Arsenic, Boron, Molybdenum, and Selenium in Successive Cuttings of Forage Crops Field Grown on Fly Ash Amended Soil

Alfalfa, birdsfoot trefoil, brome, orchard grass, and timothy were grown on soil amended with 112.5 metric tons per hectare of coal fly ash and untreated soil. Five successive cuttings of each crop were analyzed for arsenic, boron, molybdenum, and selenium. Of the fly ash treated crops boron showed a consistent increase mainly in the legumes, while selenium increased mainly in the grasses. Molybdenum showed a consistent increase in all of the cuttings of all crops grown on fly ash. Arsenic increased mostly in the first cutting of the crops. Crop yields on the two treatments appeared comparable.

As coal is pulverized and burned in electric power generating plants, the resulting fly ash is trapped by electrostatic precipitators. About 48.5 million tons of fly ash was produced in the United States in 1977 (Ash At Work, 1978). Disposal of the material is mostly in landfills with only about 13% of it utilized, largely in concrete (Buttermore et al., 1972) and as a base material in roadbeds (Ash At Work, 1969). It had been used to neutralize acidic coal mine spoils, refuse banks and wasteland areas in reclaiming them to permit establishment of cover crops to prevent erosion (Adams et al., 1972), or forage and pasture crops (Barber, 1974). Research dealing with the reclamation of soils using fly ash has been reviewed by Plank and Martens (1973).

Many elements, both essential and toxic, are typically found in fly ashes (Davison et al., 1974; von Lehmden et al., 1974; Furr et al., 1977). Possible use of fly ash as a soil amendment in agriculture has therefore been studied. The availability of a number of elements such as B, Mo, P, K, and Zn to plants grown on fly ash amended soils has been followed (Doran and Martens, 1972; Martens, 1971; Martens et al., 1970; Schnappinger et al., 1975). Furr et al. (1976) cultured a variety of vegetables and millet in potted soils containing fly ash. Among 42 elements determined, As, B, Ca, Cu, Fe, Hg, I, K, Mg, Mo, Ni, and Sb, were higher in several of the crops grown on fly ash amended soils as compared to control crops. Selenium was consistently higher in all crops grown on fly ash and its concentration in the plants was approximately proportional to the rate of fly ash addition.

Elements such as boron and selenium are deficient in many soils as regards plant and animal requirements, respectively. In the work reported, common forage grass and legume crops were field grown on fly ash amended soil, and the concentrations of arsenic, boron, molybdenum, and selenium were determined in five successive cuttings of the crops over a 2-year period of growth. The objective of the study was to determine how long one application of fly ash would continue to supply a higher concentration of these elements to forage as compared to control crops growing on the unamended soil.

EXPERIMENTAL SECTION

Two plots, each with dimensions of 3 × 6 m, were chosen for the study in Ithaca, NY. The soil was an Arkport fine sandy loam (coarse-loamy, mixed, mesic psammentic hapludalfs) comprised of 75% sand, 20% silt, 3% clay, and 2% organic matter. The pH of the soil was 6.0 and its cation-exchange capacity was 13.5 mequiv/100 g. Fly ash was obtained as freshly produced material by Milliken Station, a coal-burning electric power-generating plant located in Lansing, NY, about 32 km north of Ithaca on the eastern shore of Cayuga Lake. This power plant burns about 2300 metric tons of coal per day, yielding approximately 460 metric tons of fly ash daily. The pH of the fly ash was 5.0. Five percent (w/w) of the fly ash was spread and thoroughly mixed into the soil of one of the plots by rotary cultivation. This was equivalent to 112.5 metric tons dry weight of fly ash applied per hectare using the standard agronomic estimate of 2 million pounds dry weight of soil in an acre furrow slice. The pH of the resulting fly ash amended soil was 5.9. The other plot, untreated with fly ash, served as the control. Each plot was fertilized by mixing 2.7 kg of 15–6.5–12.5% N–P–K into the soil at the time of plot cultivation.

Table I. Total Element Content of Soil and Fly Ash

sample	As	B	Mo	Se
	parts per million (dry weight)			
soil	8.8	10	2.2	1.5
fly ash	23	14	2.9	5.1

