WORDS: coal fly ash, environmental toxicology.

INTRODUCTION
Major coal combustion residue, fly ash (FA) carries the potential for environmental contamination during the disposal of these coal combustions by-products (7). Because FA contains multiple toxic elements and 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 (8). This contamination could lead to the health, environmental, and land-use problems (9). FA is often used to amend soil as there are significant benefits that result from the application of FA as a soil amendment. These benefits include improved soil texture, increases soil nutrient holding capacity, and increased concentration of extractable potassium, calcium, magnesium, copper, iron and manganese (10). A 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 (11). These toxic metals that can be absorbed by plants through phytoremediation can then bioaccumulate in humans and other organisms in toxic levels (12). The elements this study focused on are aluminum, arsenic, cadmium, chromium, copper, lead, mercury, nickel, and vanadium as they are all naturally occurring toxic metals that can be found in coal fly ash.

MATERIAL AND METHODS
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. Over the period of five years (2010-2014) thirty plant species have been tested (cereal crops, grasses, legumes). The experiments have been conducted in three replications, and replied three times. On every petri dish 30 seeds were planted and covered with a thin layer of coal ash based growth media, and watered to approximate field capacity of growth media. The percentage of seeds germinated was determined. Plants were grown for 14-21 days (depending on the time of seedlings
The concentration of heavy metals in FA was determined by using ICP. Plant samples in our study were wet-digested in a nitric-perchloric acid mixture prior to analysis of elements (7). Chemical analysis of plant growth media and soil was performed using inductively coupled plasma (ICP) emission spectrophotometry (8). The data was analyzed statistically using ANOVA and Statistical Analysis System (13).

In leaching studiesplexiglas columns (30.4 cm long, 5-cm inner diameter) have been employed to study the transport and leaching of cations and heavy metals from a coal fly ash based plant growth media. A Fargo-Ryan soil (pH=6.1-8; organic matter=8%) has been sampled and used as a control treatment. 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 trace elements in the leachate have been determined using inductively coupled plasma (ICP) emission spectrophotometry.

RESULTS AND DISCUSSION

Aluminum

Aluminum (Al) is the most abundant element in Earth’s crust (14). Al occurs naturally in the United States soils at the levels of 7-100 g/kg (15). What we found in our fly ash based plant growth media that the concentration of Al was up to 10.766%. The highest concentration of Al in our leaching studies was 10.68 mg/l. The highest Al accumulation in plant tissues determined by inductively coupled plasma (ICP) was in winter wheat at 1161 mg/kg and barley at 1052 mg/kg. The concentration of Al in our coal ash based plant growth media didn’t exceed values found in soils (8). Despite this, the concentrations of Al in plant tissues in our experiments were high, but were approximately three times lower than the highest concentrations of Al found in plant tissues: 3410 mg/kg in grasses and 3410 mg/kg in clovers (16, 17).

The concentration of Al in the United States drinking water ranges from 0.001-1 mg/L (16). 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 (18). 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.

The concentration of Al in mammalian tissues ranges between 0.9 and 4.4 mg/kg, being the highest in skin, hair, and the lowest in heart and brain (19). There is increasing awareness and concern of the Al toxicity to human population and ecosystems due to acid rain (20). 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 (15).

Arsenic

Arsenic (As) is found in United States soils with average values of 2-4 mg/Kg (21). Agricultural practices may be a significant source of As, and its contents may be elevated by using pesticides, sludge, and manure (16). Increased contents of As in agricultural soils have become a significant problem. This issue is especially severe in the case of soils that are highly modified by anthropogenic activities, especially in the areas of rapid economic development. The concentration of As over 650 mg/kg has been reported for highly polluted soils.

The average concentration in U.S. surface and groundwater is 1ppb (21). In some countries, such as U.S., Argentina, Chile, New Zealand, Taiwan, India, and Bangladesh, elevated concentrations of As in groundwater has been reported due to weathering and leaching of As from As-rich geological formations, mining activity, waste disposal, and from thermal springs (16).

Arsenic is a common constituent of plants, but little is known about its biochemical role. Plants take up As passively with the water flow. Some plant species (e.g. Douglas fir) express a great capability to accumulate As. Contents of As in food plants varies, and most commonly is in a range of 10-60 µg/kg, with the tendency to be increased in green vegetables (16).

