

VI.9

Agricultural utilization of coal combustion residues

Urszula Kukier and Malcolm E. Sumner

VI.9.1. Introduction

Coal-fired electric power plants generate enormous amounts of waste products whose physical and chemical properties vary depending on the coal composition and specific conditions of the process. Because these materials are potentially valuable soil amendments, knowledge of their characteristics and interactions with soils and plants is essential for maximizing their environmental sound use. A great diversity in coal combustion technologies and technical solutions to air pollution control results in a variety of waste products. This chapter will cover three types of coal combustion residues widely differing from each other in their physical and chemical properties.

VI.9.2. Characterization of coal combustion waste products

Coal combustion in traditional powder-fed boilers produces two types of residues: fly ash, which is a fine fraction dispersed in the flue gas, and bottom ash collected in the boiler. Fly ash is separated from flue gas by electrostatic precipitators or a variety of mechanical methods. Typical partitioning between fly and bottom ash in pulverized coal-fired boilers is 8:2 (Santhanam et al., 1979). Fly ash particles have a spherical shape typical of dust particles generated by thermal processes involving melting, evaporation and subsequent condensation of constituents. The majority of the particles have sizes $< 100 \mu\text{m}$. Silicon, Al, Fe, K and Ca followed by Na and Ti are major components of the fly ash matrix with their concentrations being variable depending primarily on coal composition and combustion conditions (Table VI.9.1). Fly ash consists of an amorphous aluminosilicate glass, crystalline mineral mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) and quartz (SiO_2) with minor amounts of hematite (Fe_2O_3) and magnetite (Fe_3O_4) (Mattigod et al., 1990) and variable amounts of trace elements, some of which are essential for plants and animals and others are potentially toxic (Table VI.9.1, see also Chapter III.7).

Because of the large quantities of by-product produced, a great body of literature exists on fly ash chemical, mineralogical and physical characterization, potential beneficial utilization strategies and adverse environmental effects.

Large emissions of sulfur dioxide (SO_2) from coal combustion is one of the major atmospheric pollutants. To minimize these emissions, fluidized bed combustion (FBC) and

Table VI.9.1. Concentration of elements in coal combustion by-products.

Element	Fly ash	FBC	FGD
<i>g/kg</i>			
Al	59–143	4.0–20	0.1–1.64
Si	10–318	–	0.5–0.8
Ca	6–177	240–460	228–243
S	0.40–0.64	72–140	166–186
Fe	27.9–289	0.8–16.0	0.14–1.3
Mg	11.5–60.8	5.0–12.0	0.2–2.7
K	5.6–34.7	0.5–8.0	0.1
P	0.4–8.0	0.4–0.5	<0.1–0.2
<i>mg/kg</i>			
B	10–770	95–170	75
Se	1.2–17.0	0.16–0.58	<1.0–5.2
As	2.3–312	<0.1–0.3	0.14–5.73
Mo	6.5–41	0.12–0.28	0.35–1.7
Ni	1.8–115	13–29	–
Zn	14–406	29–105	2.9
Cd	0.1–3.9	0.5	–
Cu	45–616	12–19	0.6–3.2
Pb	3.1–241	1.5–7.5	–

Furr et al., 1977, 1978; Mattigod et al., 1990; Sumner, 1993; Kukier and Sumner, 1994; Alcordo and Rechcigl, 1995.

wet scrubbing technologies have been developed (Alcordo and Rechcigl, 1995). In the former, a mixture of ground coal and limestone or dolomite is injected into the combustion chamber so that combustion is accompanied by simultaneous absorption of evolved SO_2 . FBC residue is a mixture of coal ash, products of the desulfurization reaction and unreacted sorbent. Anhydrite (CaSO_4) being a product of the reaction is the dominant mineral followed by lime (CaO) and small amounts of portlandite ($\text{Ca}(\text{OH})_2$) both originating from thermally transformed calcite (CaCO_3) used as sorbent. Typically, FBC residues have pH values > 12 and electrical conductivities of about 11 dS/m (Reichert and Norton, 1996). The significant content of lime makes this by-product a potential substitute for agricultural lime. The ash component is a carrier of trace elements whose content may vary (Table VI.9.1). Because combustion temperature in the FBC process (about 900°C) is much lower than that in a traditional boiler, volatile trace elements are likely to be retained in the FBC residues.

The wet scrubbing of SO_2 in flue gas is an alternative way of minimizing emissions. In this technology, SO_2 is removed by bubbling through a dolomitic or calcitic limestone slurry (Santhanam et al., 1979; Alcordo and Rechcigl, 1995). Gaseous SO_2 dissolves in the water and reacts with the sorbent. Traditional scrubbing technologies produce a mixture of various proportions of calcium sulfite (CaSO_3) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) known as flue gas desulfurization (FGD) waste. Modern forced oxidation desulfurization technology based on the same principle goes a step further and by forced oxidation converts CaSO_3 to

gypsum. The proper adjustment of reaction parameters results in a wallboard quality gypsum with very minor amounts of unspent sorbent (CaCO_3). The quality of this FGD by-product is comparable to that of mined gypsum.

Concentrations of trace elements in FGD by-products depend on their contents in the coal, sorbent material and quality of the process make-up water (Table VI.9.1). Ash can significantly contribute to the total concentrations of trace elements in FGD residue. The ash becomes mixed with FGD by-product when a scrubber is used for the simultaneous removal of fly ash and SO_2 or when fly ash collected separately is mixed with FGD sludge. In the forced oxidation technologies both practices are to be avoided in order to maintain a quality of by-product gypsum.

