International Journal of Advanced Research in Biological Sciences
ISSN: 2348-8069
www.ijarbs.com

Review Article

Environmental health aspects of coal fly ash (FA) phytoremediation, plants biofortification, and biofuel production

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Abstract

This project focuses on the environmentally friendly utilization of coal combustion residue, fly ash (FA), containing significant amounts of heavy metals, and on combining FA utilization with biofuel production and plant biofortification with iron (Fe), zinc (Zn), and selenium (Se). The issue of combining coal FA phytoremediation with biofuel (bioethanol) production and plants biofortification has not yet been explored. The overall hypothesis is that FA can be safely utilized as plant growth media for phytoremediation, biofuel production and biofortyfication of selected plants. The aims of research in this area are: 1) determination of the environmental safety of different growth media composed of FA, soil, and sewage sludge (SS); 2) studying the influence FA, soil and/or SS composed media on the germination, growth, and uptake of heavy metals, boron (B), and Se by the plants useful for bioethanol production; 3) investigation of the influence of FA, soil and/or SS composed media on the germination, growth, uptake of Fe, Zn, heavy metals, B, and Se by selected cereal crops; biofortification study; and 4) assessment of the resistance/adaptation to high concentrations of FA in growth media among the varieties of selected plant species grown to maturity. Such research will contribute to the utilization of FA as a component of growing media for plants used for bioethanol production and plants biofortification with selected elements without compromising environmental health.

Keywords: Coal fly ash, Phytoremediation, Agronomic biofortification, Biofuel production.

Introduction

The intensive use of coal in the United States for electrical power generation will increase the amount of coal residue which needs to be safely disposed (Twardowska and Stefaniak 2006). 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 (Sajwan et al. 2006).

It is widely known that FA particles emitted from coal-fired plants contain several toxic trace metals (Shannon & Fine 1974, Bern 1976, Hodgson et al. 1982, Alva et al. 2000, Bilski et al. 2010, Bilski et al. 2011a,b, Soumaila et al. 2011). 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 liming purposes and to enhance Ca and Mg contents in the soil (Plank & Martens 1973, Rai 1987, Pathan et al 2003, Schlossberg et al. 2006**,** Bilski et al 2011a). FA utilization as a soil amendment raises the problems of FA influence on soil properties and leaching of toxic FA-components through the soil profile (Bilski et al. 2013a,b). It indicates also the necessity to take precautions against the excessive accumulation of heavy metals by plants grown on a media with FA. Pollutants associated with FA include several elements (Ti, Mn, Cu, Cr, Zn, As, Se, Co, Cd, Hg) whose excessive presence in the environment may become toxic (Carlson 1990, Sandhu et al. 1993, Schwab et al. 1993, Bilski et al. 1995, Alva et al. 2000, Kabata-Pendias & Pendias 2001, Ugurlu 2004, Li & Chen 2006, Bilski et al. 2011b).

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 (Ziemkiewicz and Knox 2006, Bilski et al 2013a,b).
There are reports on beneficlal influence of sewage sludge added to coal ash to establish plant growth media (Bilski and Alva 1995, Alva et al. 2000). Fermented sewage sludge has been used as fertilizer, and added to coal ash can bind harmful trace elements, increase useful concentrations of nitrogen, phosphorus and organic matter in FA/sewage sludge constructed plant growth media (Bilski 2014, data not published).
A vegetative cover is a remedial technique utilized on FA landfills for soil stabilization and for the physical and chemical immobilization of contaminants (Bilski et al. 1995, Koo et al. 2006, Kramer 2007, List 2007, Bilski et al. 2010, Bilski et al. 2011a, Bilski et al. 2012 a,b,c,d,e,f,g). 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 (Koo et al. 2006, Bilski et al. 2010, Bilski et al 2011a,b, Bilski et al 2012c,d). It creates z platform to include at least some of bioethanol producing plants, such as corn, reed canary grass, cord grass, sorghum, switchgrass, and miscanthus into FA phytoremediation project. Studies on the effects of coal fly ash on growth and mineral nutrition of various plants have shown the potential benefit of different soil-FA mixtures on plant germination rates and productivity Elseewi et al. 1980, Wong & Wong 1989, Menon et al. 1993, Kramer 2007, Kraft 2011, Kraft 2012).

The increase of elemental concentration in plants as a result of FA addition to growth media is not consistent and differs widely among plant species (Bilski et al 2010, Bilski et al, 2012c,d). The concentrations of Se and B, and sometimes Fe and Zn, however, are usually greater in plants grown on FA amended soil as compared to the soil. This regularity should be taken into the consideration in all attempts to use FA as a component of growth media for plants. It also allows to combine FA phytoremediation with a very important issue related to human health: plant biofortification with Fe, Zn, and Se. Iron (Fe), zinc (Zn), and selenium (Se) deficiencies are serious public health issues and important soil constraints to crop production, particularly in the developing world (Ihnat 1989, Warren 1989, Cakmak 2010, Lyons et al., 2004, Bilski et al. 2012d).

