

Prospects for enhancing carbon sequestration and reclamation of degraded lands with fossil-fuel combustion by-products[☆]

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Abstract

Concern for the potential global change consequences of increasing atmospheric CO₂ has prompted interest in the development of mechanisms to reduce or stabilize atmospheric CO₂. During the next several decades, a program focused on terrestrial sequestration processes could make a significant contribution to abating CO₂ increases. The reclamation of degraded lands, such as mine-spoil sites, highway rights-of-way, and poorly managed lands, represents an opportunity to couple C sequestration with the use of fossil-fuel and energy by-products and other waste material, such as biosolids and organic wastes from human and animal sewage treatment facilities, to improve soil quality. Degraded lands are often characterized by acidic pH, low levels of key nutrients, poor soil structure, and limited moisture-retention capacity. Much is known about the methods to improve these soils, but the cost of implementation is often a limiting factor. However, the additional financial and environmental benefits of C sequestration may change the economics of land reclamation activities. The addition of energy-related by-products can address the adverse conditions of these degraded lands through a variety of mechanisms, such as enhancing plant growth and capturing of organic C in long-lived soil C pools. This review examines the use of fossil-fuel combustion by-products and organic amendments to enhance C sequestration and identifies the key gaps in information that still must be addressed before these methods can be implemented on an environmentally meaningful scale.
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1. Introduction

Atmospheric CO₂ concentrations and other so-called greenhouse gases have, due in large part to fossil-fuel combustion, increased considerably since the early to

mid 1800s and are projected to accelerate during the coming century (e.g. IPCC, 1995; Houghton et al., 2001). It is estimated that in the United States alone, CO₂ emissions increased more than eightfold between 1990 and 1998 (Fig. 1; Marland et al., 2001). Such increases are believed to have the potential to cause unprecedented regional and global climatic and related environmental changes, including increased global temperatures, altered patterns of regional precipitation and cloud cover, rises in sea level, and increased frequency and severity of extreme weather events (e.g. Easterling

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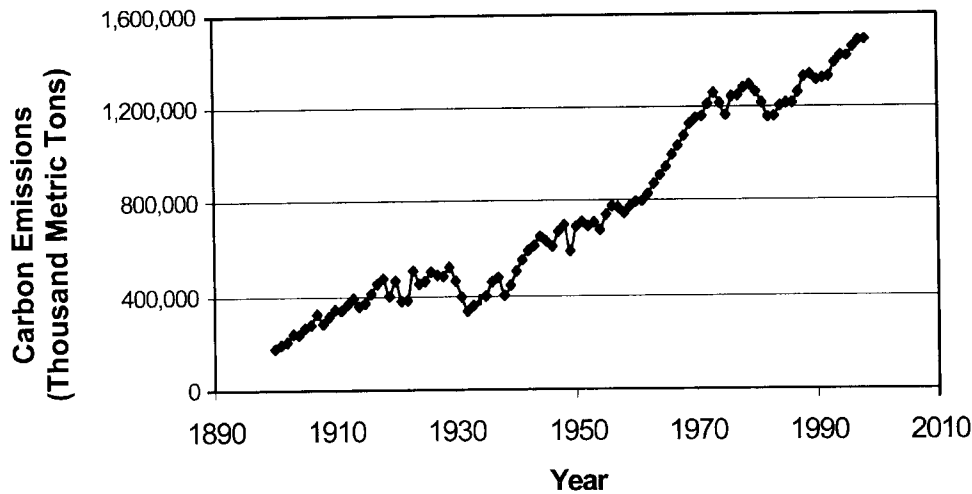


Fig. 1. Carbon dioxide emissions from the United States during the period of 1890–1998 (Marland et al., 2001) show a substantial and continuing upward trend despite the oil shock of the 1970s and a significant switch from burning of coal to petroleum as the major contributor to emissions.

et al., 2000). These projections have prompted scientists from multiple disciplines to consider options for minimizing future increases in global CO_2 concentrations through a variety of concepts concerning the implementation and research of mitigation programs. A few of the C management strategies being considered to accomplish this goal include the development of more energy-efficient fossil-fuel-fired power plants, buildings, appliances, transportation vehicles, and more efficient technologies for the production and delivery of electricity and fuels. In addition, increased attention is also being given to the development of renewable energy resources, including solar, wind, geothermal, as well as an emerging emphasis on dedicated bioenergy crops (e.g. Tuskan and Walsh, 2001).