VI.9.3. Fly ash

Various techniques including electron microscopy, diffractometry and chemical extraction have been employed to study the structure of fly ash spheres and the distribution of elements within fly ash particles. According to a generally accepted model, three different regions can be distinguished in the majority of fly ash particles. The particle core composed of amorphous aluminosilicate glass is surrounded by a network of mullite crystals covered by an external layer of deposits. This unique structure is a result of the melting of coal mineral admixtures, evaporation and subsequent condensation occurring during combustion. Phyllosilicates present in coal particles are melted in the furnace, and form spherical drops. Thermal transformation of these minerals leads to the formation of glass and mullite. Many other minerals and chemical compounds from coal volatilize in the combustion zone and condense on earlier solidified glassy particles as the flue gas cools down. The external layer of the fly ash particles has a composition different than the glassy core. Elements concentrated on the particle surfaces comprise the most environmentally relevant fraction because they are in contact with water and their release is controlled primarily by precipitation/dissolution processes. The glassy core and mullite have low solubilities even in relatively concentrated inorganic acids. Elements present in the aluminosilicate glass are protected from contact with water and their release to the environment is controlled by the rate of weathering of the material. Hansen and Fisher (1980) estimated that more than 70% of As, Se, Mo, Zn and Cd present is concentrated on the surfaces of fly ash particles. Over 70% of Na, K, Mg and Fe is associated with the aluminosilicate matrix while Mn, Cr, Cu, Co, Ba, Pb and Ni exhibit intermediate tendencies being approximately equally distributed between the aluminosilicate matrix and non-matrix material. Gladney et al. (1978) suggested that B is also a particle surface enriched element.

VI.9.3.1. Influence on plant elemental uptake and yield

Numerous experiments have been carried out in order to compare plant availability of macro- and micronutrients from fly ashes to that of fertilizers commonly used for correction of deficiencies. Potassium is more available to plants from KCl than from equivalent rates supplied as fly ash (Martens et al., 1970) while S availability was equivalent to that of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Fly ash applied at rates 1–2% by weight of

soil corrected S deficiency (Elsewii et al., 1978) and dramatically increased yields of alfalfa (*Medicago sativa* L.) and Bermuda grass (*Cynodon dactylon* L.). Doran and Martens (1972) used fly ash for correction of Mo deficiency in alfalfa grown on an acid soil and found it to be as effective as $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$. As demonstrated by Schnappinger et al. (1975), Zn plant availability from an acid fly ash was approximately equal to that of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$. Alkaline fly ashes, although higher in Zn, decreased the yield of corn (*Zea mays* L.) partly due to Zn deficiency induced by high pH. Fly ashes containing 232 and 370 mg/kg of B increased yield of alfalfa grown on a B deficient soil over a three-year period (Plank and Martens, 1974) with availability from fly ash being comparable to $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$. Mulford and Martens (1971) obtained similar results. The B status of fly ash amended soils has been extensively studied because of the potential yield responses and risks of plant injury if applied in excessive rates. The yield response curve is steep under both conditions of deficiency and excess (Sale et al., 1996). The hot water soluble B (HWSB) is the most widely accepted estimate of the plant available B. Good agreement between HWSB in fly ash amended soils and B uptake by alfalfa (Plank and Martens, 1974) and corn (Kukier and Sumner, 1994) has been obtained (Fig. VI.9.1). In a greenhouse study, Kukier and Sumner (1994) were able to predict the levels of HWSB in soil amended with a wide variety of fly ashes from an assay of the fly ash using the procedure developed for soils. The pH of solution obtained from fly ash boiling should be adjusted to the soil pH before amendment with fly ash. This method can be adapted for field conditions where it could be useful for estimation of safe application rates. In the case of very alkaline fly ash, correction for the change in soil pH would be necessary. Leaching and weathering of fly ash under natural conditions prior to a soil application effectively reduces B toxicity (Aitken and Bell, 1985; Kukier and Sumner, 1994). An alternative solution is to apply the material well in advance (few months) of planting to allow sufficient time for B leaching.

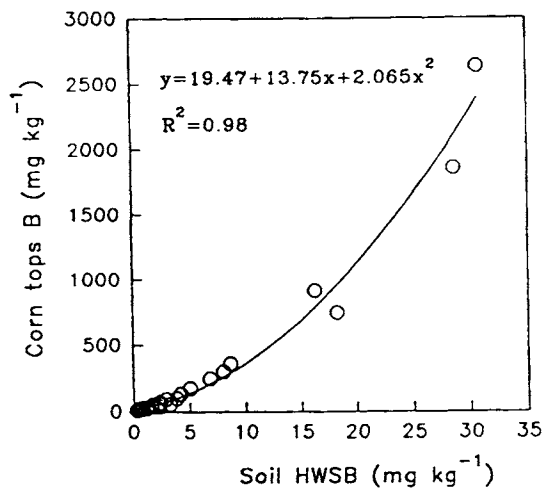


Figure VI.9.1. The relationship between hot water extractable boron in soil amended with different rates of fly ashes and FGD product and corn tissue B (Kukier and Sumner, 1994).

Selenium, while not essential for plants, is essential for animals. Selenium deficiency is a widespread problem with the level in about 30% of the forage and grain crops in the USA being below the optimum for animal nutrition (Mengel and Kirkby, 1987). Combs et al. (1980) in a feeding trial showed high Se bioavailability from corn produced on fly ash amended soil with the Se-enriched diet promoting chick growth and plasma Se-dependent glutathione peroxidase. The high plant availability of Se in fly ashes makes this material a potential source for deficient soils.

Furr et al. (1977) found a high correlation between total Se in 15 fly ashes and the Se content in cabbage grown in an amended soil. Shane et al. (1988) found Se uptake by broccoli, endive, lettuce, onions, spinach, tomatoes and perennial ryegrass from a growth medium amended with soft coal fly ash was proportional to the fly ash rate except for broccoli. Increased concentrations of Se from 0.5 to 2.0 mg/kg were detected in five successive cutting of the ryegrass indicating persistence of the effect. We came to similar conclusions based on a pot study with Cecil soil (Typic Kanhapludult) amended with increasing rates of five fly ashes in which corn shoots Se content was directly proportional to the Se rates applied in fly ash but was independent of other fly ash properties (Fig. VI.9.2). If more studies confirm this phenomenon, it would be possible to develop Se uptake equations specific for the soil–crop system which could be useful for the prediction of appropriate fly ash application rates.

