Elemental Content of Apple, Millet, and Vegetables Grown in Pots of Neutral Soil Amended with Fly Ash

A. Keith Furr, Thomas F. Parkinson, Don C. Elfving, Walter H. Gutenmann, Irene S. Pakkala, and Donald J. Lisk*

A variety of vegetables, millet, and apple trees were cultured on potted soils amended with coal fly ash. Analysis of plant tissues for 38 elements showed enhanced absorption of B, Cu, Co, Fe, Mg, Mn, Mo, Se, and Zn associated with the fly ash amendment. The magnitude of absorption of specific elements was influenced by soil pH.

Coal-burning power plants produce fly ash which is trapped by electrostatic precipitators. Millions of tons of this material are produced annually in the United States (Brackett, 1970). While a small percentage of the total fly ash produced is utilized as a base material for roadbeds, ("Ash At Work", 1969) and as a constituent in concrete and ceramic products, the bulk of it is disposed of in landfills. Other possible uses for fly ash have been investigated. It has been used as an alkaline amendment to neutralize acidic coal mine spoils to permit plant growth to control erosion (Adams et al., 1972). Since fly ash contains nutrient elements essential for plant growth (Davison et al., 1974; von Lehmden et al., 1974), it has been used to establish crops (Barber, 1974) and as a fertilizer supplement to correct plant deficiencies of several elements (Doran and Martens, 1972; Martens, 1971; Martens et al., 1970; Schnappinger et al., 1975).

In an earlier study (Furr et al., 1975), yellow sweet clover (*Melilotus officinalis*) found growing on a deep bed of coal fly ash contained concentrations of many elements, notably selenium, much higher than clover growing on soil. In the work reported, a variety of crops were grown in the greenhouse in a potted soil amended with coal fly ash. The edible plant portions were then analyzed for 38 elements to determine their extent of plant absorption in relation to the element content of the fly ash.

EXPERIMENTAL SECTION

The fly ash used was freshly produced material obtained at Milliken Station, a coal-fired electric power generating plant located in Lansing, New York, about 20 miles north of Ithaca on the eastern shore of Cayuga Lake. This plant burns about 2500 tons per day of coal strip-mined in Pennsylvania, West Virginia, Maryland, and Ohio (Furr et al., 1977) for a daily production of 500 tons of fly ash. The pH of the fly ash was 4.5. (Fly ashes derived from eastern United States coals tend to be acidic.) The soil was a Teel silt loam, pH 6.9, which originated from alluvial deposits near Varna, New York. It had an exchange capacity of 13.9 mequiv/100 g. The soil was air-dried, sifted through a 2-mm screen, and mixed by quartering. Ten percent (w/w) fly ash was thoroughly mixed with the soil (224 metric tons per hectare or 100 tons per acre) in a cement mixer. The pH of the resulting fly ash–soil mixture was 6.5. Soil alone was used as the control. Potted apple trees (see below) were grown on the Teel soil and also on a Darien gravelly silt loam (pH 5.5, exchange capacity, 20.8 mequiv/100 g) sampled near Ithaca, New York. The pH of the resulting mixture of the Darien soil containing 10% w/w fly ash was 5.3.

The crops grown were "Empire" and "McIntosh" apple cultivars (*Malus domestica* Borkh.) on semi-dwarfing MM-106 root stocks, "Long Tendergreen" bush bean (*Phaseolus vulgaris*), "Green Winter" cabbage (*Brassica oleracea* var. *capitata*), "Scarlet Nantes" carrot (*Daucus carota* var. *sativa*), Japanese millet (*Echinochloa crusgalli*

Table I. Elemental Analysis of Soils and Fly Ash

element	element concn, ppm, dry wt in: Teel silt loam	Darien gravelly silt loam	fly ash
Al	51420	43600	138100
As	0.0	1.4	42
Au	0.01	0.01	0.03
B	6.0	9.4	17
Ba	375	290	784
Br	4.6	6.0	1.1
Ca	6040	4200	18900
Ce	86	70	192
Cl	260	169	716
Co	11	14	29
Cr	59	60	140
Cs	4.1	6.4	9.3
Cu	152	90	97
Dy	13		32
Eu	0.8		1.7
Fe	27500	36000	68070
Hf	11	4.3	6.5
K	18080	11521	18640
La	25	18	49
Lu	0.3	0.7	1.0
Mg	44600	6910	35200
Mn	691	316	214
Mo	2.9		9.9
Na	6647	4100	1275
Rb	110	115	177
Sb	2.0	1.2	5.9
Sc	6.1	5.9	19
Se	0.3	0.3	12
Sm	24	0.4	43
Sr	400	215	1000
Ta	0.6	1.1	1.2
Th	16	10	43
Ti	3984	2910	7962
U	2.4	1.9	8.1
V	84	52	299
W	1.2	3.1	3.9
Yb	2.4	1.4	5.0
Zn	70	122	200

Office of Occupational Health and Safety (A.K.F.) and Nuclear Reactor Laboratory (T.F.P.), Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061; Departments of Pomology (D.C.E.) and Food Science, Pesticide Residue Laboratory (W.H.G., I.S.P., and D.J.L.), New York State College of Agriculture and Life Sciences, Cornell University, Ithaca, New York 14853.

