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## Multielement Uptake by Vegetables and Millet Grown in Pots on Fly Ash Amended Soil

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Forty-two elements were determined in beans, cabbage, carrots, millet, onions, potatoes, and tomatoes grown on potted soil amended with 10% by weight of fly ash. Thirty-two elements were present at higher total concentrations in the fly ash than in the soil. As, B, Ca, Cu, Fe, Hg, I, K, Mg, Mo, Ni, Sb, and Se were higher in concentration in the edible portions of at least three of the crops grown on fly ash amended soil as compared to the control crops. The extent of plant absorption of selenium was roughly proportional to the rate of application of fly ash. The effect of the fly ash amendment on crop yields was variable.

It has been estimated that about 29 million tons of fly ash will be produced by coal-burning, electric power-generating plants in the United States during 1975 (Brackett, 1970). Fly ash has been used as an additive to concrete and ceramics (Buttermore et al., 1972), as a filtering aid in the processing of municipal sewage (Lukz, 1972), and as a base material in roadbeds ("Ash at Work", 1969). Since these applications consume only a small fraction of the total production its possible use in agriculture has been investigated. In the past the bottom ash from coal burned in homes was commonly put on gardens and, to a small extent, the public uses fly ash, privately hauled from power plants, for that purpose today. Fly ash has been added as an alkaline amendment to coal mine spoils and refuse banks to permit their reclamation for

plant growth to stop erosion (Adams et al., 1972). It has been used in several areas in England to reclaim land for the growth of forage and pasture crops (Barber, 1974). The use of fly ash to improve soils has been reviewed (Plank and Martens, 1973).

Analysis of fly ashes (Davison et al., 1974; von Lehmden et al., 1974) indicates that a great number of essential and toxic elements may be present. Limited data have been obtained on the absorption of elements by forage grown on fly ash amended mine spoils (Adams et al., 1972). It has been added to soil to correct plant deficiencies of boron, molybdenum, phosphorus, potassium, and zinc (Doran and Martens, 1972; Martens, 1971; Martens et al., 1970; Schnappinger et al., 1975). In a recent paper (Furr et al., 1975), 35 elements were determined in fly ash, sweet clover grown on it, and tissues of guinea pigs fed the clover as 45% of their diet for 90 days. Several elements including selenium and rubidium were found to be greatly elevated in the fly ash grown clover and the tissues of guinea pigs consuming the clover as compared to the controls. The objective of the work reported here was to study the extent of absorption of a range of elements by plants representing major classes of edible garden crops

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grown on a fly ash amended soil.

#### EXPERIMENTAL SECTION

About 200 lb of fly ash was obtained as freshly produced material by Milliken Station, a coal-burning electric power-generating plant located in Lansing, N.Y. about 20 miles north of Ithaca on the eastern shore of Cayuga Lake. This power plant produces about 500 tons of fly ash per day. The pH of the material was 4.5. The fly ash was mixed by quartering. The soil was an Arkport fine sandy loam, pH 5.5, and with a cation exchange capacity of 13.5 mequiv/100 g sampled near Ithaca, N.Y. The soil was air-dried, sifted through a 2-mm screen, and mixed by quartering. Ten per cent (w/w) fly ash was thoroughly mixed with the soil (or 100 dry tons of fly ash per acre) in a cement mixer. The pH of the resulting fly ash-soil mixture was 5.2. Soil alone was used as the control.

The crops used were: "Tendercrop" bush bean (*Phaseolus vulgaris*), "Golden Acre" cabbage (*Brassica oleracea* var. *capitata*), "Scarlet Nantes" carrot (*Daucus carota* var. *sativa*), Japanese millet *Echinochloa crusgalli* var. *frumentacea*), "Downing Yellow Sweet Spanish" onion (*Allium cepa*), Katahdin potato (*Solanum tuberosum*), and "Vendor" tomato (*Lycopersicon esculentum*). All of the crops were grown in 9-in. plastic pots containing 6 kg of the soil mixtures except for potatoes which were grown in 12-in. pots containing 12 kg. The number of plants grown in each pot were: bean, 2; cabbage, 1; carrot, 3; millet, 5; onion, 3; potato, 1; and tomato, 1. All treatments were replicated twice.

