EFFECTS OF FLY ASH ON MICROBIAL CO_2 EVOLUTION FROM AN AGRICULTURAL SOIL

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Abstract. Unweathered, acidic fly ash from a coal-fired power plant was applied to alfalfa meal-amended agricultural soil at levels equivalent to 0, 100, 400, and 700 tonne ha^{-1}. Amended soils were placed in respirometer jars and monitored for CO_2–C evolution over a 37-day period. Fly ash applications of 400 and 700 tonne ha^{-1} reduced CO_2–C production significantly compared to 0 and 100 tonne ha^{-1} treatments. Carbon dioxide-carbon from all treatments was considerably greater than that from soil treated with 1000 ppm $CdCl_2$. The results suggest that soil heterotrophic microbial activity may be impacted minimally by relatively low levels of fly ash application, but may be inhibited by higher levels of fly ash. Several metals were present at potentially toxic levels in the fly ash employed and may have accounted for the inhibition of CO_2–C evolution. The availability of some of these metals was indicated in companion plant uptake experiments.

1. Introduction

Many industrial waste products are deposited on soils deliberately either as a beneficial amendment or for waste disposal, or inadvertently through spills, atmospheric deposition, inadequate waste management, etc. One such waste product with potentially beneficial applications is fly ash, a solid, essentially inorganic by-product of coal combustion removed by electrostatic precipitation from stack emissions at coal-fired generating stations. Fly ash varies in chemical composition depending on the parent coal and the operating conditions of the furnace. In general, approximately 95 to 99% of fly ash consists of oxides of Si, Al, Fe, and Ca, and about 0.5 to 3.5% consists of Na, P, K, and S (Tolle *et al.*, 1982a; Adriano *et al.*, 1980). Trace elements, including nearly all the elements occurring naturally in soils, make up the remainder of fly ash. Also, low levels of radionuclides present in coal may be enriched in some fly ashes.

Utilities collect considerable quantities of fly ash; total ash production in the United States may reach 180×10^6 tonne by the year 2000 (Halow, 1982). The ash must be disposed of in landfills, settling ponds, or by utilization in industrial processes. Land application of fly ash as an agricultural amendment or in strip mine reclamation may be an alternative means of disposal. Numerous studies have demonstrated that coal ash can benefit soil and spoils as a conditioner, diluent, neutralizing agent, or micro-nutrient supplier (Keefer *et al.*, 1980; Capp, 1978; Fail and Wochok, 1977; Martens, 1971). However, a number of environmental impacts have been identified that can result from the use of fly ash as a soil amendment and most of these impacts are associated with

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trace elements such as B, Se, Mo, As, Cd, and Ni (Page *et al.*, 1979). Adriano *et al.* (1980) reviewed the various aspects of land disposal of fly ash and found little information concerning the effects of fly ash on soil microorganisms. If fly ash is to be considered as a soil amendment, perhaps especially in agricultural soils, potential impacts on soil microbiological processes need to be evaluated as part of an effort to maintain soil fertility and plant productivity.

The objective of this research was to examine the influence of fly ash amendments on the metabolic activity of heterotrophic soil microorganisms in an agricultural soil. Carbon dioxide evolution was chosen as the indicator of microbial activity. Monitoring CO_2 evolution from soil is a relatively simple procedure which has been used widely in one form or another in both effects-testing (e.g. pesticides) and in biodegradation experiments (Anderson, 1982; Singh and Gupta, 1977; Stotzky, 1965). During microbially mediated biodegradation of carbonaceous compounds (i.e., the biological oxidation of reduced C compounds such as soil organic matter), CO_2 is liberated and O_2 is consumed according to the generalized reaction: $(CH_2O)_x + O_2 \rightarrow CO_2 + H_2O +$ - intermediates + cellular biomass + metabolic energy. The implication of altered rates of CO_2 evolution from soil is that an ecosystem-level process has been affected, specifically C cycling. However, this effect on C cycling may have ramifications on the mineralization of other plant-essential elements, such as P, N, S, and K, contained in the soil.

2. Materials and Methods

A Crosby-Lewisburg silt loam soil complex (Crosby: fine, mixed, mesic Aeric Ochraqualf; Lewisburg: fine, mixed, mesic Typic Hapludalf) with the selected physicochemical parameters shown in Table I was used in these experiments. Soil was collected from the plow-layer (top 20 cm) of a fallow agricultural field, sieved to pass a 2 mm-mesh stainless steel sieve, and stored at its field moisture content in a polyethylene bag at 4 C. Air drying of the soil was avoided.