The crops planted were "Honeyoye" alfalfa (*Medicago sativa*), "Empire" birdsfoot trefoil (*Lotus corniculatus*), brome (*Bromus* cv. Saratoga), "Penn Mead" orchard grass (*Dactylis glomerata*), and "Climax" timothy (*Phleum praetense*). In the spring of 1977, each crop was planted in an area with dimensions of 1 × 3 m in each of the plots using a mechanical seeder. The rates of seeding in kilograms/hectare were alfalfa, 14; birdsfoot trefoil, 9; brome, 9; orchard grass, 7; and timothy, 7. Five successive cuttings of each crop were taken, two in the summer and fall of 1977 and three (spring, summer and fall) during 1978. Each crop was fertilized with 35 g of soluble 20–8.7–16.6% N–P–K between cuttings. Total rainfall for the periods of May through October during which the forage was harvested in 1977 and 1978 was respectively 73.2 and 40.9 cm. Owing to the low rainfall during 1978, the crops were irrigated as necessary. At the time of cutting, the entire crop on each plot was harvested, dried, milled, mixed, and subsampled for analysis. Arsenic was determined by dry ashing (Evans and Bandemer, 1954) the samples, distilling arsine, and analysis using the silver diethyldithiocarbamate spectrophotometric procedure (Fisher Scientific Co., 1960). Boron was determined by the curcumin spectrophotometric procedure (Greweling, 1966). Molybdenum was determined by the thiocyanate method of Greweling (1966). Selenium was determined by a modification of the method of Olson (1969) employing wet digestion of the sample and measurement of the fluorescence of piazselenol resulting from reaction of selenium with 2,3-diaminonaphthalene. Soil reaction (pH) was determined by the method of Peech et al. (1953).

RESULTS AND DISCUSSION

The growth of the plants on the control and fly ash treated plots was comparable with no visible evidence of nutrient deficiency or phytotoxicity. Table I lists the concentrations of arsenic, boron, molybdenum, and selenium in soil and fly ash. On a total basis each element was higher in content in the fly ash than the soil.

In Table II are given the total concentrations of these elements in successive cuttings of the forage crops grown

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Table II. Total Element Concentrations in Five Successive Cuttings of Forage Crops Field Grown on Soil Amended with 112.5 Metric Tons per Hectare of Coal Fly Ash and on Soil Alone (Control)

		parts per million (dry weight)							
		arsenic		boron		molybdenum		selenium	
crop	cutting	control	fly ash	control	fly ash	control	fly ash	control	fly ash
alfalfa	1	0.2	0.4	34	40	0.4	1.8	0.07	0.13
	2	0.1	0.2	34	28	0.8	2.3	0.10	0.10
	3	0.2	0.1	25	26	0.5	2.6	0.06	0.07
	4	0.02	0.1	30	39	0.3	1.2	0.05	0.05
	5	0.02	0.02	35	42	1.0	1.4	0.05	0.05
birdsfoot trefoil	1	0.2	0.8	35	37	1.0	6.2	0.09	0.22
	2	0.02	0.2	30	30	2.0	7.0	0.11	0.12
	3	0.02	0.1	20	23	1.3	4.9	0.08	0.08
	4	0.02	0.02	35	43	1.0	2.7	0.07	0.07
	5	0.02	0.02	33	40	0.8	3.0	0.09	0.11
brome	1	0.2	0.4	14	18	0.7	3.0	0.12	0.28
	2	0.02	0.02	4.5	4.2	1.3	3.1	0.23	0.43
	3	0.1	0.02	7.5	8.8	0.2	1.2	0.08	0.26
	4	0.02	0.02	14	15	0.8	1.6	0.18	0.51
	5	0.2	0.1	13	13	1.6	3.5	0.15	0.62
orchard grass	1	0.2	1.0	9.0	25	1.1	6.8	0.11	0.50
	2	0.02	0.1	4.7	4.5	2.3	6.4	0.21	0.55
	3	0.02	0.1	6.9	5.2	1.4	4.8	0.18	0.35
	4	0.02	0.1	12	11	0.9	1.9	0.30	0.56
	5	0.2	0.2	8.7	10	1.7	4.1	0.30	0.64
timothy	1	0.2	0.4	14	24	0.9	2.0	0.08	0.27
	2	0.1	0.2	5.0	6.0	1.6	4.1	0.22	0.46
	3	0.1	0.02	9.4	7.6	1.1	2.4	0.25	0.37
	4	0.02	0.02	17	17	1.3	2.0	0.28	0.41
	5	0.02	0.2	15	15	1.4	2.3	0.25	0.53

Table III. Statistical Level of Significance (p Value) of Results

crop	As	B	Mo	Se
legumes (all cuttings)	0.02	0.05	0.01	0.01
grasses (all cuttings)	0.05	n.s.[a]	0.01	0.01

[a] Not significant.

on the fly ash amended soil or soil alone. Wilcoxson's signed rank test (Steel and Torrie, 1960) for detecting real differences between paired treatments showed the concentrations of each of the elements to be significantly higher when the grasses or legumes were grown on the fly ash amended soil. The only exception was boron which was not significantly higher in the grasses with all cuttings taken into account. Table III lists the levels of statistical significance (p values).