Five grams of 15-15-15 fertilizer was thoroughly mixed into the top 3 in. of soil in the 9-in. pots. Twice these weights of fertilizers were mixed with the soil in the 12-in. pots. All plants were fertilized once each week during the 11th, 12th, and 13th weeks of growth with a solution containing reagent grade  $\text{KH}_2\text{PO}_4$  (0.001 M),  $\text{KNO}_3$  (0.005 M), and  $\text{Ca}(\text{NO}_3)_2$  (0.005 M); 250 ml was added to the 9-in. pots and 500 ml was added to the 12-in. pots. All plants were watered daily, care being taken to avoid splashing soil on the aerial portions of the plants.

At maturity the crops were harvested and only the edible plant portions were collected for analysis. In the case of millet this included the entire aerial portion of the plant (stems plus grain). Prior to analysis all crop portions were thoroughly rinsed with distilled water to remove adhering dust. Carrots, onions, and potatoes were thoroughly brushed, rinsed, and then peeled. The respective replicated edible plant portions were combined and subdivided by homogenizing in a blender or chopping in a food cutter with stainless steel surfaces. The food material was freeze-dried in polystyrene containers, mixed, and subsampled for analysis.

Subsamples of soil, fly ash, and crop material were analyzed for 33 elements using nondestructive neutron activation analysis as previously described (Furr et al., 1975).

Cadmium, lead, zinc, copper, nickel, chromium, selenium, boron, and arsenic were determined by other methods. The determination of cadmium, lead, and zinc was performed by dry ashing the sample up to 475 °C followed by analysis by conventional stripping voltammetry using a Princeton Applied Research Corp. Model 174 Polarographic analyzer (Gajan and Larry, 1972). Following dry ashing, copper, nickel, and chromium were determined by furnace atomic absorption using a Perkin-Elmer Model 303 spectrophotometer equipped with an HGA-2000 furnace.

The determination of selenium was performed by a modification of the method of Olsen (1969) employing wet digestion of the sample and measurement of the

Table I. Elemental Analysis of Soil and Fly Ash

Element	Element concn, ppm, dry wt in	
	Soil	Fly ash
Al	39 400	110 100
As	2.9	139
Au	0.004	0.08
B	13.0	10.2
Ba	331	1 020
Br	3.5	7.4
Ca	3 410	7 250
Cd	0.1	0.5
Ce	76.6	223
Cl	82	67
Co	9.3	48.5
Cr	43.3	167
Cs	2.6	9.2
Cu	47	327
Fe	24 900	86 600
Hf	8.5	6.2
Hg	0.1	0.3
I	1.2	1.2
K	14 100	15 000
La	24.6	72
Lu	0.4	1.2
Mg	7 470	11 700
Mn	278	119
Mo		11.5
Na	6 210	1 180
Ni	17.2	6.6
Pb	13.1	14.5
Rb	115	162
Sb	0.8	5.3
Sc	8.7	37.7
Se	0.3	16.8
Sm	5.0	16.3
Sn	12	27
Sr		59
Ta	0.6	1.6
Th	15.0	56
Ti	3 292	8 310
U	1.4	7.2
V	67	253
W	2.1	9.8
Yb	2.0	5.9
Zn	180	15.7

fluorescence of piazselenol resulting from reaction of selenium with 2,3-diaminonaphthalene. Boron was determined by the curcumin spectrophotometric procedure (Greweling, 1966). 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). Soil reaction (pH) was determined by the method of Peech et al. (1953).

