

## Elemental Composition of Potted Vegetables and Millet Grown on Hard Coal Bottom Ash-amended Soil

Earle E. Cary,<sup>1</sup> Mason Gilbert,<sup>1</sup> Carl A. Bache,<sup>2</sup> Walter H. Gutenmann,<sup>2</sup> and Donald J. Lisk<sup>2,3</sup>

<sup>1</sup>*U.S. Plant, Soil and Nutrition Laboratory, U.S. Department of Agriculture, and*

<sup>2</sup>*Toxic Chemical Laboratory (C.A.B., W.H.G., E.J.L.), New York State College of Agriculture and Life Sciences, Cornell University, Ithaca, NY 14853*

Much attention has been devoted recently to studies of the elemental composition and properties of soft coal fly ash (DAVISON et al., 1974; KLEIN et al., 1975; FISHER et al., 1976; FURR et al., 1977), largely a waste product of coal-fired electric power generating plants. This is understandable since about 60 million tons are produced in the United States annually (*Ash at Work*, 1981) and proper disposal of it remains a problem. Since only about 17% of that produced is used as an additive to concrete and in road construction, other uses have been proposed such as a possible fertilizer material in agriculture. Studies of the movement of nutrient and toxic elements from soft coal fly ash-amended soils in pots (FURR et al., 1976) and field plots (FURR et al., 1978) into vegetable, forage and grain crops has been reported.

Owing to predicted future shortages of petroleum and natural gas, a slow trend is emerging toward the use of hard coal for domestic heating purposes. Very little has been reported on the growth and composition of crops cultured on soil amended with the bottom ash resulting from burning hard coal. Yet the practice of disposing of such ash by incorporating it in garden soils was formerly a common practice. Limited studies were conducted in Poland on the suitability of growing a variety of crops on disposal sites containing hard coal ash but little was reported on elemental plant composition (MACIAK et al., 1976a, 1976b, 1976c). In the work reported, a variety of vegetables and millet were grown in pots of soil amended with hard coal bottom ash and the magnitude of absorption of 23 elements by the plants was studied.

### EXPERIMENTAL

The ash was obtained as bottom ash resulting from burning hard coal in homes in Ithaca, New York. The coal was deep-mined near Hazelton, Pennsylvania. The coal contained 0.57% sulfur and 61.4% ash. The ash was pulverized in a hammermill through a 3 mm screen and mixed. The pH of the ash as determined by the method of PEECH et al. (1953) was 7.0. The soil was a Honeyoye silt loam (Glossoboric hapludalfs, fine loamy, mixed mesic), pH 6.9, containing 4.8% organic matter and with a cation exchange capacity of 17 milliequivalents per 100 grams. The soil was air-dried, sifted through a 2 mm screen and mixed by quartering. Ten percent w/w (224 metric tons per hectare or 100 tons per acre) of the ash was mixed with the

<sup>3</sup>Correspondence and offprint author.

soil in a cement mixer. The pH of the resulting ash-soil mixture was 7.2. The crops grown were 'Long Tendergreen' 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*). All of the crops were grown in 7.6 liter plastic pots except potatoes which were grown in 11.4 liter pots. The weights of the growth media contained in the 7.6 and 11.4 liter pots were, respectively, 7.5 and 12.0 kg. Equal weights of the Honeoye soil alone was used for growth of the control crops. The number of plants grown in each pot were: bean, 3; cabbage, 1; carrot, 10; millet, 5; onion, 10; potato, 1; and tomato, 1. All treatments were replicated 4 times. The plants were fertilized weekly with 1,000 ml (1,500 ml for the 11.4 liter pots) of a solution containing reagent grade  $\text{KH}_2\text{PO}_4$  (0.001 M) and  $\text{KNO}_3$  (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 analysis. Prior to analysis, all crop portions were rinsed with distilled water to remove adhering dust. Carrots, onions and potatoes were brushed, rinsed and peeled. The total respective, replicated, edible 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. Samples of the soil and ash were also taken for analysis.