Another potential approach to mitigating rising CO_2 concentrations currently of interest, and one that is designed to complement the development of energy-efficient technologies, is the enhanced storage or sequestration of C in terrestrial ecosystems (e.g. Paustian et al., 1998; Reichle et al., 1999). One aspect of the terrestrial sequestration approach envisions the use of soil and vegetation functioning as long-term storage pools for atmosphere-derived C. To accomplish this, increased sequestration of C can be conceptually achieved by enhancing the natural biological processes that assimilate CO_2 (i.e. increased productivity of lands) and then allocating the assimilated C to long-lived plant tissues and/or pools of soil organic matter (SOM) resistant to microbial decomposition. Thus, the use of terrestrial C sequestration strategies for slowing increased atmospheric CO_2 and its potential environmental and economic consequences would require a

plant- and soil-based program of C management that can successfully be implemented across multiple ecosystems and land-use categories. This is especially important if continued fossil-fuel use is necessary during a transition to other types of energy systems (e.g. renewable). Although a key objective in C management research is to enhance the natural capacity of plants and soils to sequester C, the functionality of C storage in terrestrial ecosystems as a whole is a poorly understood process. Many facets of terrestrial C sequestration have been explored, including the use of forest ecosystems, grasslands (Fisher et al., 1994; Richter et al., 1994; Post and Kwon, 2000; Conant et al., 2001), and agricultural applications. However, there is a long history of research on the reclamation of degraded and disturbed lands, and although few of these studies have focused on the effects of amendments on C budgets, there is reason to believe that new C management strategies could enhance C sequestration on such lands (e.g. Akala and Lal, 2000, 2001; Bendfeldt et al., 2001). Worldwide, for example, nearly 2×10^9 ha of lands are considered to be degraded to some degree (Oldeman and Vanengelen, 1993) and may be capable of sequestering as much as 3 PgC yr^{-1} (Lal et al., 1998). In the United States, approximately 4×10^6 ha ($\sim 0.4\%$ of the surface area of the United States) consists of previously mined lands (USDA, 1979) or rural highway rights-of-way (US DOT, 1999; calculated assuming a 10- to 20-m average width of non-road right-of-way). If we estimate that poorly managed lands account for 1.4×10^8 ha of US land (based on world estimates of degraded land at $\sim 15\%$, Oldeman and Vanengelen, 1993) and use the estimates for C sequestration potential by degraded lands

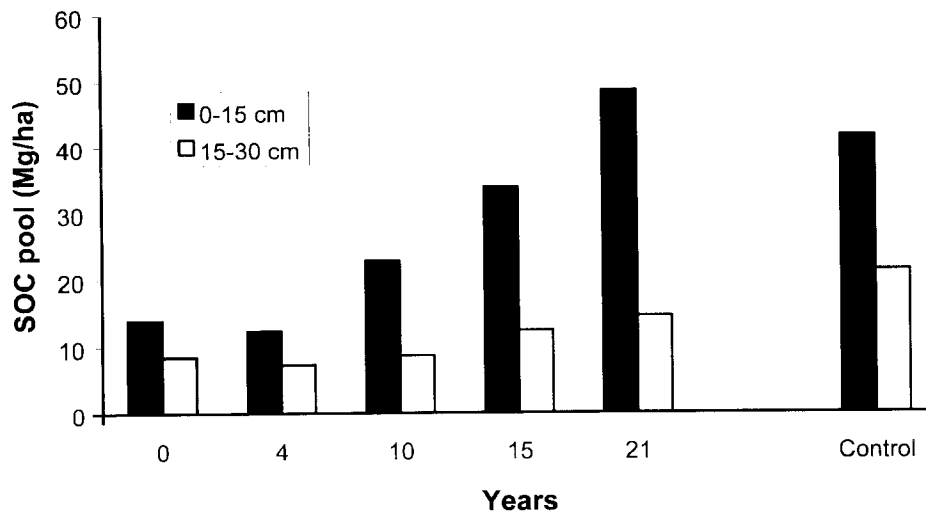


Fig. 2. Accumulation of SOC in reclaimed mine soils planted as forest in southeastern Ohio during a 21-year period after reclamation (Akala and Lal, 2001). The control plot was a 65-year-old forest.