#### RESULTS AND DISCUSSION

Table I lists the total elemental concentrations found in the soil and fly ash. Thirty-two elements were present at higher concentrations in the fly ash than in the soil. In Table II are presented the concentrations of those elements in the crops which were found at higher concentrations in three or more of the crops grown on fly ash amended soil as compared to the corresponding controls. Most of the elements in Table II were also higher in total concentration in the fly ash as compared to the soil (see Table I). The enhanced uptake of the elements such as boron, potassium, and molybdenum by crops grown on the fly ash amended soil supports the reported use of fly ash to correct deficiencies of these elements in plants (Doran and Martens, 1972; Martens, 1971; Martens et al., 1970). As noted earlier (Martens, 1971; Schnappinger et al., 1975) fly ash has been used to correct zinc deficiency in plants. The fly ash used in this study was particularly low in total zinc (Table I) and this element did not increase consistently in the crops

Table II. Element Concentrations (Parts per Million, Dry Weight) in Edible Portions of Crops Grown in Pots on Soil (Control or Fly Ash) Amended with 10% (by Weight) Fly Ash

Element	Beans		Cabbage		Carrots		Millet		Onions		Potatoes		Tomatoes	
	Control	Fly ash	Control	Fly ash	Control	Fly ash	Control	Fly ash	Control	Fly ash	Control	Fly ash	Control	Fly ash
As	0.01	0.2	0.1	0.2	0.01	0.2	0.2	1.0	0.1	0.03	0.1	0.1	0.1	0.1
B	16	24	23	24	19	17	22	22	---	22	6	10	4	15
Ca	2 670	2 900	4 500	4 950	1 650	3 700	2 090	2 090	4 210	7 150	237	200	780	980
Cu	3.2	1.3	3.0	1.1	2.0	2.4	2.8	2.8	3.4	2.0	3.1	5.5	2.2	3.3
Fe	108	92	78	267	143	49	85	85	100	120	49	63	173	114
Hg	0.2	0.1	0.1	0.3	0.1	0.7	0.2	0.2	0.3	0.3	0.1	0.2	0.1	0.3
I	0.7	0.5	0.3	0.7	0.9	---	0.1	0.1	0.7	2.6	0.0	0.3	0.4	0.6
K	16 300	19 500	31 200	27 200	25 300	20 500	12 200	14 900	14 900	16 300	21 500	23 800	22 200	25 100
Mg	1 340	1 590	2 160	1 320	730	3 100	2 550	1 480	1 480	1 160	740	1 200	880	1 080
Mo	0.9	3.2	1.0	2.2	0.2	0.3	1.2	0.4	0.7	0.4	0.2	0.6	0.5	0.8
Ni	3.9	4.3	1.9	1.3	2.7	1.4	0.7	2.9	2.2	2.9	0.6	0.7	0.5	0.8
Sb	0.4	0.4	1.4	2.0	0.9	1.1	0.6	2.2	0.8	2.2	0.4	0.7	2.5	1.1

Table III. Selenium (Parts per Million, Dry Weight) in Edible Portions of Crops Grown Twice in the Same Pots of Soil (Control or Fly Ash) Amended Once with 5 or 10% (by Weight) Fly Ash

Crop	First year crop			Second year crop		
	Control	5% fly ash	10% fly ash	Control	5% fly ash	10% fly ash
Beans	0.02	0.20	0.47	0.01	0.21	0.64
Cabbage	0.01	0.24	0.95	0.02	0.18	0.43
Carrots	0.00	0.12	0.19	0.01	0.33	0.81
Millet	0.02	0.43	0.90	0.03	0.23	0.40
Onions	0.00	0.19	0.30	0.02	0.18	0.37
Potatoes	0.01	0.16	0.49	0.02	0.21	0.30
Tomatoes	0.01	0.20	0.33	0.02	0.12	0.15

grown on the fly ash amended soil.

Cadmium did not increase in the crops as a result of the fly ash amendment. Owing to the current emphasis being placed on this toxic element, however, its concentration as found in the plants is worth reporting. Cadmium concentrations (parts per million, dry weight) in the crops from the control and fly ash treatments, respectively, were as follows: beans, 0.1 and 0.1; cabbage, 0.2 and 0.2; carrots, 1.1 and 0.6; millet, 0.2 and 0.2; onions, 0.6 and 0.4; potatoes, 0.4 and 0.2; and tomatoes, 0.1 and 0.1.