TABLE I

Selected physicochemical characteristics of Crosby-Lewisburg silt loam soil used in CO_2 evolution experiments

Parameter	Value
pH	6.5
Cation exchange capacity	10 meq 100 g^{-1}
Organic matter	2–3%
Field capacity	25.7%
Field moisture content	11.6

Fly ash for this research was obtained directly from the electrostatic precipitator of a coal-fired power plant in central Ohio. The ash had a pH (1 : 1 ash : distilled water) of 4.9 and an elemental composition compared to soil as shown in Table II. This

TABLE II

Concentrations of selected elements in the fly ash and the soil used in this experiment as determined by spark source mass spectroscopy*

Element	Concentration (ppm)	
	Fly ash	Soil
As	300.0	5.0
B	300.0	20.0
Cr	500.0	50.0
Co	100.0	5.0
Cu	700.0	30.0
Pb	140.0	2.0
Hg	3.0	<0.3
Mo	70.0	3.0
Ni	500.0	20.0
Sr	2500.0	300.0
Tl	40.0	0.1
Sn	20.0	2.0
U	60.0	1.0
Zn	1000.0	10.0

* All values are ±50%.

particular ash was used in concomitant field and laboratory experiments in which agricultural crops were grown in the presence of various levels of fly ash and examined for productivity and trace element uptake (Tolle *et al.*, 1982b, 1983; Van Voris *et al.*, 1982). The level of fly ash dosing of the soil (on a gram fly ash/gram soil basis) was the same in the field crop experiments as in the CO_2 evolution experiments, thus facilitating the interpretation of the CO_2 evolution results from an agroecosystem perspective.

Carbon dioxide evolution experiments were conducted in acid-washed 0.95 L glass jars. One-hundred g of soil (oven-dry weight basis), amended with 1.0 g finely ground alfalfa meal, were amended further with fly ash at levels equivalent to 0, 100, 400, or 700 tonne ha^{-1}, or with $CdCl_2$ at a concentration in the soil of 1000 ppm. Alfalfa meal is an environmentally relevant substrate with a narrow C : N ratio and was added in order to enhance microbial activity. The $CdCl_2$ treatment was included as a microbial inhibitor (positive control) for comparison with the potential inhibition of microbial activity due to fly ash. Unamended controls received no fly ash, alfalfa meal, or $CdCl_2$. Three replicates of each treatment were used. Prior to adding the amended or unamended soils to the respirometer jars, enough distilled water, or 5% (W/V) $CdCl_2$ solution in distilled water in the case of positive controls, was added to the empty jars to bring the soils to 70% field capacity. The mixed soils were then added and an equilibration period of approximately 1 hr was allowed for the moisture to distribute throughout the soil. Evolved CO_2–C was trapped in 10.0 mL of 0.6 N NaOH contained in small wide-mouth nalgene bottles on the surface of each soil. All respirometer jars were capped and incubated in the dark at 25 C. At prescribed intervals, alkali traps were

removed from the respirometer jars and were titrated to pH 9.0 with 0.6 N HCl, after addition of 5.0 mL of 1.3 N $BaCl_2 \cdot 2H_2O$. The 0.6 N HCl solution was standardized with aminomethane (hydroymethyl) tris. Triplicate method blanks, consisting of respirometer jars containing only alkali traps, were titrated simultaneously with treatments. Titrations were performed for four consecutive days during the first week of incubations and periodically through 37 days for a total of nine titrations. Cumulative CO_2–C (mg) evolution was calculated as follows:

$$CO_2\text{–}C = \sum_{i=1}^{9} [(B - V)NE]_i$$

where

V = mL acid for end-point titration of the alkali in the CO_2 traps from treated soils,
B = mL of acid for end-point titration of the alkali in the CO_2 traps from method blanks,
N = normality of acid, and
E = equivalent weight of CO_2–C, i.e., 6 mg meq^{-1}.

3. Results

Cumulative CO_2–C production decreased with increasing fly ash application. High doses (400 and 700 tonne ha^{-1}) of fly ash significantly ($p < 0.05$) inhibited cumulative CO_2–C evolution (Figure 1 and Table III), whereas the 100 tonne ha^{-1} application of fly ash showed little effect on cumulative CO_2–C loss. Total CO_2–C production was