(i.e. $1.5 \text{ MgC yr}^{-1} \text{ ha}^{-1}$) derived from Akala and Lal (2000), degraded lands in the United States could sequester approximately 11 PgC over 50 years, which is a small but significant fraction of the total needed to stabilize global atmospheric CO_2 levels.

Despite the fact that degraded mine lands are often characterized by acidic pH, low levels of key nutrients, poor soil structure, and limited moisture-retention capacity (Barnhisel et al., 2000), there does appear to be significant C sequestration potential (e.g. Akala and Lal, 2001). Addition of energy-related by-products can address these adverse conditions through a variety of mechanisms, including improvement of the soil structure, direct or indirect contribution to the releasing of nutrient elements in the soil, and the stabilization of toxic metals in soil.

The additional costs associated with more intensive reclamation strategies may be counterbalanced if coupled with the additional objective of C sequestration. Indeed, various countries are considering programs of long-term economic incentives for C sequestration and these could be available in the future (e.g. Walsh, 1999). Thus, a focus on C sequestration may ensure the long-term success of soil reclamation efforts as the potential for C accumulation in reclaimed soils under forests appears great (e.g. Fig. 2).

In this review, we explore the prospects for enhancing both C sequestration and the reclamation of degraded lands with fossil-fuel combustion by-products. Our approach is to suggest that restoration of degraded soils represents a unique opportunity to couple C sequestration with the use of fossil-fuel combustion by-products and other waste materials while achieving ecological,

environmental, and societal benefits. Although gains in C sequestration potential for degraded lands in the continental United States may be relatively modest, the use of industrial by-products to restore degraded lands offers both environmental and economic benefits as well as scientific challenges.

2. Fossil-fuel combustion by-products as amendments

The two major coal combustion by-products that have potential for use in prompting C sequestration are fly ash and flue-gas desulfurization (FGD) by-products. Fly ash is a coal combustion residue with an aluminosilicate composition comparable to that of soil (Adriano et al., 1980; El-Mogazi et al., 1988; Qafoku et al., 1999; Dick et al., 2000). Variable amounts of unburned C is present with quartz, mullite, hematite, and magnetite, but the majority of fly ash consists of amorphous aluminosilicate glassy spheres (Qafoku et al., 1999). FGD by-products, which are produced by newer SO_2 scrubbing technologies, such as pressurized fluidized bed combustion (PFBC) and lime injection multistage burners (LIMB), are primarily composed of alkaline materials consisting of excess sorbent (calcite or dolomitic limestone, CaO , $\text{Ca}(\text{OH})_2$ and MgO), S-bearing compounds (CaSO_4 , CaSO_3 and MgSO_4), and fly ash (Crews and Dick, 1998). In 1996, 54 Mg of fly ash and 22 mg of FGD by-products were produced in the United States, of which less than 25% of the fly ash and less than 7% of FGD by-products were reused (American Coal Ash Association, 1997). The remainder was disposed in landfills. Whereas fly ash is used mainly for engineering purposes to modify texture in soils and as a source of

trace nutrients for plants. FGD by-products are of interest mainly as liming agents and sources of divalent cations for improvement of soil pH and aggregation (American Coal Ash Association, 1997).

Low pH appears to be a major negative determinate in natural revegetation of surface-mined coal lands (Skousen et al., 1994). Coal combustion residues can contribute Ca^{2+} and other basic cations to improve soil structure and increase the pH of acidic soils. FGD has been able to supply base cations and trace elements for growth of commercially important tree species (Crews and Dick, 1998). For example, sulfur present in FGD by-products can offer nutritional value for plants (increases in barley production have been observed with fly ash addition in Se-deficient soil (Sale et al., 1996)). In addition, coal combustion by-products can supply micronutrients to areas where plant growth is limited by specific trace elements. Micronutrient amendment from coal fly ash mixed with sewage biosolids was applied to an acid B-deficient loamy soil in China with a resulting higher yield for cucumber (*Cucumis sativus*) and corn (*Zea mays*) than either the control treatment or a B-containing fertilizer (Jiang et al., 1999).