The highest concentration of arsenic recorded in fly ash was 83.746 mg/Kg. The highest As concentration in our leachates from coal ash in our studies was 1.58 mg/l, which is lower than the global median concentration of As in seawaters (3.7 µg/l), and higher than the world average level of As in river waters, estimated at 0.62 µg/l (22). The concentration of As in our coal ash based plant media and in our soil used as control (Fargo Clay) was below ICP detection limits.

When As builds in the system of animals and humans, it can have varying harmful effects. At low levels As impacts the gastrointestinal system (G.I. track) causing nausea and vomiting, abdominal pain, and/or diarrhea (21). As can also cause a decrease in the production of blood cells and damage blood vessels.
(21). When As reaches higher levels it can alter ones mental state, cause organ failure and cause skin, liver, bladder, and lung cancers.

**Beryllium**

The concentration of beryllium in soils has not been investigated on a large scale. Beryllium (Be) is commonly found in rocks, coal, oil, soil, and volcanic dust. Be is similar to Al in geochemical behavior and can substitute for Si and Al in some minerals (16). Beryllium is the lightest of the alkaline earth and although widely distributed, exists in relatively small quantities. The average concentration occurring in United States soils is 3 mg/kg (23). Be concentration in waters ranges broadly. Its common contents are established for the range of 0.008- 0.6 µg/l. In acidic conditions, Be might be easily mobilized from fly ash and slag, and its increased levels (in many cases more than 800 µg/l) in aquatic environment around coal power plants might be a reason for serious concerns.

The highest concentration of Be in fly ash in our study was 3.9 mg/kg. The highest concentration of Be leached from coal ash (based media was 0.05 mg/l. Be was below ICP detection limits in the plant tissues of plants grown on coal fly ash. The concentration of Be in our coal fly ashes was only slightly higher than the concentration spotted in the soils.

Be is mainly harmful when it is inhaled causing pneumonia symptoms and Chronic beryllium disease. Chronic beryllium disease resembles severe allergies that develop granulomas (23). Be can cause fatalities when exposed to a high enough dosage through the lungs, as there have been no effects reported when Be was ingested.

**Cadmium**

Cadmium (Cd) is most commonly found in ores with zinc, copper and lead. Cd occurs in the United States soils at the average level of 0.255 mg/kg (24). Anthropogenic sources of Cd in soils are of a great concern (16). The level of Cd in soils contaminated with sewage sludge may reach 3400 mg/kg, contaminated with coal fly ash – 13 mg/kg, and excessive usage of phosphorus fertilizers may lead to Cd concentration in the soil of up to 300 mg/kg. Average Cd levels in water in the United States are less than 0.1 µg/l (25, 26).

The highest concentration of Cd in fly ash in our study was 3.896 mg/kg. The highest level of Cd in the leachates from coal ash leached was 0.016 mg/L. Concentrations of Cd in growth media was below ICP detection limits. Our results indicate that in our experimental conditions there was no endangerment of transferring Cd contamination to the environment.

Cd is a heavy metal with severe risks to animal and human health. Cd causes kidney, bone, and pulmonary damage. Kidney damage is the main problem with Cd as it bioaccumulates there. In Japan where there is heavy Cd poisoning Itai-Itai disease is common where we find people with extreme skeletal decalciification and an increase in bone fracture rates (26). In rats there was reproductive system concerns such as low birth weights and spontaneous abortions.

**Chromium**

The world median content of chromium (Cr) in soils has been determined as 54 mg/kg (16). Its content in soils is determined mainly by its abundance in the parent material. The Cr concentration in soils may be elevated due to pollution from such sources as pigments by products and tannery wastes, leather manufacturing wastes, and municipal wastes. Cr concentration in United States soils varies from 2-60 mg/Kg (27, 28).

The median Cr content in river waters has been determined at 0.7 µg/l, with the range of 0.04- 1.3 µg/l, reaching the concentration up to 47 µg/l in polluted rivers (29).

The highest level of Cr composition in our fly ash recorded was 76.660 mg/kg. The highest level of Cr leached from fly ash in our studies was 0.035 mg/l. With ICP detection we found oats to have the highest concentration at 43.2 mg/kg and winter wheat at 36.26 mg/kg. As compared to a range of Cr in plant tissues determined at up to 0.35 mg/kg (16), the concentration of Cr in plant tissues in our study was elevated and should be a matter of concern and requiring further investigations.