An extensive review of the effects of fly ash on plant elemental uptake (Adriano et al., 1980) indicated a consistent increase in plant uptake of B, Mo, Se, As, S and Sr from fly ash amended soils. All anionic species from this list belong to the group of elements highly concentrated on the surfaces of fly ash particles. Other elements including essential plant nutrients such as P, K, Cu, Mg, Mn, Cu, Fe and Zn do not exhibit consistent uptake patterns. Depending on the composition of fly ash, soil properties and plant species, various effects on crop yields have been observed.

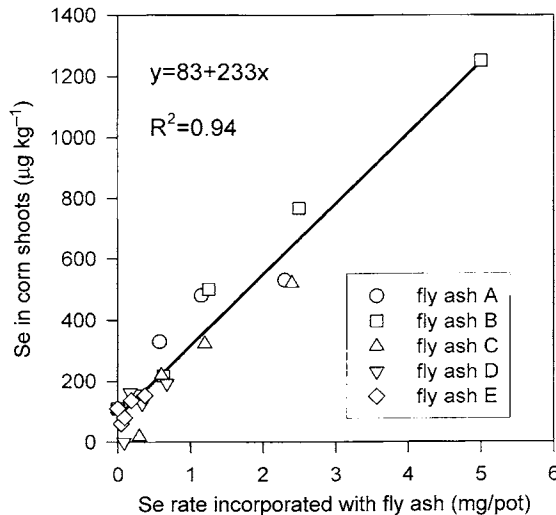


Figure VI.9.2. The relationship between Se rate incorporated with different fly ashes and Se concentration in corn shoots.

VI.9.3.2. Effects on soil physical properties

The effect of fly ash application on soil water content depends on fly ash rate and soil texture. Chang et al. (1977) reported that addition of less than 10% (by volume) of fly ash to soils of various textures (10–55% clay), resulted in a slight reduction in water contents at 20 centibars suction in all soils, except the heaviest. Increased amendment rates, up to 25 and 50% by volume, resulted in significant increases in water contents of almost all soils; however, the amount of plant available water did not change appreciably. Campbell et al. (1983) noted a marked increase in plant available water after addition of 10% fly ash by weight to a sand, which they attributed to an increase in capillary pores. A spectacular example of improving soil water characteristics was demonstrated by Jacobs et al. (1991) in a field study. Fly ash applied to Bayer loamy sand (Typic Hapludalf) and Crosswell sand (Entic Haplorthod) in bands significantly increased corn yield by improvement of the soil water regime. The saturated hydraulic conductivity of the sand was dramatically decreased by additions of fly ash in excess of 10% by weight (Campbell et al., 1983). Chang et al. (1977) observed an increase in hydraulic conductivity in all soils studied from applications of 2.5–5% of alkaline fly ash, above which dramatic decreases in the hydraulic conductivities of the heavy soils (> 50% clay) were observed due to a pH rather than soil texture effect. They hypothesized that the pozzolanic reaction of the fly ash caused a clogging of soil pores. It is also likely that clay dispersion played a role in the drastic reduction in hydraulic conductivity of acidic soils. Inconsistent responses of agricultural soils to the application of fly ash indicate the need for further research in order to establish management practices that can assure beneficial modification of soil physical properties. In contrast to agricultural land, potting mixtures and artificial soils create a market for fly ash that can be used to improve their texture and water-holding capacity (Schlosserg et al., 2001).

VI.9.3.3. Observed and potential adverse effects

Although fly ash may have positive effects on soil quality and subsequently on crop yield, various constraints limit its use in agriculture. For example, an improvement in soil water-holding capacity, which requires high fly ash application rates, may result in toxic concentrations of B. Alkaline fly ash used as a lime substitute may add excessive amounts of Mo whose availability increases with pH promoting toxicity. There are numerous examples in the literature demonstrating that improvement of one soil parameter was associated with changes in other soil properties leading to yield reductions or deterioration in crop quality. Many reports emphasized elevated concentrations of elements potentially toxic to animals and humans or adverse balances among elements (Furr et al., 1977; Adriano et al., 1980). Improper Cu:Mo ratios in crops is a common example of such a disorder (Sale et al., 1996).

Because fly ash contains almost all elements and their concentrations depend on coal source, periodic monitoring of the chemical composition should be undertaken to ensure safe utilization.

The situation is further complicated by soil factors that affect plant uptake of elements potentially toxic to animals and human. Kukier et al. (1995) found that As concentrations in corn tops were affected not only by fly ash application rate but also by the addition of

K-fertilizer (Fig. VI.9.3). This could not be attributed to a “dilution effect” because dry matter values were equal for both K treatments at fly ash rates exceeding 3 g/kg soil. Therefore, the effect should be rather attributed to a modification of the uptake mechanism. This example shows that establishing of a safe application rate is a complicated issue and experimentally determined values may vary for the same soil under different management conditions.

Soil microbial population is an important factor influencing cycling of essential elements (C, N, S and P) in soil and the biosphere. Microbial counts, respiration and enzyme activities are the parameters commonly used for evaluation of microbial activity and growth. The changes in soil enzyme activity reflect changes in soil quality (Dick, 1992) and can be a measure of its deterioration. Arthur et al. (1984) found that CO₂ evolution from alfalfa meal and fly ash amended soil was significantly reduced at the higher rates (400–700 t/ha fly ash) indicating a decreased rate of organic carbon mineralization. Reduction of oat grain and alfalfa yields in accompanying field experiment with the same fly ash was noted at these rates. Yield reductions were associated with a B toxicity in plants and an excessive uptake of Mo, Se and As at levels potentially toxic to livestock. Therefore, it was concluded that a CO₂ evolution test may be suitable for prediction of potential phytotoxicity of fly ash.

Soil microbial activity expressed by a microbial respiration and enzyme activity in a fly ash amended Glynwood soil (Aquic Hapludalf) was investigated by Pichtel and Hayes (1990). An alkaline fly ash had no adverse effect on soil respiration at all rates applied (5, 10 and 20% by weight). At the 5% rate, bacterial numbers increased probably due to addition of nutrients but actinomycetes and fungi declined. At the higher rates, numbers of organisms declined in all populations. The decline in fungi was attributed to an increase in soil pH as these organisms are alkali-intolerant. Soil phosphatase, arylsulfatase, dehydrogenase, catalase and invertase activities were strongly inhibited at the 20% rate. Decrease in phosphatase activity was linked to the P added with fly ash, which interferes with activity and production of this enzyme. Overall, it seems that, the adverse effects of fly ash on crop yield and quality are usually observed at lower fly ash rates than those on soil microbial populations.