Exploiting the genetic variability and biotechnological approach to the development of plants with high Fe, Zn, and Se content may be an effective method to improve the human nutrition, but, unfortunately, it is not very cost effective and requires significant amount of time. Agronomic approaches such as application of Fe, Zn, and Se to plant growth media, called "agronomic biofortification" (Cakmak 2009, Lyons et al. 2004), seems to be a very cost-effective, fast and practical approach to improve Fe, Zn, and Se concentration in cereal crops.

It is important to highlight, that the use of agronomical biofortification might be especially desirable in various developing countries. Most of farmers in such countries (e.g., African countries) cannot afford application of mineral fertilizers, and it would be desirable find a solution through the application of some cheap materials which would serve as potential fertilizers, would contain a variety of micronutrients, and would be considered as non-toxic from environmental heath point of view. Coal combustion residues seem to meet these criteria (Bilski and Alva 1995, Bilski et al. 2011a,b, Bilski et al. 2012).

Bilski et al. (2011b, 2012c) didn't identify any agro-toxicological effects of coal FA phytoremediation by cereal crops. This research is encouraging, because it shows not only that plants are able to grow in such adverse conditions as the presence of up to 100% of FA in growth media, but that the transfer of heavy metals present in FA does not indicate the possiblility of dangerous heavy metals transmission to a food chain, which would be detrimental to environmental health.

The research outlined above clearly indicates that the chemical composition of FA and the amount of FA added to soils are important factors in determining the risk for the transfer of heavy metals to the plant-animal-human food chain. There are, therefore, several areas of research that need immediate attention: (a) the levels of heavy metals uptake by plants and the transfer of heavy metals to animals consuming these plants; (b) the chemical reactions in soils amended with FA of different chemical composition; (c) differences in the tolerance of plant species and varieties to soluble salts and toxic elements found in soils amended with different rates of FA; (d) development of models to determine the potential contamination of ground water as a function of plant uptake and the mobility of toxic elements (in particular heavy metals) within FA-amendments with different chemical composition.

Although research on FA caught the attention of North Dakota's scientific community and led to the establishing of the Coal Ash Research Center at the University of North Dakota, the research on coal FA is predominantly focused on solid state chemistry, crystal chemistry, and X-ray diffraction analysis of FA. Research on FA utilization in ND is focused on the utilization of coal FA as a cement additive and as a soil stabilization material. North Dakota coal- lignite is extraordinarily variable in its mineral composition. Thus, ND FA mineral composition is also very variable (Benson *www.anl.gov/PCS/acsfuel/ preprint %20archive/Files/Merge/Vol-28_2-0003.pdf*).

Leaching studies with the utilization of ND FA from Coal Creek and Stanton showed significant concentrations (in µg/L) of Cd (3.6 and 2.3, respectively), Cr (84.6 and 91.2), and Se (18.0 and 20.1) in the leachates (Bin-Shafique et al. 2006).

The environmental health issues of the utilization of a FA as plant growth media in ND remains unexplored, despite the fact that coal generates 91% electricity in this state.

Leaching of heavy metals from FA/soil/sphagnum peat moss composed media

The utilization of FA as a growth medium for plants is an attractive alternative to disposal of FA in landfills (Plank et al. 1975, Scanlon & Duggan 1979, Carlson & Adriano 1993, Bilski & Alva 1995, Alva et al. 2000, List 2007, Bilski et al 2011a, b). The necessity to undertake precautions against water contamination as a result of FA usage has been suggested by numerous investigators (Carlson & Adriano 1993, Menon et al. 1993, Bilski et al. 1995, Ugurlu 2004, Twardowska & Stefaniak 2006, Bilski et al. 2013a, b).

These precautions were the rationale for such study of the usage of FA as a prospective growth media component for various crops. The study was devoted to the tests of leaching through the soil profile of some metallic elements (Cu, Mn, Fe, Pb, Zn, Cr, and Se), which are present in FA. The elemental analysis in this study was obtained by inductively coupled plasma (ICP) emission spectrophotometry.

The objective of this study was to examine the transport and leaching of various elements including heavy metals in coal FA, coal FA mixed with Sphagnum Peat Moss- SPM. (50% FA+ 50% SPM), and FA mixed with SPM and soil (30%FA+ 30% SPM + 30% soil). The study was conducted in the absence of plant cover, thus would represent the maximum potential for leaching. The presence of crop could considerably alter the leaching of metals. These studies have been described by Bilski et al (2013a,b).