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Table II. Element Concentrations (parts per million, dry weight) in Harvested Portions of Crops Grown the First Year in Potted Soil (control) or Soil Amended with 10% (by weight) Fly Ash

plant sample	Co	Cu	Fe	Mg	Mn	Mo	Zn
apple[a] twigs on Teel soil control	0.1	3.3	52	1588	23	0.3	25
apple twigs on Teel soil fly ash	0.3	6.8	148	2676	29	3.4	34
apple twigs on Darien soil control	0.3	0.9	69	2159	245	0.3	43
apple twigs on Darien soil fly ash	0.6	3.0	94	2473	289	0.6	58
apple leaves[b] on Teel soil control	0.2	3.3	158	2520	31	0.3	19
apple leaves on Teel soil fly ash	0.4	6.6	87	3347	38	1.5	20
apple leaves on Darian soil control	0.4	4.0	241	2179	591		26
apple leaves on Darien soil fly ash	0.7	10.0	192	2230	568		30
apple fruit on Teel soil control	0.5	2.0	86	221	4.3	0.2	20
apple fruit on Teel soil fly ash	0.4	2.2	86	338	1.4	1.8	21
beans control	0.4	8.0	96	2128	15	2.8	35
beans fly ash	0.7	8.7	167	2726	18	17	56
cabbage control	0.2	20	132	3357	44	0.7	32
cabbage fly ash	0.5	10	108	2694	34	23	36
carrot control	0.3	2.9	90	1130	8.1	0.2	24
carrot fly ash	0.3	6.9	105	1327	13.3	1.0	31
millet grain control	0.2	3.5	49	1757	23	1.2	37
millet grain fly ash	0.1	7.6	56	1490	28	2.4	60
onion control	0.2	1.6	37	450	7.6		16
onion fly ash	0.3	2.6	80	1030	17	1.2	54
potato control	0.2	9.3	30	1430	6.4	0.2	29
potato fly ash	0.3	10	302	1182	6.5	2.7	38
tomato control	0.6	18	35	2595	46	1.8	29
tomato fly ash	0.6	7	200	1742	24	2.5	39

[a] All apples were cultivar Empire. [b] Shoot leaves.

var *frumentacea*), "1620 Pedro" onion (*Allium cepa*), "Katahdin" potato (*Solanum tuberosum*), and "New Yorker" tomato (*Lycopersicon esculentum*). All of the crops were grown in 7.6-L plastic pots containing 8 kg of growth medium, except apple, cabbage, and potato, which were grown in 11.4-L pots containing 13 kg of medium. The number of plants grown per pot were: apple, 1; beans, 3; cabbage, 1; carrots, 7; millet, 5; onions, 3; potato, 1; and tomato, 1. All treatments were replicated four times. All plants were fertilized weekly with 1000 mL (2000 mL for the 11.4-L pots) of a solution containing reagent grade KH_2PO_4 (0.001 M) and KNO_3 (0.005 M) (Hoagland and Arnon, 1950). All plants were watered daily.

At maturity the crops were harvested and only the edible plant portions of the vegetables and millet were collected for analysis. In the case of millet, the straw and grain were harvested separately. Shoot leaves, spur leaves, and twigs of the apple trees were collected. 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 plant portions were combined and subdivided by homogenizing in a blender or chopping in a food cutter. The plant material was freeze-dried in polystyrene containers, mixed, and subsampled for analysis.

After harvesting the first crops of vegetables and millet, the remaining plant portions were incorporated into the soil in which it was grown and the mixtures were stored moist in the unheated greenhouse during the following fall and winter to simulate field practice. The following spring, the contents of each pot were emptied, lumps were broken up, and the material was again placed in the respective pot and seeded with the same crop which was similarly grown to maturity a second time. The apple trees were also cultured for a second year in the same pots and samples again taken from all of the crops as described above.