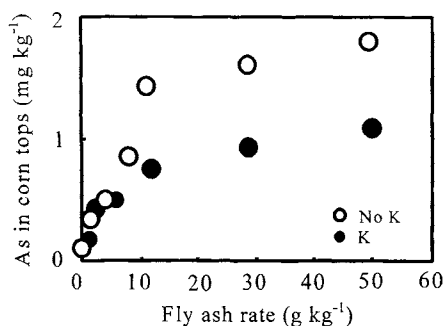


Figure VI.9.3. Effect of K fertilizer and fly ash rate on As concentration in corn shoots (Kukier et al., 1997).

VI.9.4. Forced oxidation FGD gypsum

Gypsum is applied to soils to supply S and Ca for crops, ameliorate subsoil acidity and improve soil physical condition and is recognized as a valuable soil amendment, being used on a commercial scale in many countries. The gypsum produced by a forced oxidation technology has a commercial-grade quality and can substitute mined gypsum in industrial and agricultural applications. Typically, FGD materials have smaller particle sizes than mined gypsum, which affects the dissolution kinetics as demonstrated by Bolan et al. (1991). The dissolution rate of the FGD material was only slightly lower than that of reagent grade gypsum but much higher than that of phosphogypsum and gypsum, which was attributed to a high external surface area of FGD product. This is considered an advantage because a rapid dissolution provides a better protection against crust formation as a rain event occurs and promotes movement of Ca^{2+} and SO_4^{2-} to subsoil. The following section will discuss the beneficial effects of gypsum application and the mechanisms involved. Because forced oxidation FGD gypsum is a recently developed product, most studies on its agricultural utilization are still in progress and few results have been published. For that reason, some examples of the effects of mined gypsum will be presented keeping in mind that FGD by-product has the same or even a better quality than mined gypsum.

VI.9.4.1. Amelioration of subsoil acidity

Highly weathered acid soils are characterized by high levels of Al and often insufficient amounts of Ca. Excessive amounts of Al and insufficient supply of Ca restrict root growth in a subsoil and result in crop susceptibility to drought periods and inhibited nutrient uptake.

Acidity of the topsoil can be ameliorated by application of lime. The Ca applied in this compound remains in the zone of incorporation and for that reason is not an effective ameliorant for subsoil acidity (Sumner, 1993). This can be partly attributed to the low solubility of CaCO_3 but also to the lack of a stable soluble anion that would have to accompany the migrating Ca^{2+} cation in order to maintain soil electroneutrality (Pavan et al., 1984). Surface application or incorporation of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) into topsoil was demonstrated to be a cost-effective way of ameliorating subsoil acidity. Both Ca^{2+} and SO_4^{2-} easily migrate down the soil profile changing subsoil chemical properties. Positive crop responses are usually observed after one or two years depending on soil texture, mineralogy and precipitation regime. Both ions, Ca^{2+} and SO_4^{2-} , are involved in reducing Al toxicity. Calcium displaces Al on soil exchange sites increasing Ca and decreasing Al saturation. This was demonstrated in a field experiment on an acid Tupelo soil (Vertic Palequilt) amended with commercial-grade FGD gypsum, which was surface incorporated at the rate of 20 t/ha. Deep sampling after 16 months revealed a substantial increase in soil exchangeable Ca and a decrease in exchangeable Al to a depth of 50 cm (Fig. VI.9.4). Alleviation of Al toxicity and improved Ca status in the subsoil result in greater root growth as demonstrated in a number of studies with mined gypsum (Sumner, 1993, 1995) and FGD gypsum (Wendell and Ritchey, 1996). This, in turn, enables a better extraction of water and plant nutrients stored in the subsoil and increases crop yields especially if drought events occur (Sumner, 1993; Farina et al., 2000).

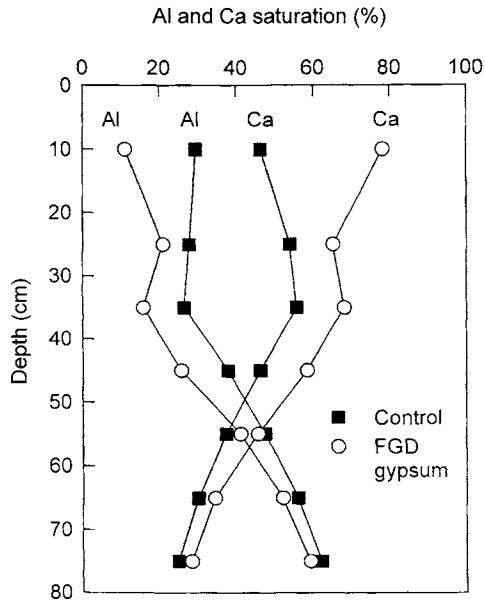


Figure VI.9.4. Al and Ca saturation in the profile of soil amended with 10 t/ha rate of FGD.

Displaced Al is leached out of the root zone or precipitates in a form of various aluminosilicate minerals such as alunite $KAl_3(OH)_6(SO_4)_2$, basaluminite $Al_4(OH)_{10}SO_4 \times 5H_2O$ and jurbanite $AlOHSO_4 \times 5H_2O$. Toxicity of Al in soil solution is reduced by a formation of $AlSO_4^+$ complex. Reeve and Sumner (1972) suggested that ligand exchange of SO_4^{2-} for OH^- on iron and aluminum oxide surfaces would increase soil cation-exchange capacity by creation of a net negative charge. The released OH^- groups would react with Al to form non-toxic $Al(OH)_3$. This process is known as the “self liming effect”.