The benefits of fly ash incorporation to soil structure are well known. Ash additions to an easily clodded, clay loam soil decreased bulk density, increased aggregation, and decreased the modulus of rupture (Sale et al., 1997). Fly ash has been shown to increase porosity, water-holding capacity, pH, conductivity, and dissolved SO_4^{2-} , CO_3^{2-} , HCO_3^- , Cl^- , and basic cations, although the effect is decreased in high-clay soils (Matsi and Keramidas, 1999). Soil depth appears to be a positive factor in establishing white pine (*Pinus strobes*) on mine-spoil (Andrews et al., 1998). Thus, fly ash incorporation within increased depths of soil, or the effective rooting zone, could be beneficial.

The net positive results of nutrient and soil structure changes with fly ash amendment have been seen in a number of studies with several types of plants. At low levels of application to barley (*Hordeum vulgare* L. var. Ledue), fly ash resulted in increased plant heights and grain yields (Sale et al., 1996). Application of 50% fly ash to soil resulted in increased growth and yield of wheat (*Triticum aestivum*), with effects comparable to those of soil with compost and an NPK (nitrogen–phosphorus–potassium) fertilizer (Tripathy and Sahu, 1997). In another study on wheat, increased growth was seen with addition of fly ash and fly ash leachate (Karpate and Choudhary, 1997). With tomatoes (*Lycopersicon esculentum*), an increased yield was observed in loam soil amended with up to 60% (v/v) of coal fly ash (Khan and Khan, 1996). The addition of low-B fly ash increased biomass of rye grass (*Lolium perenne* L.) up to 80% over controls in Red Mediterranean acid soils (Matsi and Keramidas, 1999). However, many coal fly ashes are high enough in soluble salts and B to

limit plant growth in sensitive species at application rates as low as 10% (Daniels et al., 1999). Therefore, utilization of large amounts of fly ash as a soil amendment may be limited with certain combinations of ashes, soil conditions, and plant materials.

3. Organic amendments with combustion products

The potential for coal combustion by-products to enhance C sequestration in degraded lands may be most fully realized when these inorganic by-products are applied in conjunction with organic amendments, including mulch from biomass, agricultural residues, and process waste materials, such as biosolids and pulp and sludge from paper production (Haering et al., 2000). These organic amendments can have beneficial effects that complement and extend those of the inorganic fly ash material. Fly ash mixed with sandy loam soil at a 1:3 ratio and further amended with composted lawn clippings resulted in high yields that were correlated with higher K, Ca and N levels and lower B levels (Menon et al., 1992). Mixing composted lawn clippings and fine fly ash (20%) from the US Department of Energy (DOE) Savannah River Site (SRS) increased mustard (*Brassica integrifolia*) and collard green (*Brassica oleracea viridis*) yields but depressed yields of string beans (*Phaseolus vulgaris*), bell pepper (*Capsicum frutescens*), and eggplant (*Solanum melongena esculentum*) as a result of B accumulation (Menon et al., 1993).

Potential benefits also include improving soil structure, moisture-retention capacity, and soil fertility. Inorganic and organic amendments both contribute to soil tilth but do so by different mechanisms that act in a complementary fashion. The Ca^{2+} from fly ash promotes flocculation between soil particles and stabilizes soil structure through cation bridging, while organic matter can sorb to mineral surfaces and create a more reactive network for water, air, and nutrient interactions in the soil. The organic matter also contributes additional pH buffering capacity. The interaction of organic matter with soils is enhanced by Ca^{2+} , thus the addition of both organic and inorganic amendments would provide synergistic benefits to soil improvement.

Microbial mineralization of organic matter releases nutrient elements to the soil solution for plant uptake. In addition, organic matter can bind essential metal nutrients, acting as a metal/ion buffer in soil to make micronutrients available to plants. For example, organic matter can complex soil-phase Fe and make it available for uptake by plants.

Organic matter can also stabilize toxic metals in soil, thereby reducing their migration to groundwater and reducing their uptake and toxic effects in plants. In addition, SOM has been demonstrated to bind a variety of metals that are sometimes present in fly ash and

FGD by-products, such as Zn, Ni, Pb, Cd, Cu and B. For example, in field experiments at metal-contaminated and metal-amended sites, the addition of humic materials reduced uptake of a suite of heavy metals (Ni, Cr, Cu and Zn) in clover by 60% and decreased the concentration of metals leached into soil solution by 50–90%. Biomass production also tripled in the humic-treated contaminated soil (McCarthy, 1998). Even greater reductions in metal uptake and larger increases in biomass were observed in greenhouse studies (Wong, 1995; Chu and Poon, 1999).