Subsamples of soil, fly ash, and crop material were analyzed for 35 elements using nondestructive neutron activation analysis as previously described (Furr et al., 1976a). Arsenic, boron, and selenium were determined by other methods. Arsenic was determined by dry ashing (Evans and Bandemer, 1954) the samples, distilling arsine,

Table III. Boron and Selenium in Edible Portions of Vegetables and Millet Cultured on Fly Ash Amended Soil

	boron (ppm, dry wt)		selenium (ppm, dry wt)	
crop	control	fly ash	control	fly ash
	First Year Crop			
bean	21	29	0.03	1.4
cabbage	22	46	0.05	3.1
carrot	14	19	0.02	1.2
millet grain	4.7	4.5	0.03	1.2
millet straw	7.5	26	0.04	0.6
onion	13	17	0.02	2.4
potato	3.5	4.0	0.03	2.4
tomato	12	15	0.02	1.1
	Second Year Crop			
bean	24	26	0.02	1.1
cabbage	22	29	0.03	1.7
carrot	15	23	0.01	1.8
millet grain	3.7	3.5	0.02	1.5
millet straw	8.0	17	0.02	0.6
onion	14	11	0.01	2.1
potato	4.5	5.0	0.02	1.1
tomato	10	15	0.01	1.8

and analysis using the silver diethyldithiocarbamate spectrophotometric procedure (Fisher Scientific Co., 1960). Boron was determined by the curcumin spectrophotometric procedure (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 total elemental concentrations found in the soils and the fly ash are given in Table I. Thirty-two elements were present at higher concentrations in the fly ash than in either soil. Table II lists the elements which were found at higher concentrations in most of the plants grown on fly ash amended soil during the first growing season as compared to the respective control crop. In general the

Table IV. Boron and Selenium in Foliar Portions of Apple Seedlings Cultured on Fly Ash Amended Soil

variety	tree part	soil pH	boron (ppm, dry wt) control	boron (ppm, dry wt) fly ash	selenium (ppm, dry wt) control	selenium (ppm, dry wt) fly ash
			First Years Growth			
Empire	leaves (ES)[a]	6.9[b]	22	44	0.01	0.30
	leaves (LS)[c]		29	34	0.04	0.16
	twigs (LS)		24	36	0.01	0.15
	leaves (ES)	5.5[d]	30	54	0.03	0.11
	leaves (LS)		30	36	0.01	0.06
	twigs (LS)		27	34	0.01	0.06
McIntosh	leaves (ES)	6.9	24	48	0.02	0.24
	leaves (LS)		30	40	0.03	0.23
	twigs (LS)		20	30	0.01	0.14
	leaves (ES)	5.5	44	52	0.03	0.03
	leaves (LS)		30	52	0.04	0.12
	twigs (LS)		22	34	0.02	0.07
			Second Years Growth			
Empire	leaves (ES)	6.9	30	45	0.07	0.23
	twigs (ES)		20	40	0.03	0.11
	fruit (without seeds)		11	46	0.01	0.03
	seeds		e	e	0.02	0.21
	leaves (ES)	5.5	30	58	0.07	0.16
	twigs (ES)		21	33	0.01	0.04
McIntosh[f]	leaves (ES)	6.9	30	58	0.05	0.25
	twigs (ES)		21	38	0.01	0.10
	leaves (ES)	5.5	27	53	0.07	0.11
	twigs (ES)		16	34	0.02	0.03

[a] Sampled early season before extensive translocation of nutrients from leaves to roots. [b] Teel silt loam. [c] Sampled late season after appreciable translocation. [d] Darien gravelly silt loam. [e] Insufficient sample for analysis. [f] No apples were produced on the 'McIntosh' trees.

accumulation of the elements Co, Fe, Mn, and Zn were higher in apple twigs and leaves when grown on the more acid Darien soil, while Mg and Mo were absorbed more efficiently from the more neutral Teel soil (Allaway, 1975).

Table III lists the concentrations of boron and selenium in vegetables and millet grown successively for 2 years in the same growth medium. In most instances the presence of fly ash in the soil caused a notable increase in the concentration of these elements in the edible portions of the crops which was maintained through the second year of growth. Selenium was considerably higher in concentration in these crops grown on the 10% fly ash amended Teel soil (pH 6.5) than it was in the same respective crops grown successively earlier (Furr et al, 1976b) on an Arkport fine sandy loam (pH 5.5) amended with 10% fly ash. The total selenium content of the formerly (Furr et al., 1976b) and presently used fly ashes were, respectively, 16.8 and 12 ppm. This may have been due to greater leaching losses of selenium in the Arkport soil but moreso to the possibly greater availability of selenium to plants at more neutral soil pH values (Selenium, 1976).