VI.9.4.2. Improvement of soil physical properties

The Ca^{2+} in gypsum promotes flocculation of clay particles, which in turn affects various physical properties of soils containing appreciable amounts of water-dispersible clay. Sodic and many highly weathered acid soils are very susceptible to clay dispersion under conditions of low electrolyte concentration. The energy of raindrops destabilizes aggregates, and clay particles, which separate from other fractions, seal pores to form a layer of reduced permeability at the soil surface (crust). The process is rapid and causes drastic reductions in water infiltration rate accompanied by increased run-off and erosion (Sumner, 1993). Gypsum applications increase final infiltration rates substantially (Miller, 1987, 1988; Miller and Scifers, 1988). Soil losses were reduced from 266, 1315, 1135 and 939 to 96, 732, 442, and 50 kg/ha, respectively. Preventing crust formation by placing gypsum over the row prior to planting improves seedling emergence (Miller, 1988).

Gypsum was also demonstrated to be effective in reducing mechanical impedance of subsoil hardpans (Radcliffe et al., 1986; Sumner et al., 1990) through clay flocculation and improved chemical conditions in the subsoil. Physical, chemical and biological factors working in concert lead to aggregation of the subsoil material, which in turn promotes a better plant rooting and increased stability of the structure.

VI.9.4.3. Observed and potential negative effects

The high application rates of gypsum required for the amelioration of the subsoil acidity may induce losses of Mg and K from the topsoil due to exchange of the Mg^{2+} and K^+ by Ca^{2+} on the soil exchange sites. Increased mobility and solubility of both cations in soil column amended with gypsum FGD material was reported by Wendell and Ritchey (1996). Severity of the losses depends upon gypsum application rate and soil texture (Fig. VI.9.5).

As mentioned earlier, leaching of Al beyond the root zone is one of the mechanisms alleviating Al toxicity in acid subsoils. This may potentially pose a risk of groundwater contamination with Al. A column study (Wendell and Ritchey, 1996) demonstrated that FGD gypsum dramatically increased concentrations of the Al in leachates. These results may not be directly applicable to field conditions but they indicate the need for further research to answer this question.

These adverse effects are not specific to FGD gypsum and are also observed with mined and any other gypsum materials. They can be overcome by application of K and Mg fertilizers shortly after gypsum application.

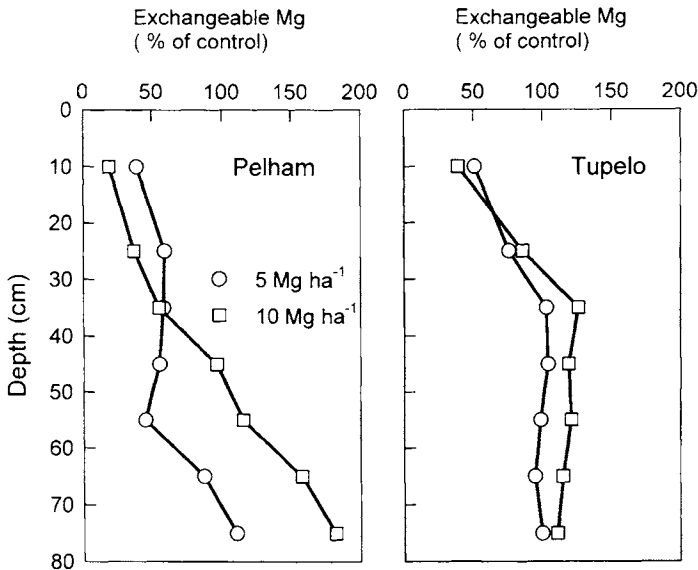


Figure VI.9.5. Distribution of exchangeable Mg in the profiles of soils amended with FGD material.

A salinity problem, which may be potentially associated with high rates of FGD products, is more specific to this material. The electrical conductivity of the mined gypsum saturated extracts is about 2 dS/m while that of FGD gypsum may exceed 30 dS/m. This is due to the presence of soluble salts other than gypsum from process make-up water that is recirculated in order to minimize the volume of wastewater. It is not expected to pose any significant risk to crops and the environment when FGD gypsum is applied at low rates of 0.5–1 t/ha as a source of Ca and S for crops but at high rates a period of time for leaching to take place before planting may be necessary.

A long-term mesocosm study of FGD residue application to South Carolina coastal plain soils showed a short term improvement of the yield of several crops. However, leachate salinity was significantly increased, and both crops and soil were enriched in trace elements As, B and Se; for this reason, 220 T/ha was assumed to be upper limit for the application of this material (Punshon and Adriano, 2001).

In some cases, FGD gypsum is stored in the same settling pond with fly ash, which is a carrier for trace elements. Application of such mixtures may add significant loads of trace elements. Kukier et al. (1997) demonstrated increased plant available As in the mixed vs. the pure FGD gypsum. Although some beneficial effects may result from joint application of both materials, extreme caution is recommended because the agronomic value of FGD gypsum may be offset by the fly ash component.

VI.9.5. Fluidized bed combustion (FBC) material

VI.9.5.1. Beneficial effects

The FBC products are composed mainly of CaSO_4 , CaSO_3 , CaO and MgO and ash. Their CaCO_3 equivalent typically varies from 50 to over 80% (Stout et al., 1979; Korcak, 1985); therefore their primary agricultural function is a substitute for lime on arable land and orchards (Korcak, 1988; Stehouwer et al., 1999). For this purpose, FBC materials are applied at rates from several to over 70 t/ha. An attempt to apply FBC waste at disposal rates higher than 100 t/ha was also reported (Mays et al., 1991). In every case, except for the highest disposal rates, positive effects were observed. The FBC materials increase soil pH and Ca and Mg levels in plants and soil. No excessive plant uptake of trace elements was reported in any of the field or pot studies. It was established (Terman et al., 1978; Stout et al., 1979) that FBC products may correct S deficiency. The availability of S from this material was comparable to that of Na_2SO_4 and elemental S.

High application rates 100 t/ha of FBC products can be used in orchards. The FBC material is surface applied beneath the trees. In addition to improving Ca status in soil and trees and the liming effect, it provides weed control (Korcak, 1993). A similar method was used with good results for tomato production. The FBC by-product was equal to or better than standard black plastic mulch, bare soil and rolled newspaper in terms of yield and fruit firmness.