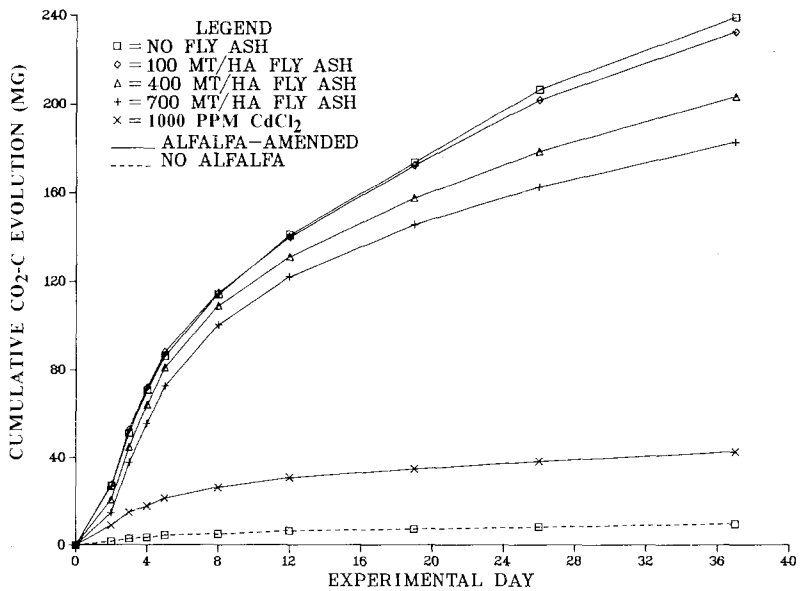

Fig. 1. Cumulative CO_2–C from alfalfa-amended soil in the presence or absence of fly ash. Table III indicates the statistical evaluation of these data.

TABLE III

Influence of fly ash application on CO_2–C production parameters

	Fly ash (tonne ha^{-1})[a]			
	0	100	400	700
CO_2–C produced up to day 2 (mg)	27.0 (a)	27.4 (a)	20.6 (b)	14.6 (c)
CO_2–C produced from day 2 to day 3 (mg)	24.2 (a)	25.3 (b)	24.1 (a)	23.0 (c)
Rate of decline (b) in equation where CO_2–C production = at^b	− 0.821 (a)	− 0.866 (a)	− 0.991 (b)	− 1.064 (c)
Total CO_2–C production (mg)	239.3 (a)	232.7 (a)	203.6 (b)	182.9 (c)

[a] Within rows, values with common letters did not differ significantly at the 95% confidence level.

described by the linear regression equation $Y = 239.450 - 0.0828X$, where Y is the total CO_2–C production (mg) and X is the level of fly ash application (tonne ha^{-1}).

Daily CO_2–C production can be divided into two distinct phases: an initial build-up period from day 0 until day 2, and a declining phase from day 2 until the end of the experiment. Up to day 2, CO_2–C production in the 100 tonne ha^{-1} fly ash treatment was not significantly different ($p < 0.05$) from the undosed control, while both the 400 and 700 tonne ha^{-1} treatments differed significantly ($p < 0.05$) from the control and from each other. At day 3, only the 100 and 700 tonne ha^{-1} treatments differed significantly ($p < 0.05$).

After day 3, daily CO_2–C production declined in all treatments and was described by the model: CO_2–C production = at^b, where t is time in days and a and b are constants. The rate of decline in daily production of CO_2–C, measured by b, was estimated for each replicate respirometer jar and increased (b became more negative) with increased fly ash application: $b = -0.830 - 0.000\,35X$, where X is the level of fly ash application (tonne ha^{-1}). All treatments differed significantly ($p < 0.05$) from each other and from the control in their rate of decline in CO_2–C production, with the exception that the 100 tonne ha^{-1} treatment did not differ from the control. These relationships are summarized in Table III.

4. Discussion

The results of this experiment indicate that unweathered, acidic fly ash applications of up to 100 tonne ha^{-1} in an agricultural soil had no measurable impact on soil heterotrophic microbial activity as determined by cumulative CO_2–C production. Application of fly ash at levels of 400 and 700 tonne ha^{-1} inhibited CO_2–C production from alfalfa meal-amended soils. Nevertheless, CO_2–C production was substantially greater in all fly ash treatments compared to $CdCl_2$-treated controls or to control soils which received no alfalfa meal. Thus, mineralization of organic C apparently proceeded, though at reduced rates, even in the highest dosed soils. The results suggest the need to assess the effects on microorganisms due to various fly ash and soil or spoil combinations,

especially at higher levels of application, since the maintenance of active populations of soil microorganisms is critical to nutrient mineralization and cycling and thus to long-term soil fertility.

The levels of fly ash employed in this research were not unlike those reported in the literature, especially with respect to land reclamation. For example, up to 1972-tonne ha^{-1} of fly ash were applied to coal spoils by Adams *et al.* (1971); Jones and Amos (1976) added 430 tonne ha^{-1} of fly ash to three different agricultural soils. The levels of fly ash chosen for the work reported here were based on concomitant field and soil microcosm (intact soil core) studies to determine potential toxicity effects and trace element uptake in agricultural forage crops amended with fly ash (Tolle *et al.*, 1982b). In these companion studies, fly ash applications were chosen in order to provide soil concentrations of plant-available boron of 4, 17, and 33 ppm (fly ash at 100, 400, and 700 tonne ha^{-1}, respectively). Yields of oat grain and alfalfa were reduced markedly in the presence of 400 or 700 tonne ha^{-1} of fly ash in both field plots and soil microcosms, as shown in Table IV (Tolle *et al.*, 1982b). Trace element uptake was also determined and at high fly ash doses was found to be great enough to induce plant toxicity in the case of B, and livestock toxicity in the cases of Mo, Se, and As. Thus, at least some of the metals added to soils in the form of fly ash are biologically available.