The same method, based on leaching column, was successfully employed in similar investigations, ranging from the tests of heavy metals leaching, to the herbicides components leaching through the soil profile (Alva & Gasho 1991, Reddy et. al 1992, Bilski & Alva 1995, Alva et al. 2000, Dissette et al. 2010).

The concentrations of all tested elements in the soil control were lower than in coal FA. 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.These results are presented in Table 1.

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.

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.

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	50% FAND +50% SPM	33% FAND+ 33% SPM+ 33%S	FAVC	50% FAVC+ 50% SPM	33% FAVC+ 33% SPM+ 33% S
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

S – soil control;
FAND - fly ash from semi-bituminous coal (obtained from NDSU power plant);
FAVC - fly ash from lignite coal (obtained from VCSU power plant).

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).

Testing the influence of various FA rates in FA/soil composed media on the germination, growth, and uptake of heavy metals, boron (B), and selenium (Se) by the plants.

Similar tests and greenhouse experiments have been previously performed to predict plant responses to various toxic environmental factors (Foy 1983, Bilski & Foy 1987, Bilski 1990, 2011b, Alva et al. 2000).

The growth media containing 0, 10, 20, 30, 40, 50, 60, 70, 80 90 and 100% FA and the tolerance to mentioned above media of the following plant species: barley, Sudan grass, ryegrass, rape, alfalfa, and canola. has been tested. The presence of FA in growth media even up to 40% did not have detrimental effect on the germination rate and dry matter accumulation of all plants. Barley was the only plant of plants used, which was able to sustain seedlings growth on media consisting on FA alone.

The results of trace elements analysis is shown in Table 2.

Table 2: Concentration of trace elements in soil, FA and plants

	Al	B (mg/kg)	Ba	Co (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Mo (mg/kg)	Sr (mg/kg)	Ti	V (mg/kg)
Soil	1.43%	19	0.19%	6.81	17.3	15.8	2.9	200	0.05%	27.3
FA	6.28%	1230	0.35%	12.29	39.6	32.9	10.3	4300	0.14%	83.8
Highest concentration in plants	1991 mg/kg	468	221 mg/kg	1.99	4.41	11.7	7.9	500	135.5 mg/kg	3.95

Preliminary results of chemical analysis of FA and harvested young plants implicate that plants do not accumulate toxic amounts of heavy metals even being grown on media containing 100% FA. Our research results indicate that coal FA might be used as a plant growth media additive. However, additional studies should be undertaken to determine the effects of FA on plants grown till maturity.

Testing the biofortification of cereal crop plants with Fe, Zn, and Se by the utilization of coal FA as plant growth media.

The laboratory tests used in this study have been described in Bilski et al 2012d).

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*).

This study demonstrated, that cereal crops can grow on growth media composed exclusively of coal combustion by-products, and that these crops are able to accumulate elevated amounts of Fe, Zn and Se, as compared to plants grown on the soil used as control. Accumulated levels of these elements may justify treating the process of cultivating cereal crops on coal ash piles not only as a phytoremediation process, but also as means of agronomic biofortification of planted crops. 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 addition, we should be extremely aware of the necessity for close and continuous monitoring of coal the presence of potentially toxic micronutrients in coal ash. Such presence might be one of major limiting factors to the cultivation of cereal crops on coal combustion byproducts piles.

Future experiments

1.Studying of heavy metals leaching from FA/soil/sewage sludge composed media

This experiment will be similar to the experiment performed in our laboratory as described by McLean et al 2010a,b, 2011). Sewage sludge, as sphagnum peat moss (SPM), contains significant amounts of organic material, and replacing SPM with SS is more environmentally friendly approach, since SS will not deplete the natural environment. In addition, in order to avoid any sanitary issues related to the utilization of SS, SS will be substitutes with a Milorganite fertilizer containing 91.4% of sewage sludge from Milwaukee, WI.

In a separate experiment, the transport and leaching of various elements including heavy metals in coal FA alone, and coal FA mixed with the increased concentrations of soil will be examined.

2.Studying the influence of various FA rates in FA/soil composed media (up to 100% of FA), and in FA/soil/sewage sludge composed media on the germination, growth, and uptake of heavy metals, boron (B), and selenium (Se) by the plants useful for bioethanol production.