High solubility of some components in FBC materials providing electrolytes concentrations sufficient for the flocculation of clay particles can be used for the improvement of water infiltration and the reduction of erosion in variable-charge and swelling soils but with some limitations (Reichert and Norton, 1996). The FBC bottom ash

used in the study was a combination of coal ash, unreacted sorbent material and anhydride (CaSO_4). Unlike gypsum, which does not change soil pH, FGD bottom ash increases pH and produces a much stronger electrolyte concentration upon dissolution. Application of FBC bottom ash has two opposite effects on clay dispersion. The increase in pH promotes clay dispersion by generation of negative charge while the increase in electrolyte concentration tends to flocculate clay particles. Reichert and Norton (1996) studied the effect of surface application of 5 t/ha FBC bottom ash on infiltration rate and erosion of seven variable charge soil series from Hawaii, Puerto Rico, Georgia, Brazil and Australia. The FBC ash increased infiltration and reduced erosion only on the soils whose pH was little affected by the application of the by-product. On the permanent charge soils, which respond with a small increase in charge as pH increases, a consistent positive effect expressed in reduced surface sealing and erosion was observed after FBC waste application (Reichert and Norton, 1994).

VI.9.5.2. Potential and observed adverse effects

Very high disposal rates (up to 500 t/ha) of FBC by-product on arable land had an adverse effect on crop yield and soil quality including excessively high pH levels and crust formation due to a pozzolanic effect of the material (Mays et al., 1991).

The potential adverse effect on groundwater quality associated with application of large quantities of FBC product was evaluated by Sidle et al. (1979). Only the Ca, Mg, Mn and SO_4^{2-} concentrations increased in FBC-amended soil. Movement of Ca and Mg could be considered a beneficial effect for subsoil. Concentrations of Mn and SO_4^{2-} in the percolate were within the range for drinking water. No evidence for downward migration of B, Cd, Co, Cu, K, Na, Ni, Pb and Zn was observed.

McCarty et al. (1994) studied the effect of lime (CaCO_3) and FBC fly and bed ashes applied at the rates appropriate for substitution as lime on the soil enzyme activity. Significant effects on enzyme activity were observed at 2.8 t/ha rates of FBC products and 4.5 t/ha of CaCO_3 . The FBC products influenced enzyme activity in a similar manner to CaCO_3 , which suggests that the influence of the by-products on the enzyme activity was partly due to their liming effect. It appears that in some situations it is very difficult to distinguish the effects of coal combustion by-products from those of traditional fertilizers and lime.

The potential effect on the food chain was studied by Whitsel et al. (1988). Pigs were fed for 8 weeks on a diet produced on soil amended with FBC material. Increased As in urine was the only adverse effect of the diet. None of trace elements investigated (Fe, Mn, Cu, Zn, Cd, Pb and Se) exceeded normal levels in pig organs. A significant depression in weight gain of pigs fed an FBC produced diet was observed when compared to a lime treatment. No explanation of this adverse effect was provided.

VI.9.6. Closing comments

Based on the available literature, it appears that among the coal combustion residues reviewed, fly ashes have the most variable characteristics; therefore their beneficial agricultural utilization should be preceded by a careful evaluation of potential effects on

soil, crop and environment. Co-utilization with other waste materials such as biosolids or manure seems to be a promising alternative (Schumann and Sumner, 2000). Fly ash as a component in such a mixture serves as a dewatering and deodorizing agent and would stabilize P. The organic components are supposed to reduce the toxicity of trace elements present in fly ash. Recent reports give equivocal evidence concerning the environmental effect of biosolids/fly ash mixture. On the one hand, mixture application was found to reduce concentrations of plant available trace elements (Bhumbla et al., 2001). On the other hand, Yuncong et al. (2001) observed an increased phytoavailability of Zn, Ni and Mo in soil amended with a large amount of composted mixture of fly ash and biosolids. Increased mobility of Pb and Zn, following fly ash compost application could pose a risk of groundwater contamination. These results indicate that there is a need to develop guidelines for fly ash application to the agricultural land, either as a sole component or as a mixture with biosolids.

More research is needed in order to explore the possibilities of the agricultural utilization of gypsum-like materials. A greater number of field studies on the environmental impacts of coal combustion by-products is necessary to test under natural conditions hypotheses developed as a result of laboratory studies.

Acknowledgements

We acknowledge the kind assistance of Dr. Rufus Chaney, Beltsville, MD, who gave us access to his literature files on coal combustion by-products and discussed interpretations of the research on food chain transport of trace elements in coal combustion by-products.

References

- Adriano, D.C., Page, A.L., Elseewi, A.A., Chang, A.C., Straughan, I., 1980. Utilization and disposal of fly ash and other coal residues in terrestrial ecosystems: a review. *J. Environ. Qual.*, 9, 333–344.
- Aitken, R.L., Bell, L.C., 1985. Plant uptake and phytotoxicity of boron in Australian fly ashes. *Plant Soil*, 84, 245–257.
- Alcordo, I.S., Rechcigl, J.E., 1995. Phosphogypsum and other by-product gypsums. In: Rechcigl, J.E. (Ed.), *Soil Amendments and Environmental Quality*, Lewis Publishers, Boca Raton, FL, pp. 365–425.
- Arthur, M.A., Zwick, T.C., Tolle, D.A., van Voris, P., 1984. Effects of fly ash on microbial CO₂ evolution from an agricultural soil. *Water Air Soil Pollut.*, 22, 209–216.
- Bhumbla, D.K., Sekhon, B.S., Sajwan, K.S., 2001. Trace elements bioavailability in mine soils treated with sewage sludge and fly ash mixtures, pp. 368–368. *Biogeochemistry of Trace Elements. ICOBTE 2001 Conference Proceedings*, July 29–August 2, 2001, University of Guelph, Ontario, Canada, p. 669.
- Bolan, N.S., Syers, J.K., Sumner, M.E., 1991. Dissolution of various sources of gypsum in aqueous solutions and in soils. *J. Sci. Food Agric.*, 57, 527–541.
- Campbell, D.J., Fox, W.E., Aitken, R.L., Bell, L.C., 1983. Physical characteristics of sand amended with fly ash. *Aust. J. Soil Res.*, 21, 147–154.
- Chang, A.C., Lund, L.J., Page, A.L., Warneke, J.E., 1977. Physical properties of fly-ash amended soils. *J. Environ. Qual.*, 6, 267–270.
- Combs, G.F., Jr., Barrows, S.A., Swader, F.N., 1980. Biologic availability of selenium in corn grain produced on soil amended with fly ash. *J. Agric. Food Chem.*, 28, 406–409.
- Dick, R.P., 1992. Soil enzyme activities as process level biological indexes of soil quality. *Agron. Abstr.*, 253.
- Doran, J.W., Martens, D.C., 1972. Molybdenum availability as influenced by application of fly ash to soil. *J. Environ. Qual.*, 1, 186–189.