TABLE IV

Comparison of plant yields in soil core microcosms and field plots when treated with fly ash, based on predicted values obtained by linear regression[a]

Fly ash treatment (tonne ha^{-1})	Predicted microcosm yields (percent of control)	Predicted field plot yields (percent of control)
Oat grain		
100	88.1	155.0
400	19.0	4.4
700	0.43	0.57
Alfalfa		
100	57.0	64.0
400	7.4	11.0
700	0.44	0.57

[a] Within each of the four treatment groups, all values differ significantly ($p < 0.05$) from each other and from controls, with the following two exceptions:
(1) The yields of oat grain at 100 tonne ha^{-1} fly ash microcosms and field plots were not significantly different ($p > 0.05$) from the respective controls, and
(2) The yields of oat grain in the 400 and 700 tonne ha^{-1} fly ash in field plots were not significantly different ($p > 0.05$).

Interestingly, reduced CO_2–C production from fly-ash amended soils in respirometer jars (Figure 1) generally agreed with the reductions in crop yields at similar levels of fly ash amendment. This agreement suggests that respiration measurements are relevant to ecosystem-level processes, such as predicting the response of higher plants to the presence of a potentially toxic soil amendment. Thus, a short-term CO_2 evolution

experiment may be a substitute and/or a range-finding test for longer-term phytotoxicity studies, e.g. predicting the effects on plant growth of land farming waste products.

Figure 1 also illustrates the well-known stimulatory effect on CO_2–C production from soils due to the addition of organic matter. We have found in these and other experiments that the addition of an environmentally relevant organic substrate with a relatively narrow C : N ratio, as opposed to a compound like glucose or cellulose, improves the suitability of soil respiration as an effects test without resulting in nutrient immobilization. In preliminary experiments with fly ash (Arthur and Zwick, 1982), the normal rate of CO_2–C evolution from the Crosby-Lewisburg silt loam soil was so low as to essentially preclude distinguishing between treatment levels and controls. For example, Figure 1 shows the low level of CO_2–C evolution from soil when no alfalfa meal was added. In contrast, treatment effects were clearly distinguishable when the metabolic potential of soil microorganisms was more fully realized by the addition of alfalfa meal.

The experimental design used in this work was simple and short-term. No identification of effects on other microbial processes was attempted, nor were there attempts to identify the mechanisms or agents specifically responsible for reduced CO_2–C production. Many of the elements present in fly ash are potentially toxic to microorganisms. For the most part, the concentrations of several microbially important metals were at least an order of magnitude greater in fly ash than in the Crosby-Lewisburg silt loam soil used (Table II). The biological availability and effects of these metals depend on such factors as concentration, pH, and oxidation state (Summers and Silver, 1978; Bowen, 1966) and considerable work has been done with many of these elements individually or in limited combinations. For example, Ross *et al.* (1981) found reduced CO_2 evolution from soils treated with 10 or 100 ppm Cr(VI) or 100 ppm Cr(III). The fly ash used in our experiments contained 500 ppm Cr (Table II), although the oxidation state was not determined explicitly. Jordan and Lechevalier (1975) reported reduced numbers of bacteria and actinomycetes on soil dilution plates when 6.5 to 13 ppm Zn were added to the medium. In soils, the biologically effective concentrations are probably quite different than *in vitro*, but considering that the fly ash used in our experiments contained 100 ppm Zn (Table II) there is a potential for Zn toxicity in the fly ash-amended soil, especially at the higher rates of application used. In addition to the presence of individual elements at concentrations which may be toxic, the combination of several metals at relatively high concentrations may elicit unique effects. Experiments are being developed in our laboratory to study these interactions, as well as fly ash effects on other microbial processes such as N transformations in soils.

The results of this study suggest that soil heterotrophic microbial populations, as measured by the production of CO_2–C from soils, should be minimally affected by low (100 tonne ha^{-1}) levels of unweathered, acidic fly ash amendment. However, at high levels of amendment (400 or 700 tonne ha^{-1}), soil microorganisms may be adversely affected. Long-term experiments using weathered ash unweathered fly and with different soils and spoils, and studies of other microbial processes may be useful to assess further the suitability of land-disposal of large quantities of fly ash.

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