In general, arsenic concentration in the respective crops fluctuated little with treatment except for the increase shown in the first cutting of the fly ash grown crops. The increase in boron concentration above that in the corresponding control crops was most dramatic in the first cutting only of the grasses on the fly ash treatment. Molybdenum increased consistently in all cuttings of all crops grown on fly ash. Selenium consistently showed a higher concentration in all cuttings of the fly ash grown grasses than in the control crops, while with legumes the increase was mainly confined to the first cutting. One might assume that the reason for this is that the shallow roots of grasses would remain largely in the top soil containing the fly ash, while the roots of deep rooted legumes would mainly occupy the top soil layer only during their early stages of growth. Perhaps, however, owing to leaching downward, boron showed an increase in concentration in the fly ash grown legumes during the third, fourth, and fifth cuttings. The control grasses were much more efficient selenium accumulators than the control legumes, while just the reverse was true for boron.

From the standpoint of animal nutrition, molybdenum and particularly selenium are present in many crops in the northeastern United States in concentrations deficient for farm animal requirements. Fly ash therefore may be a useful soil amendment for boosting molybdenum in forage crops and selenium, particularly in grasses. As regards plant nutrition, boron is deficient in many northeastern soils and fly ash might therefore be a useful fertilizer, especially for grasses.

This study indicates that one application of fly ash will continue to release elements such as boron, molybdenum, and selenium through five successive cuttings of specific forage crops. One would, of course, have to monitor the elemental composition of the fly ashes and crops subsequently grown. For instance, when molybdenum is sufficiently high in the diet it can induce a copper deficiency in cattle (Underwood, 1971). Selenium may also be toxic to animals at concentrations above about 5 ppm (Allaway, 1975). Fly ashes vary greatly not only in elemental composition, but also pH (Furr et al., 1977), and their effect on availability of other nutrient elements in the soil would therefore also have to be considered. Soil properties would also have to be considered. Leaching of elements would expectedly be more prevalent in the sandy soil used in this study. Fixation and a lower plant availability of elements in fly ash might be predicted for a soil higher in clay or organic matter. Soils of higher pH would tend to increase the availability of molybdenum and selenium for crop absorption. It is noteworthy that, in an earlier study (Furr et al., 1978), only rarely were other toxic elements such as cadmium, mercury, or antimony found slightly elevated in these grass and legume forage crops when grown on fly ash amended soil.

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In Vitro Metabolism of Carbaryl by Liver Explants of Bluegill, Catfish, Perch, Goldfish, and Kissing Gourami

The purpose of this study was to demonstrate the metabolic role of livers of five species of fish toward insecticide carbaryl (Sevin), 1-naphthyl *N*-methylcarbamate. Carbaryl (naphthyl-^{14}C or *N*-methyl-^{14}C) was applied to a growth medium containing liver explants of the five species. Each mixture was incubated for 18 h after which the medium was analyzed by diethylaminoethyl (DEAE)–cellulose column chromatography. Based on the metabolic profile analysis, hepatic tissues from each species all performed the metabolic processes of demethylation and/or hydrolysis, hydroxylation, and oxidation, followed by conjugation. The most significant common metabolite in all species chromatographed as a dihydrodihydroxycarbaryl glucuronide.

Sullivan et al. (1972a) reported a potential in vitro method for the selection of species metabolically similar to man for use in chronic toxicity studies. The technique is simple, rapid, reproducible, and organ specific (Chin et al., 1974, 1979) and therefore is very practical in estimating major metabolic differences among test species without resorting to the actual dosing of animals with test chemicals. The purpose of this study is to elucidate the metabolic role of livers of several species of fish using the in vitro method because increased importance of metabolic fate studies have been emphasized in fish in recent years.

As a prototype the carbamate insecticide carbaryl (Sevin) 1-naphthyl *N*-methylcarbamate was used because extensive metabolic information is available in man and in many other species as reviewed by Knaak (1971). The designation of major metabolites of carbaryl is based on chromatographic behavior and fluorescence characteristics rather than actual isolation and structural verification of the metabolites.

MATERIALS

1-Naphthyl-^{14}*C* *N*-methylcarbamate (carbaryl) of specific activity 30 μCi/mg and 1-naphthyl *N*-methyl-^{14}*C*-carbamate of specific activity 11.3 μCi/mg were provided by the Union Carbide Corporation Technical Center, South Charleston, WV. The carbogen used was the commercially available oxygen/carbon dioxide mixture (95:5). Trowell (1959) T8 medium and penicillin–streptomycin mixture (Catalog No. 12603F) were purchased from Microbiological Associates, Bethesda, MD. Kissing gourami (*Helostoma temmincki*), weighing 6–8 g, and goldfish (*Carassius auratus*), weighing 28–33 g, were purchased from a local pet shop. Because these fish had very small amounts of liver, respective liver specimens from these fish

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