Table IV lists the concentrations of boron and selenium in foliar portions of the apple trees. Both elements were higher in the various tree parts grown on the fly ash treatment as compared to the respective control in virtually all instances. These higher element concentrations appeared to be sustained through the first as well as the second year of growth. In general selenium tended to be higher and boron lower in the samples cultivated on the fly ash treated neutral soil vs. the same samples cultured on the fly ash amended acid soil during the first year. There appeared to be no consistent relationship between levels of the elements in leaves as a function of early or late season sampling. Although only a few apples were produced on the "Empire" trees during the second year, the concentration of selenium in the seeds appeared far higher than in the fruit, most probably since the element tends to be associated with the protein fraction of biological material. Therefore selenium also tended to be higher in the leaves than in the corresponding twig samples.

In summary, the addition of fly ash to soil was associated with increased absorption of a number of elements by vegetables, millet, and apple trees. Absorption of boron, molybdenum, and selenium was noted earlier (Furr et al., 1977) to be enhanced in cabbage grown on soil amended with any of a number of fly ashes resulting from combustion of widely different coal sources. Since certain of the elements studied here are essential for plant or animal nutrition, the use of fly ash might serve to correct soil deficiencies of these elements. Application rate would, however, have to be closely controlled to obviate possible accumulation of toxic levels of elements such as selenium. The possible modifying effects of fly ash on soil physical properties also remains to be comprehensively studied.

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Lead Content of Vegetables, Millet, and Apple Trees Grown on Soils Amended with Colored Newsprint

Don C. Elfving, Carl A. Bache, and Donald J. Lisk*

Apple trees, vegetables, and millet were grown successively for 2 years in pots in an acid or a neutral soil in which was incorporated 10% by weight of pulverized colored magazines and newsprint. Analysis of harvested mature plant material indicated that small quantities of lead may be absorbed by plants when grown on such paper-amended soils.

Millions of tons of waste paper result annually in the United States. The material is disposed of by incineration, in landfills, and recycling for various uses. Burning waste paper is being prohibited in many communities. Also areas suitable for landfills are dwindling. Since recycling of waste paper presently utilizes only a relatively small percentage of the total available, other uses for it have been proposed. One such possible use is as a soil mulching material in agriculture.

A toxic element of concern in paper is lead which is used as a dye in the inks. Its concentration may range up to about 500 ppm in colored newsprint (Serum et al., 1973; Heffron et al., 1977). In the work reported, a number of vegetable species, millet, and apple trees were grown in potted soils amended with colored newsprint. Lead was then determined in the edible harvested plant material to learn the possible extent of absorption of lead as a function of time and soil pH.

EXPERIMENTAL SECTION

The colored paper used derived from magazines, rotogravure sections of newspapers, brochures, and catalogs. Staples were removed, and about 75 kg of the paper was pulverized in a hammer mill equipped with a 0.32-cm mesh sieve. The paper was thoroughly mixed by quartering. The soils used were a Mardin silt loam (Typic Fragiochrept, coarse-loamy, mixed, mesic),pH 5.6, with an exchange capacity of 15.6 mequiv/100 g sampled near Dryden, New York, and a Teel silt loam (Fluvaquentic Eutrochrept, coarse-loamy, mixed, mesic), pH 7.2, with an exchange capacity of 13.9 mequiv/100 g. The Teel soil originated from alluvial deposits in the vicinity of Varna, New York. The soils were air-dried, sifted through a 2-mm screen, and mixed by quartering. Ten percent (w/w) of the paper was thoroughly mixed with each of the soils in a cement mixer. Ten percent (w/w) pulverized virgin bond paper containing no ink was similarly mixed with the above soils to serve as controls.

The crops used were 'Empire' and 'McIntosh' apple (*Malus domestica* Borkh.) on M-7A rootstock, '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*), '1620 Pedro' onion (*Allium cepa*), 'Katahdin' potato (*Solanum tuberosum*), and 'New Yorker' tomato (*Lycopersicon esculentum*). The crops were seeded in pots with the exception of apple, cabbage, onion, and tomato which were planted as transplants. All of the crops were grown in 7.6-L plastic pots except apple and potato which were grown in 11.4-L pots. The weights of the growth media contained in the 7.6- and 11.4-L pots were, respectively, 5.8 and 9.3 kg for the Mardin soil and 6.8 and 11.5 kg for the Teel soil. The numbers of plants grown in each pot were apple, 1; bean, 3; cabbage, 1; carrots, 10; millet, 5; onion, 3; potato, 1; and tomato, 1. All treatments were replicated four times. The plants were fertilized weekly with 1000 mL (1500 mL for the 11.4-L pots) of a solution containing reagent grade KH_2PO_4 (0.001 M) and KNO_3 (0.005 M) (Hoagland and Arnon, 1950). All plants were watered as necessary.

At maturity the crops were harvested. Only the edible portions were collected for the determination of lead. Since

Departments of Pomology (D.C.E.) and Food Science (C.A.B., D.J.L.), Pesticide Residue Laboratory, New York State College of Agriculture, Cornell University, Ithaca, New York 14853.