Beneficial effects of mixing fly ash with biosolids appear to include reduction in certain metal toxicities from contaminated sewage biosolids, increased supply of nutrients, and addition of buffering capacity. There is a reduction of metal uptake (e.g. Zn, Cd, Cu) in plants grown in fly ash and sewage biosolids compared with those grown without fly ash and sewage biosolids (Wong, 1995; Chu and Poon, 1999). This has been observed in sandy soils perhaps as a result of an increase in soil pH (Vallini et al., 1999).

In addition to reducing metal toxicity, sewage biosolids have been mixed with alkaline industrial by-products to make a commercial soil substitute that has beneficial effects on moisture-holding capacity when applied at rates of 500 t acre⁻¹ (Logan and Harrison, 1995). Fly ash mixed with poultry manure or sewage biosolids (1:1) was beneficial to growth of sudangrass (*Sorghum bicolor*) at 25 t acre⁻¹, and fly ash mixed with dairy manure increased growth at rates to 50 t acre⁻¹ (Sajwan et al., 1996). These beneficial effects have been seen in other studies with varying amounts of fly ash but occasionally with B toxicity at high applications (Wong et al., 1998; Wong and Su, 1997a; Chu and Poon, 1999). The sewage biosolids also contributed significant amounts of PO₄, while the fly ash provided a pH buffering capacity to counteract the increase in acidity during the initial decomposition of organic matter (Wong and Su, 1997b). One of the few long-lasting effects of sewage biosolids in reclamation of mine soil was an increase in available phosphate (Bendfeldt et al., 2001).

Organic amendments are often useful in conjunction with fly ash in successful mine reclamation activities. However, application rates must be controlled. For example, yields of barley silage on a mine-spoil increased at intermediate fly ash amendment rates (200 t ha⁻¹ or less) but decreased at rates of 400 t ha⁻¹ or more. Addition of compost and krill manure proved effective in increasing vegetation at a mine reclamation site in South Africa where Se levels in grass leaves may have been toxic (Van Rensburg et al., 1998). Application of gypsum reduced Se levels in plants grown on a coal ash landfill (Woodbury et al., 1999), but other questions related to Se accumulation remained unanswered. In FGD sludge pond revegetation, growth

of grasses (but not shrubs) was increased by amendments with manure, wood shavings, and fly ash (Salo et al., 1999).

Use of FGD by-products combined with organic amendments has also been shown to be an effective mine reclamation approach in recent studies in Ohio (Beeghly et al., 1995; Stehouwer et al., 1995; Stehouwer, 1997a,b; Dick et al., 2000; Hao and Dick, 2000). Greenhouse and field studies were conducted on various mine-spoil materials using mixtures of FGD by-products (PFBC, LIMB, Spray Dryer) with either compost derived from yard trimmings or sewage sludge. FGD applications were shown to be effective with or without the organic additions, but the compost/sludge decreased the potential for metal toxicity and increased the depth at which the treatment was effective. Hao and Dick (2000) noted that the O₂-scavenging and antibacterial properties of CaSO₃ and FGD by-products also significantly delayed the onset of mine-spoil acidification and suggested that deep incorporation of FGD by-products would be very effective in this regard.

4. Issues involved in by-product amendments

The literature suggests the great potential for the addition of a suite of amendments containing both organic and inorganic energy-related by-products to improve degraded land and to beneficially utilize energy by-products. However, the optimal strategy for rapid enhancement of C sequestration is not currently known. As yet, there are still critical knowledge gaps related to appropriate materials to be added, the method of addition, and the management of the sites.

Fly ash and FGD by-product mixtures may have to be tailored to site conditions. For example, fly ash can improve soil tilth by promoting aggregation of soil particles. However, for degraded lands lacking small-size soil particles, while silt-size fly ash particles can increase the moisture-retention capacity of the soil, addition of large amounts of alkaline fly ash may increase the soil pH, soluble salts, or B too much for some desirable crops. For example, in later stages of a C-enhancement strategy, woody plants may be desirable to store biomass in both aboveground and belowground C pools. However, many of the pine trees typically grown in the Southeast require acid soils and thus will not thrive if fly ash additions raise the pH above 6.0. Furthermore, while adsorption of organic matter to soil is somewhat greater under slightly acid conditions, alkaline pH promotes leaching of SOM, thus potentially reducing both C sequestration and soil fertility (Senesi and Loffredo, 1999).