The soil, ash and crop samples were analyzed for 22 elements using several methods. 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). Nickel was determined by wet ashing the sample with  $\text{HNO}_3$  and  $\text{HClO}_4$ , isolation using dimethylglyoxime (ZACHARIASEN et al., 1975) and electrothermal atomic absorption analysis using a Perkin Elmer Model 303 spectrophotometer equipped with an HGA-2200 furnace and a background corrector. Selenium was determined by a modification of the method of OLSON (1969) employing wet digestion of the sample and measurement of the fluorescence of piasselenol resulting from reaction of selenium with 2,3-diaminonaphthalene. The remaining elements in plants were ashed in  $\text{HNO}_3$ :  $\text{HClO}_4$  (5:1 v/v). Samples were taken to near dryness before diluting with 0.4 N HCl. Soil and ash samples were finely ground and 0.2 g of material was digested in a teflon-lined bomb with  $\text{HF}$ ,  $\text{HCl}$  and  $\text{HNO}_3$  at  $140^\circ\text{C}$  for 14 hours. The ash solutions were then analyzed by inductively coupled argon plasma emission spectrometry utilizing both an Applied Research Laboratory Model 34000 equipped for vacuum operation and a Model 975 Jarrell Ash instrument with a nonadjustable cross-flow nebulizer.

## RESULTS AND DISCUSSION

The plants grew comparably on the control and ash treatments. There were no visible indications of nutrient deficiencies or

phytotoxicity. The results of elemental analysis of the soil and bottom ash are listed in Table 1. All of the elements were higher in concentration in the ash than the soil except calcium, magnesium, manganese, potassium, sodium and zinc. Volatile elements such as selenium and sulfur would expectedly vaporize during coal combustion and therefore be low in bottom ash.

TABLE 1

Elemental composition of soil and bottom ash.

Element	Soil	Bottom ash
<u>Parts per million (dry wt)</u>		
As	1.0	2.6
B	10.1	14.8
Cd	9.0	20.0
Co	<3.0	112
Cr	<4.0	311
Cu	45.0	188
Mn	421	83.0
Mo	22.0	65.0
Na	1275	24.0
Ni	<15.0	333
Sc	13.0	27.0
Se	0.23	0.55
V	14.5	400
Zn	82.1	63.0
Zr	3.4	111
<u>Percent (dry wt)</u>		
Al	3.89	9.04
Ca	0.74	0.14
Fe	2.16	2.72
K	2.12	2.07
Mg	0.60	0.29
P	0.25	0.30
S	0.24	0.31
Ti	0.36	1.01

The elemental composition of the plant material as produced in the control and ash treatments is given in Table 2. Most elements showed no consistent increase in concentration in the ash-grown plants. Boron, chromium, molybdenum, potassium, sodium and selenium were higher in at least five of the crops grown on ash-amended soil than the respective control crops. Molybdenum and selenium were higher in all seven crops grown on the ash treatment. Boron, molybdenum and selenium were also found to be higher in crops grown on soil amended with soft coal fly ash (FURR et al., 1976,

TABLE 2

Elemental composition of edible portions of crops.