- Elseewi, A.A., Bingham, F.T., Page, A.L., 1978. Availability of sulfur in fly ash to plants. *J. Environ. Qual.*, 7, 69–73.
- Farina, M.P.W., Channon, P., Thibaud, G.R., 2000. A comparison of strategies for ameliorating subsoil acidity: I. Long-term growth effects. *Soil Sci. Soc. Am. J.*, 64, 646–651.
- Furr, A.K., Parkinson, T.F., Hinrich, R.A., VanCampen, D.R., Bache, C.A., Gutenmann, W.H., St. John, L.E., Jr., Pakkala, I.S., Lisk, D.J., 1977. National survey of elements and radioactivity in fly ashes; absorption of elements by cabbage grown in fly ash–soil mixtures. *Environ. Sci. Technol.*, 11, 1194–1201.
- Furr, A.K., Parkinson, T.F., Gutenmann, W.H., Pakkala, I.S., Lisk, D.J., 1978. Elemental content of vegetables, grains, and forages field-grown on fly ash-amended soil. *J. Agric. Food Chem.*, 26, 357–359.
- Gladney, E.S., Wangen, L.E., Curtis, D.B., Journey, E.T., 1978. Observation of boron release from coal-fired power plants. *Environ. Sci. Technol.*, 12, 1084–1085.
- Hansen, L.D., Fisher, G.L., 1980. Elemental distribution in coal fly ash particles. *Environ. Sci. Technol.*, 14, 1111–1117.
- Jacobs, L.W., Erickson, A.E., Berti, W.R., MacKellar, B.M., 1991. Improving crop yield potentials of coarse textured soils with fly ash amendments. *Proceedings of the 9th International Ash Use Symposium, Vol. 3 EPRI GS-7162, American Coal Ash Assoc., Washington, DC*, pp. 59–1–59–16.
- Korcak, R.F., 1985. Effect of coal combustion wastes used as lime substitutes in nutrition of apple in three soils. *Plant Soil*, 85, 437–441.
- Korcak, R.F., 1988. Fluidized bed material applied at disposal levels: effects on an apple orchard. *J. Environ. Qual.*, 17, 469–473.
- Korcak, R.F., 1993. Utilization of fluidized bed combustion byproducts in horticulture. *Proceedings of the Tenth International Ash Use Symposium, Vol. 1, EPRI Publ. No. TR-101774, Amer. Coal Ash Assoc., Washington, DC*, pp. 12–1–12–9.
- Kukier, U., Sumner, M.E., 1994. Boron availability to plants from coal combustion by-products. *Water Air Soil Pollut.*, 87, 93–110.
- Kukier, U., Ishak, C.F., Sumner, M.E., Miller, W.P., 1995. Arsenic distribution in soil profiles amended with coal combustion by-products. In: Hatcher, K.J. (Ed.), *Proceedings of Georgia Water Resource Conference, Carl Vinson Institute of Government, University of Georgia, Athens, GA*, pp. 394–397.
- Kukier, U., Sumner, M.E., Miller, W.P., 1997. The effect of fly ash amendment on arsenic levels in soil and plants. *Proceedings of Fourth International Conference on the Biogeochemistry of Trace Elements (Extended Abstracts)*, June 23–26, Berkeley, California.
- Martens, D.C., Schnappinger, M.G., Jr., Zelazny, L.W., 1970. The plant availability of potassium in fly ash. *Soil. Sci. Soc. Am. Proc.*, 34, 453–456.
- Mattigod, S.V., Rai, D., Eary, L.E., Ainsworth, C.C., 1990. Geochemical factors controlling the mobilization of inorganic constituents from fossil fuel combustion residues: I. Review of the major elements. *J. Environ. Qual.*, 19, 188–201.
- Mays, D.A., Giordano, P.M., Behel, A.D., Jr., 1991. Impact of fluidized bed combustion waste on metal content of crops and soil. *Water Air Soil Pollut.*, 57–58, 307–317.
- McCarty, G.W., Siddaramappa, R., Wright, R.J., Codling, E.E., Gao, G., 1994. Evaluation of coal combustion by-products as soil liming materials: their influence on soil pH and enzyme activities. *Biol. Fertil. Soils*, 17, 167–172.
- Mengel, K., Kirkby, K.D., 1987. *Principles of Plant Nutrition*, International Potash Institute, Bern, Switzerland.
- Miller, W.P., 1987. Infiltration and soil loss of three gypsum-amended Ultisols under simulated rainfall. *Soil Sci. Soc. Am. J.*, 51, 1314–1320.
- Miller, W.P., 1988. *Use of Gypsum to Improve Physical Properties and Water Relation in Southeastern Soils*, Publ. No. 01-020-082, Florida Institute of Phosphate Research, Bartow.
- Miller, W.P., Scifers, J., 1988. Effect of sodium nitrate and gypsum on infiltration and erosion of a highly weathered soil. *Soil Sci.*, 145, 304–309.
- Mulford, F.R., Martens, D.C., 1971. Response of alfalfa to boron in fly ash. *Soil Sci. Soc. Am. Proc.*, 35, 296–300.
- Pavan, M.A., Bingham, F.T., Pratt, P.F., 1984. Redistribution of exchangeable calcium, magnesium, and aluminum following lime and or gypsum application to a Brazilian Oxisol. *Soil Sci. Soc. Am. J.*, 48, 33–38.
- Pichtel, J.R., Hayes, J.M., 1990. Influence of fly ash on soil microbial activity and populations. *J. Environ. Qual.*, 19, 593–597.
- Plank, C.O., Martens, D.C., 1974. Boron availability as influenced by application of fly ash to soil. *Soil Sci. Soc. Am. Proc.*, 38, 974–977.