Cr is required as a trace element for the human diet (28). High concentrations of Cr may impact human health including creating ulcers in the stomach, cardiovascular collapse, cause miscarriages, and damage DNA (27). At high doses Cr is lethal, with its toxic effects observed if consumed at a level of 70-100 mg/kg. In animals there were observed harmful effects of Cr on the respiratory system and a weakened immune system.

**Copper**

Copper (Cu) is found in rock, soil, water sediment, and at low levels in the air (30). The average concentration of Cu in United States soils ranges from 5-70 mg/kg. Cu concentration in the soil is closely associated with soil texture and usually is the lowest in light sandy soils and the highest in heavy, loamy soils. Soil contamination by Cu has been the subject of detailed studies. Several significant sources such as fertilizers, sewage sludge, agrochemicals, industrial by-product wastes and the quality of irrigation waters have contributed to increased Cu levels in agricultural soils (16).
Copper levels in Lakes and Rivers average 10 ppb, and the Environmental Protection Agency (EPA) regulates drinking water at 1.3 mg/L of Cu (16). The highest recorded Cu composition in fly ash in our studies was 243.5 mg/kg. The highest concentration of Cu leached from tested by us coal fly ashes was 0.729 mg/L. Although the concentration of Cu in coal ash reached the level spotted in Cu contaminated soils, levels of Cu leached from fly ash were within the limits allowed for drinking water. When we looked at the Cu composition in plant matter there was no difference between plants grown on 100% fly ash and 100% soil.

Copper is an essential element for all living organisms at low levels, but becomes toxic at high levels (ATSDR 2004). Humans consume about 1 milligram of copper a day which is excreted through urine and feces, keeping the Cu level generally constant.

Lead

Lead (Pb) is a heavy metal that is harmful when ingested. Natural levels of Pb in United States soil range from 50-400 mg/kg (31). Lead near industrial facilities has been spotted in the concentrations of Pb as high as 11,000 mg/kg (32). EPA has set for Pb concentration in drinking water, as up to 15 µg/l (33). Relatively high Pb concentrations, between 5 and 30 µg/l, have been measured in several thousands of samples of surface waters and groundwater in the USA (16).

We found in our tests that the highest concentration of Pb in our fly ash was 106.3 mg/kg, and the highest Pb concentration in leachates from coal ash was 14 µg/l. The concentration of Pb in plant matter was below ICP detection limits. Our results showed the concentration of lead in coal ashes relatively low, within the range spotted in the soil, and almost no intake of lead by plant seedlings grown on coal ash based media. In addition, we didn’t notice any significant leaching of Pb from coal ash, and the levels of lead in the leachedate were within values obtained in surface waters and groundwater in the US.

Exposure to lead can happen from contaminated water, soil, paint chips, inhalation of soil and/or dust, and ingestion of food (31). This exposure to Pb can lead to lead poisoning. Early symptoms of lead poisoning are often not noticed as they resemble other illnesses with symptoms such as: fatigue, irritability, appetite loss, insomnia, stomach discomfort and/or constipation (31). When lead poisoning becomes more severe, it leads to poor muscle condition, nerve damage to sensory organs and nerves, increase in blood pressure, hearing and vision impairment, and restarted fetal development. Lead poisoning in children causes brain damage, anemia, behavioral problems, liver damage, kidney damage, hearing loss, developmental delays, and hyperactivity. In extreme cases Pb may cause death.

Mercury

Mercury (Hg) is a metal that is liquid at room temperature. Average concentration of Hg in United States soils varies greatly and ranges from 20-636 mg/kg, and the concentration in surface water are on average less than 5 parts per trillion (34). Mercury is highly bioavailable and easily accumulates in fish (16). High Hg concentrations in fish tissues are reported in acidic lakes, and Hg content in fish tissues may reach up to 0.5-1.0 mg/kg in fish species being on the top of food chain, such as walley and pike.

The results of our studies showed the concentrations of Hg in fly ash was below detection limits, and the highest leaching concentration in the leachates from coal ash was 0.009 mg/l, which may raise some concerns, as we compare such concentration to a concentration in surface waters. The concentration of mercury in plant tissues in our studies was below detection limits.