Element	Beans		Cabbage		Carrots		Millet		Onions		Potatoes		Tomatoes	
	Control	Ash	Control	Ash	Control	Ash	Control	Ash	Control	Ash	Control	Ash	Control	Ash
Parts per million														
Al	7.8	3.8	8.6	4.8	8.6	18	9.9	3.9	7.7	30	3.0	2.4	6.9	13
As	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.4	0.4
B	16	15	14	12	13	15	2.8	5.6	9.1	9.3	3.8	4.1	6.5	7.4
Cd	0.1	0.3	0.5	0.3	0.4	0.4	0.3	0.1	0.3	0.4	0.4	0.4	0.4	0.7
Co	0.2	0.3	0.5	0.4	0.6	0.6	0.7	0.5	0.4	0.8	0.7	0.7	0.6	1.1
Cr	0.2	0.3	0.5	0.3	0.6	0.7	0.6	0.6	0.5	0.9	0.6	0.7	0.7	1.4
Cu	4.9	4.5	2.0	1.8	3.9	3.7	16	21	3.8	3.8	8.5	8.7	3.0	4.6
Fe	72	60	29	26	32	27	24	26	27	30	31	31	46	48
Mn	17	16	15	14	7.5	6.9	12	14	6.6	8.7	7.7	8.5	10	11
Mo	4.0	13	3.8	12	0.8	1.2	1.7	3.8	1.0	2.6	1.4	2.4	1.1	3.0
Na	9.1	12	224	250	1140	1000	64	85	162	164	60	60	58	145
Ni	0.8	0.7	0.1	0.1	0.1	0.2	0.3	0.4	0.1	0.2	0.1	0.2	0.1	0.1
Sc	0.1	0.1	0.2	0.1	0.2	0.2	0.2	0.1	0.1	0.2	0.2	0.2	0.2	0.3
Se	0.01	0.04	0.03	0.1	0.01	0.04	0.02	0.03	0.02	0.1	0.02	0.1	0.02	0.03
Tl	0.6	0.9	1.9	1.4	1.4	1.8	1.8	1.4	1.3	2.7	1.5	1.4	1.4	2.8
V	0.3	0.4	0.9	0.6	0.8	1.0	0.9	0.7	0.6	1.1	0.8	0.8	0.8	1.5
Zn	26	24	14	12	13	13	39	37	18	16	16	17	8.1	16
Zr	0.2	0.7	1.5	1.0	1.5	1.7	1.8	1.1	1.0	2.0	1.5	1.4	1.4	2.7
Percent														
Ca	0.44	0.44	1.85	1.69	0.26	0.26	0.57	0.87	0.49	0.40	0.05	0.05	0.05	0.08
K	2.15	2.06	2.67	2.69	2.28	2.19	0.78	1.04	2.00	2.04	2.89	3.12	1.49	2.95
Mg	0.24	0.23	0.20	0.20	0.14	0.14	0.26	0.27	0.09	0.09	0.15	0.16	0.14	0.16
P	0.41	0.38	0.37	0.35	0.33	0.34	0.46	0.51	0.45	0.43	0.49	0.54	0.44	0.38
S	0.11	0.11	0.50	0.47	0.13	0.12	0.10	0.12	0.38	0.35	0.12	0.13	0.04	0.09

1978; GUTENMANN et al., 1979). In the Northeastern United States, molybdenum and selenium may be present in crops in insufficient concentrations to meet farm animal requirements. Boron is sometimes deficient in Northeastern soils for plant nutrition. Hard coal bottom ash as a soil amendment might, therefore, aid in rectifying these problems in some plants. In this regard, the increases in the concentration of these elements in the ash-grown plants was not enough to cause toxicity. Fortunately toxic elements such as arsenic and cadmium showed no, or only a modest increase in various of the plants grown. It is possible that certain elements may have concentrated in other than the edible plant portions which were analyzed in the study.

From the data in this initial study, it would appear that hard coal bottom ash may be safely applied to agricultural soils. It is obvious, however, that element absorption will vary with the rate of ash application, the resultant soil pH, the specific plants involved and many other factors. Furthermore, the elemental composition of coal and, therefore, the resultant ash may vary considerably depending on the mining location and conditions during fuel combustion. For instance, it has been found that coals from various sources contain elements in the following ppm concentration ranges: arsenic (2-25); cadmium (0.2-28); chromium (5-60); nickel (10-50); selenium (4-7); titanium (500-2,000); vanadium (10-50); and zirconium (7-250)(ABERNETHY et al., 1969; KESSLER et al., 1971; GOLDSCHMIDT, 1935; and STETTLER et al., 1982).

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