In these experiments the influence of FA in various FA/soil composed media on the germination, seedlings growth and heavy metals, B and Se accumulation in the seedlings will be studied. A broad spectrum of plant species and varieties among species will be grown on media composed of FA alone or mixed with the soil. The most of plant species tested will be represented by 3-4 cultivars, common for North-Central States. The following plant species will be used: corn *(Zea mays*), reed canary grass *(Phalaris arundinacea)*, cord grass *(Spartium junceum)*, sorghum *(Sorghum bicolor)*, switchgrass *(Panicum virgatum)*, miscanthus *(Miscanthus giganteus)*, perennial ryegrass *(Lolium multiflorum)*,, barley *(Hordeurn vulgare)*,), wildrye *(Elymus arenarius)*, needlegrass *(Stipa tenacissima)*, fescue *(Festuca rubra)*. The rationale for choosing listed above plant species was their diversity of nutritional requirements combined with the fact that these species are resistant to unfavorable environmental conditions. In addition, some of these plants have a potential to be used for bioethanol production. The inclusion of varieties among the species to be tested is due to the possible wide differences in the response to mineral stress conditions among the varieties of the same species (Foy 1983, Bilski 1990). Two-thre weeks after germination, plant samples will be wet-digested in a nitric-perchloric acid mixture prior to elemental analysis (Carlson and Adriano 1991). Chemical analysis will be performed using inductively coupled plasma (ICP) emission spectrophotometry (Bilski et al.212c)

3.Biofortification Study. The goal is to study the influence of various FA rates in FA/soil composed media (up to 100% of FA) and in FA/soil/sewage sludge composed media on the germination, growth, uptake of Fe, Zn, heavy metals, boron (B), and selenium (Se) by selected cereal crops.

In this study**,** as a plant growth media, soil control, and different FA ashes will used. The most of plant species tested will be represented by 3-4 cultivars, common for North-Central States. The following plant species will be used: corn *(Zea mays*), sorghum *(Sorghum bicolor)*, barley (Hordeum vulgare), rye (Secale cereal), wheat *(Triticum aestivum*), pearl millet *(Pennisetum typhoides)*, oats *(Avena sativa)*, and triticale; a hybrid between wheat *(Triticum aestivum)* and rye *(Secale cereale)*. The growth and chemical composition of these plants will be determined during the first three weeks after germination.

4.Greenhouse study on selected plant species/varieties using FA/soil composed media to assess the resistance to high concentrations of FA in growth media among the varieties of most resistant plant species

On the basis of results of the laboratory experiments, 4-5 species represented by 1-2 most tolerant to FA varieties, will be chosen for greenhouse pot experiments. This experiment will determine (under greenhouse conditions) the maximum of FA concentration in growth media which allows for normal growth, and for the environmentally concentration of heavy metals, B and Se in plant tissues that are within acceptable limits as set by the Environmental Protection Agency.

Results and Benefits Expected

The completion of described above studies should provide information as to how much FA may be added to plant growth media in order to avoid environmental endangerment by leaching of heavy metals, B and Se through the soil.

The leaching tests will allow for determination if, and to what extent, the differences in possible leaching of tested elements (Cu, Mn, Pb, Fe, Zn, Cr, Cd, As, B, Se) are associated with FA source and with its rate as a soil amendment. These results should provide information about the safest way to use FA to protect and/or maintain healthy environmental conditions.

Such study will also determine which of tested plant species and varieties would be most suitable for planting in FA amended soils, and to determine a suitable FA/soil rate and to be used without compromising environmental health.

For each of the experiments, the data will be analyzed statistically using ANOVA and Statistical Analysis System (SAS, 2005). In addition it is planned to network with Statistical Consulting Service at one of the universities within a North Dakota State University System

Future Directions

Future research on the utilization of coal combustion residues as a growth media for plants in a way which would preserve environmental health, in investigator's opinion, will focus on several problems as follows:

1. More detailed study of the leaching of potentially toxic elements through the soil from a wide selection of FA types in FA/soil composed media. Some data suggest that it might be possible to decrease heavy metals leaching from FA by a FA/soil/organic material media composition. The ability of various organic amendments added to FA to bind toxic elements

moving downwards the soil during leaching process will be tested.

2. A wider selection of plant species/varieties will be tested with the employment of different FA/soil media to hospitalize the choice of the most resistant plants to be grown with the highest possible presence of FA in the environment.

3**.** There is a great need to investigate the problem of possible translocation of elements from FA through the food chain: to plants, animals and eventually humans, especially when plants with a great ability to accumulate heavy metals voluntarily grow over coal combustion residues. Therefore, in the future, the effects of heavy metals on the growth and function of *Drosophila melanogaster* (as a model for whole organism), and selected mammalian cell function (e.g., proliferation and apoptosis) should be studied. Furthermore, a nutrition study of adding grass grown on media containing FA to an animal feed should be undertaken.

Acknowledgments

Supported by North Dakota INBRE Grant Number P820GM103422-13 from the National Institutes of Health.

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