- Punshon, T., Adriano, D.C., 2001. Soil amendment with flue-gas desulfurization residue: mid-term physical and chemical effects on plants and soils, pp. 375–375. *Biogeochemistry of Trace Elements. ICOBTE 2001 Conference Proceedings*, July 29–August 2, 2001, University of Guelph, Ontario, Canada, p. 669.
- Radcliffe, D.E., Clark, J.L., Sumner, M.E., 1986. Effect of gypsum and deep-rooting perennials on subsoil mechanical impedance. *Soil Sci. Soc. Am. J.*, 50, 1566–1570.
- Reeve, N.G., Sumner, M.E., 1972. Amelioration of a subsoil acidity in Natal Qxisols by leaching of surface-applied amendments. *Agrochemophysica*, 4, 1–6.
- Reichert, J.M., Norton, L.D., 1994. Fluidized bed bottom-ash effects on infiltration and erosion of swelling soils. *Soil Sci. Soc. Am. J.*, 58, 1483–1488.
- Reichert, J.M., Norton, L.D., 1996. Fluidized bed bottom-ash effects on infiltration and erosion of variable-charge soils. *Soil Sci. Soc. Am. J.*, 60, 275–282.
- Sale, L.Y., Naeth, M.A., Chanasyk, D.S., 1996. Growth response of barley on unfettered fly ash-amended soil. *J. Environ. Qual.*, 25, 684–691.
- Santhanam, C.J., Lunt, R.R., Johnson, S.L., Cooper, C.B., Thayer, P.S., Jones, J.W., 1979. Health and environmental impacts of increased generation of coal ash and FGD sludges. *Environ. Health Perspect.*, 33, 131–157.
- Schlossberg, M.J., Sumner, M., Miller, W.P., Dudka, S., 2001. Utilization of coal combustion by-products (CCBP) in horticulture and turfgrass industries; technical and environmental feasibility studies, pp. 377–377. *Biogeochemistry of Trace Elements. ICOBTE 2001 Conference Proceedings*, July 29–August 2, 2001, University of Guelph, Ontario, Canada, p. 669.
- Schnappinger, M.G., Jr., Martens, D.C., Plank, C.O., 1975. Zinc availability as influenced by application of fly ash to soil. *Environ. Sci. Technol.*, 9, 258–261.
- Schumann, A.W., Sumner, M.E., 2000. Chemical evaluation of nutrient supply from fly ash–biosolids mixtures. *Soil Sci. Soc. Am. J.*, 64, 419–426.
- Shane, B.S., Littman, C.B., Essick, L.A., Gutenmann, W.H., Doss, G.J., Lisk, D.J., 1988. Uptake of selenium and mutagens by vegetables grown in fly ash containing greenhouse media. *J. Agric. Food Chem.*, 36, 328–333.
- Sidle, R.C., Stout, W.L., Hern, J.L., Bennett, O.L., 1979. Solute movement from fluidized bed combustion wastes in acid soil and mine spoil columns. *J. Environ. Qual.*, 8, 236–241.
- Stehouwer, R.C., Dick, W.A., Sutton, P., 1999. Acidic soil amendment with a magnesium-containing fluidized bed combustion by-product. *Agron. J.*, 91, 24–32.
- Stout, W.L., Sidle, R.C., Hern, J.L., Bennett, O.L., 1979. Effects of fluidized bed combustion wastes on the Ca, Mg, S, and Zn levels in red clover, tall fescue, oat and buckwheat. *Agron. J.*, 71, 662–665.
- Sumner, M.E., 1993. Gypsum and acid soils: the world scene. *Adv. Agron.*, 51, 1–31.
- Sumner, M.E., 1995. Amelioration of subsoil acidity with minimum disturbance. In: Jayawardane, N.S., Stewart, B.A. (Eds), *Subsoil Management Techniques. Advances in Soil Science*, Lewis Publishers, Boca Raton, FL, pp. 147–185.
- Sumner, M.E., Radcliffe, D.E., McCray, M., Clark, R.L., 1990. Gypsum as an ameliorant for subsoil hardpans. *Soil Technol.*, 3, 253–258.
- Terman, G.L., Kilmer, V.J., Hunt, C.M., Buchanan, W., 1978. Fluidized bed boiler waste as a source of nutrients and lime. *J. Environ. Qual.*, 7, 147–150.
- Wendell, R.R., Ritchey, K.D., 1996. High-calcium flue gas desulfurization products reduce aluminum toxicity in an Appalachian soil. *J. Environ. Qual.*, 25, 1401–1410.
- Whitsel, T.J., Reid, R.L., Stout, W.L., Hern, J.L., Bennett, O.L., 1988. Quality of diets with fluidized bed combustion residue treatment: swine trials. *J. Environ. Qual.*, 17, 556–562.
- Yuncong, L., Zhang, M., Stopella, P., Bryan, H., Zhenli, H.E., 2001. Influence of fly ash compost application on distribution of metals on soil, water and plant, pp. 374–374. *Biogeochemistry of Trace Elements. ICOBTE 2001 Conference Proceedings*, July 29–August 2, 2001, University of Guelph, Ontario, Canada, p. 669.

Further Reading

- Sajwan, K.S., Alva, A.K., Keefer, R.F. (Eds), 1999. *Biogeochemistry of Trace Elements in Coal and Coal Combustion Byproducts*. Kluwer Academic/Plenum Publishers, New York, p. 359.
- Sajwan, K.S., Alva, A.K., Keefer, R.F. (Eds), 2003. *Chemistry of Trace Elements in Fly Ash*. Kluwer Academic/Plenum Publishers, New York, p. 346.