The source, quality, and amount of organic matter amendments will also need to be selected with specific sites in mind. Biosolids, organic waste from treatment facilities, and similar waste material (swine manure,

Table 1

Ecosystem	Mean residence time (years)		Reference
	Macroaggregate	Microaggregate	
Restored prairie	140	412	Jastrow (1996)
Corn	14	61	Monreal et al. (1997)
Corn	42	691	Angers and Giroux (1996)

chicken litter) provide an excellent source of organic nutrients that can be easily used to promote plant growth and development of microbial communities (Bendfeldt et al., 2001; Wong and Su, 1997a,b; Bulluck and Ristaino, 2002). However, these readily bioavailable organic amendments may be less likely to be retained in the soil over long periods of time and thus may contribute little to long-term C sequestration. More recalcitrant, lignin-rich amendments, such as woody biomass and possibly paper and pulp mill sludge, are less labile in the soil and have a higher affinity for binding to soil particles. Microbial oxidation of the lignin to polyphenols is understood to be one of several pathways in the humification process (Senesi and Lofredo, 1999), leading to formation of recalcitrant organic C that will contribute to long-term C sequestration. It is important to consider not only the quantity but also the chemical composition of the SOM when evaluating the success of amendments in promoting long-term C sequestration. Organic C in soil can also be physically protected from degradation by forming aggregates in which primary particles and clay microstructure are bound to larger macroaggregates and in turn form microaggregates within the macroaggregates (Oades, 1984; Six et al., 2000; Jastrow, 1996). This process may be enhanced by growth of roots and fungal hyphae (Tisdall and Oades, 1982). The accrual of soil C has been linked to the mineral components of microaggregate formation through macroaggregate turnover, suggesting that organic matter associated with the aggregates becomes physically protected from decomposition (Gale et al., 2000; Jastrow, 1996; Six et al., 2000). For example, Six et al. (2000) concluded that the rate of macroaggregate turnover was reduced in no-till compared with conventional tillage cropping systems. The slower macroaggregate turnover promoted the formation of stable microaggregates in which C is stabilized and sequestered in the long-term. A number of studies have found that microaggregate formation is crucial for the long-term sequestration of C (Six et al., 1999, 2000) because microaggregates have a greater capacity to protect C against decomposition compared with macroaggregates (Balesdent et al., 2000; Besnard et al., 1996; Skjemstad et al., 1990). The higher protection of C exerted by microaggregates is demonstrated by the manyfold slower C turnover times associated

with microaggregates versus macroaggregates. For example, several investigators have estimated the mean residence time of macroaggregates and microaggregates using radiocarbon dating or changes in the $\delta^{13}\text{C}$ signatures following a transition between of C4 and C3 vegetation (Six and Jastrow, 2002).

Thus, optimizing C sequestration requires consideration of the physical structure of the soil C to evaluate the potential of a treatment to accumulate C in the soil.

In the initial stages of land reclamation, deep incorporation of amendments in soils with little organic matter may be an effective method to promote soil development. Amendments are traditionally either applied to the surface or incorporated only to shallow depths. Incorporation of amendments to greater depth (e.g. to 60 cm) could have a number of advantages to soil restoration and, more specifically, to C sequestration. Surface or near-surface applications result in very slow migration of colloidal organic or inorganic amendments to greater depths, and thus any advantage of the amendments in promoting increases in tilth and moisture-retention or in development of healthy microbial communities is greatly retarded. Similarly, roots will be able to access the improved soil only within a small, shallow soil volume. Deeper incorporation will provide access to a much larger soil volume for rooting and will provide a deep moisture reservoir, permitting plants to better tolerate dry soil conditions. Finally, deep incorporation will provide a direct insertion of organic amendments into a much larger volume of soil. C accumulation will be much more rapid because it will not depend on slow migration from the soil surface layer. Microbial degradation of the organic matter is generally thought to decrease with depth (e.g. Vinther et al., 2001), further enhancing the potential for long-term C sequestration. However, incorporation of such amendments as biosolids or fly ash will require considerable machinery plus fuel inputs, especially with many mine-spoil materials that are quite rocky and dense. The added economic incentive likely to develop for C sequestration may make more aggressive management of sites an economically feasible alternative.

Although each of these proposed amendments might increase the C sequestration potential of the degraded land, each also may have other, possibly deleterious effects. For example, while coal ash and FGD by-