Table III lists the concentrations of selenium in the crops when grown twice in the same pots containing soil alone (control), and pots containing either 5 or 10% by weight of the fly ash. After harvesting the first crops the material in the pots was kept moist in the greenhouse (unheated) during the following fall and winter to simulate field practice. At the time of the second planting, the contents of each pot was emptied, lumps were broken up, and the material (including partially decomposed roots) again placed in the respective pot, fertilized as before, and seeded. The extent of plant absorption of selenium was roughly proportional to the rate of application of fly ash.

Selenium is of special interest owing to its essentiality and toxicity. Birdsfoot trefoil (*Lotus corniculatus*), Sudan grass (*Sorghum sudanese*) seed, and the roots of mangles (*Beta vulgaris*) absorbed, respectively, the following concentrations of selenium (parts per million, dry weight) when grown to maturity on 100% fly ash from Milliken Station vs. the soil alone (control): 6.5 and 0.07; 5.3 and 0.04; 2.4 and 0.02. Yellow sweet clover (*Melilotus officinalis*) found growing on fly ash, 15 ft in depth, at the Milliken Station landfill site contained 5.3 ppm of selenium (Furr et al., 1975). White sweet clover (*Melilotus alba*) growing voluntarily on deep beds of fly ash in Lansing, N.Y. and Endwell, N.Y. contained, respectively, 14 and 69 ppm of selenium (Gutenmann et al., 1975). Indeed, the uppermost leafy portions of clover from the Endwell, N.Y. site contained over 200 ppm of selenium. Selenium above 5 ppm in livestock rations is toxic (Ehlig et al., 1968). Cabbage grown on potted soil to which fly ashes from 15 different states were added (10% by weight) absorbed selenium up to 3.7 ppm (dry weight) with a correlation coefficient (*r*) of 0.9 when comparing the concentrations of total selenium in the cabbages and that in the respective fly ashes added to the soil upon which they were grown (Gutenmann et al., 1975). Total selenium in these latter 15 fly ashes ranged from 1.2 to 16.5 ppm.

Kaakinen et al. (1975) showed that selenium was lowest in bottom ash and increased progressively in fly ashes collected downstream toward the stack. Selenium is believed likely to exist in fly ash in the elemental form and has been found 300 times more concentrated in fly ash than in the corresponding slag produced during coal combustion (Klein et al., 1975; Andren et al., 1975). This

Table IV. Yields of Edible<sup>a</sup> Portions of Crops in the Various Treatments in Table III

Crop	Av g (dry wt) per pot					
	First year crop			Second year crop		
	Con- trol	5% fly ash	10% fly ash	Con- trol	5% fly ash	10% fly ash
Beans	16.2	19.3	30.6	8.1	11.3	5.4
Cabbage	45.5	39.9	40.5	23.4	25.4	23.2
Carrots	3.5	9.6	7.5	27.4	13.6	8.1
Millet	107.0	101.0	97.0	77.0	83.3	84.0
Onions	2.0	3.0	3.0	18.9	27.1	32.9
Potatoes	78.5	63.5	53.9	65.4	41.5	68.5
Tomatoes	39.5	63.2	40.0	22.2	22.0	29.2

<sup>a</sup> Millet included stems plus grain.

elemental selenium is possibly oxidized very slowly to more water-soluble ionic forms and thus available to plants. Indeed, when 2 g of the fly ash used in this study was stirred for 8 h with 20 ml of deionized water, 0.5 µg of selenium was solubilized.

Analyses of the remaining elements listed in Table I were also conducted in the crops but have not been included either because the fly ash amendment did not result in an increase (over the control) in their absorption in more than two of the crops or analytical interferences prevented their accurate determination. Of course, any of the elements may have concentrated in plant parts other than the edible portions analyzed in this study. The average yields in grams (dry weight) per pot are listed in Table IV. The effect of fly ash on yields was variable.

The elemental composition and pH of fly ashes vary considerably. It is affected by the source of coal, methods of combustion and ash collection, and percentage of finer particles which are much higher in toxic element content (Davison et al., 1974). It is also common practice for power plants to buy coal from widely scattered sources as determined by price and sulfur content so that fly ash in any landfill is expectedly heterogeneous in composition. The safe use of fly ash in agriculture would therefore require careful and persistent monitoring of the complete elemental composition of fly ashes, that of the plants grown on them, and the tissues of foraging animals.

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