Hg exists as either Methylmercury (CH₃Hg) or elemental mercury which is liquid at room temperature. When humans are exposed to Methylmercury we find brain, nerve, and kidney damage (34). Metallic Hg, which is only harmful when inhaled in the vapor form, causes personality change, tremors, changes in vision, deafness, muscle incoordination loss of sensation, and difficulties with memory. Kidney damage can occur from any Hg ingestion, and living organisms may even be able to recover depending on the amount of damage after the Hg is removed. Pregnant women should be weary of Hg because it poses risks to the fetus as well as the infants that are breastfeeding (34). Hg is also more harmful to children than adults because their brain is still developing.

Nickel

The concentration of Nickel (Ni) in United States soils ranges from 4-80 mg/kg (NIH 2013). Nickel has become a serious pollutant that is released into the soil from the increased combustion of coal and oil, and also from sewage sludges and phosphate fertilizers. Nickel (Ni) has the ability to accumulate in plants (9, 19, 22), and the level of Ni in cereal crops ranges from 0.34 to 14.6 mg/kg. Concentration of Ni in river waters range from 0.15 to 10.39 µg/l, and the world average is 0.8 µg/l (16). The global Ni average concentration in ground water is estimated at 15 µg/l.

The highest concentration of Ni found in coal fly ashes in our studies was 43.5 mg/Kg. Such level of Ni concentration doesn’t even exceed the concentrations found in the soil. The highest concentration of Ni leached from plant growth media composed of coal fly ash was 0.580 mg/l. Such value exceeds Ni levels...
found in waters and in groundwater. The highest concentration of Ni in plants was 11.45 mg/kg, which within the range of Ni concentrations spotted in plant tissues. Nickel’s effects on health vary. The most common problem with Ni is allergic reactions as roughly as 10-20% of the human population is sensitive to Ni (16, 35). When people who are sensitive to Ni and they inhale it, the Ni can create asthma attacks. The most serious effects of Ni are chronic bronchitis, reduced lung function, and lung and nasal sinus cancers.

**Vanadium**
The vanadium (V) contents of soils are related to those of the parent rocks from which they are formed (36). Average contents of V in soils vary from 10 mg/kg in sandy soils to 500 mg/kg in calcereous soils. The soils in the USA contain V in the range of 36-150 mg/kg (36, 37). The level of V in surface water ranges from .04-220 µg/L (9, 22). Some municipal waters in the US have been found to contain V levels of between 1 and 6µg/l, and the highest concentrations of vanadium in rivers have been found in rivers in the area rich in uranium ores (16).

The highest concentration of V found in our fly ash was 305.8 mg/kg, and such concentration remains within the range of V concentration found in some soils. The highest concentration of V leached from our coal ash based plant growth media was 0.232 mg/l, and such concentration is much higher than spotted naturally in surface waters. We found that the highest vanadium concentration in plant tissues in our studies was 7.48 mg/kg in rye seedlings. Such concentration is several times higher than average concentration (10 to 700 µg/kg) reported for plants (16).

Vanadium has negative effects on animals and humans at high levels. Vanadium pentoxide causes a cough in humans. Vanadium pentoxide causes damage to lab animal’s lungs, throats, and noses as well as causing lung cancer (37, 38). Vanadyl sulfate and Sodium metavanadate have been used in experimental treatments for diabetes. These patients developed nausea, mild diarrhea, and stomach cramps while taking 13 mg of V/day orally. Lab animals treated with V had a decrease in red blood cell production, an increase in blood pressure, mild neurological effects, and developmental effects (37). There were also birth defects observed when levels of vanadium affected the mother, and occasionally when V did not affect the mother.

**CONCLUSIONS**
Our investigations lead to the conclusion, that there is a no risk or a low risk of harm coming from plants growing on coal fly ash based plant growth media. Aluminum had the highest uptake level by plants grown on coal as based growth media, and Al was determined as an element of concern. Elements that could also pose some environmental health risk are chromium, nickel and vanadium. To make a final determination, though, additional in-depth studies are required.

We also believe that the people at greatest risk of harm from the metals discussed in this paper are those who are exposed to the elements routinely. We should also have to keep in mind that coal ash is very diverse in terms of chemical composition depending on coal source, and each load of fly ash is unique in its chemical composition.

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**REFERENCES**


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