

Element Concentrations in Aqueous Equilibrates of Coal and Lignite Fly Ashes

A survey was conducted of the concentration of arsenic, boron, molybdenum, phosphorus, and selenium in aqueous equilibrates of fly ashes derived from a number of soft coals and lignites. Concentrations of boron were much higher than those of the other elements. The concentrations of water-soluble boron and molybdenum in the soft coal ashes and water-soluble selenium in the lignite ashes showed a high degree of correlation ($p < 0.01$) with the total element concentrations in the respective ash samples.

About 50 million tons of fly ash result from burning soft coal in power plants in the United States annually (Ash At Work, 1977). Only about 10% of this total is used in concrete and as a base material for road construction. The remainder is discarded in landfills. Several investigators have reported on the results of using fly ash as a soil fertilizer amendment for the growth of plants and this work has been reviewed (Adriano et al., 1978).

Several elements in coal fly ashes are important to plants and animals from a nutritional and/or toxicologic standpoint. These include arsenic, boron, molybdenum, phosphorus, and selenium. Plants growing on soils amended with fly ash have been reported to absorb levels (above controls) of arsenic, boron, molybdenum, or selenium (Erdman et al., 1978; Furr et al., 1976, 1978a,b; Plank and Martens, 1974). Animals fed forage grown on fly ash and thus containing elevated concentrations of selenium readily accumulate selenium in body tissues (Furr et al., 1978b). Selenium has been shown to be accumulated by aquatic organisms exposed to fly ash or fly ash effluents (Gutenmann et al., 1976; Cherry et al., 1976). The possible association between phosphorus in water and algal blooms is well known.

Environmentally, it is of interest to learn the equilibrium concentration of such elements in water which may have percolated through fly ash in a landfill or in the soil solution of a fly ash amended soil. In the work reported the concentrations of arsenic, boron, molybdenum, phosphorus, and selenium were determined in aqueous equilibrates of a wide range of soft coal and lignite fly ashes collected throughout the United States.

EXPERIMENTAL SECTION

The fly ashes studied were obtained by mail from a number of coal-burning power plants. A description of the power plant combustion equipment, the mining location of most of the parent coals and their total element concentration was published earlier (Furr et al., 1977). One gram of each of the fly ashes was equilibrated at room temperature for 2 h with 200 mL of distilled water in a 250-mL soft glass bottle using magnetic stirring. Cox et al. (1978) used this method for obtaining aqueous equilibrates of fly ash in a study of boron leaching. The suspensions were filtered and portions of the solution were then analyzed for arsenic, boron, molybdenum, phosphorus, and selenium. Arsenic was determined by 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 measured by a modification of the thiocyanate method of Sandell (1959). Phosphorus was determined by the spectrophotometric method of Martin and Doty (1949) employing extraction of phosphomolybdic acid into benzeneisobutyl alcohol and reduction to the heteropoly blue complex. Selenium was determined by a modification of the diamionaphthalene fluorescence method of Olson (1969).

Table I. Concentration of Elements in Aqueous Equilibrates of Soft Coal and Lignite Fly Ashes in the United States

power plant	$\mu\text{m/mL}$ in aqueous equilibrates				
	As	B	Mo	P	Se
Soft Coal Fly Ashes					
Alabama	0.07	0.72	0.05	0.03	0.00
Colorado	0.00	1.14	0.01	0.00	0.01
Delaware	0.11	0.14	0.03	0.06	0.01
Georgia	0.00	0.28	0.00	0.02	0.00
Iowa	0.08	1.62	0.05	0.10	0.00
Kentucky	0.00	0.18	0.00	0.02	0.01
Maryland	0.00	0.06	0.00	0.17	0.00
Massachusetts	0.00	0.19	0.00	0.06	0.01
Michigan (site 1)	0.00	1.05	0.02	0.01	0.02
Michigan (site 2)	0.03	1.48	0.03	0.03	0.02
Minnesota	0.00	4.23	0.04	0.01	0.02
New Hampshire	0.10	3.13	0.05	0.05	0.01
New Mexico (site 1)	0.00	0.21	0.01	0.05	0.00
New Mexico (site 2)	0.00	1.69	0.02	0.01	0.00
New York	0.00	0.16	0.01	0.07	0.01
North Carolina	0.05	0.38	0.02	0.10	0.04
Ohio	0.00	0.38	0.01	0.03	0.08
South Carolina	0.00	0.24	0.03	0.11	0.02
South Dakota	0.00	0.89	0.00	0.02	0.02
Utah	0.00	2.81	0.00	0.03	0.01
West Virginia	0.00	0.73	0.01	0.08	0.01
Wisconsin	0.06	1.38	0.08	0.01	0.01
Lignite Fly Ashes					
Minnesota (Fergus Falls) ^a	0.00	3.39	0.00	0.01	0.03
Montana (Savage)	0.00	1.73	0.01	0.01	0.01
North Dakota (Center)	0.04	7.37	0.04	0.01	0.06
North Dakota (Stanton)	0.03	3.00	0.03	0.01	0.03
Texas (Fairfield)	0.00	3.40	0.00	0.00	0.04
Poland (Konin)	0.00	0.35	0.00	0.02	0.00

^a The last six entries are power plants that burn lignite mined nearby except for Minnesota in which the mine is in Beulah, ND.

RESULTS AND DISCUSSION

The results of one analysis of each of the elements in the aqueous equilibrates of the fly ashes are listed in Table I. Boron attained the highest concentration by far. Sweet clover voluntarily grows on fly ash landfill sites (Erdman et al., 1978) probably because it has a high tolerance to boron phytotoxicity (Barber, 1974). Plants absorb appreciable quantities of boron above controls when fresh fly ash is mixed with the soil (Furr et al., 1976, 1978a). The arsenic concentrations in the aqueous extracts were low. In this regard plants have been shown to absorb only slightly higher levels of arsenic when grown on fly ash amended soil (Furr et al., 1976, 1978a).

Molybdenum concentration in the aqueous equilibrates did not appear elevated but plants growing on fly ash may absorb relatively high levels of the element (Furr et al., 1978b). When the ratio of the total concentration of copper to molybdenum in forage plants is less than 5, molybdenosis, a molybdenum-induced copper deficiency,

may reportedly occur in foraging ruminants (Erdman et al., 1978). Yet when sweet clover growing on a fly ash landfill and having a copper to molybdenum ratio of 0.39 was fed to sheep and pregnant goats for 173 days, molybdenosis in the animals was not observed (Furr et al., 1978b).

Selenium, although low in concentration in the extracts, is accumulated by plants growing on fly ash (Gutenmann et al., 1976) and is probably the element of most concern. Phosphorus was also low in concentration in the fly ash equilibrates. In contrast to selenium, however, plants grown on fly ash amended soils may show phosphorus deficiency (Adriano et al., 1978). In this regard, fly ash has the ability to fix phosphorus and has been investigated for such use in natural aquatic systems (Higgins et al., 1976; Fine and Jensen, 1976).

A highly significant correlation was found between water-soluble boron ($r = 0.83$; $p < 0.01$) and molybdenum ($r = 0.94$; $p < 0.01$) in the soft coal fly ashes and the respective total concentrations of these elements in these same ashes reported earlier (Furr et al., 1977). A highly significant correlation was also found between water-soluble selenium ($r = 0.89$; $p < 0.01$) in the lignite fly ashes and total selenium in the ashes. The total concentrations of selenium in the lignite ashes were in parts per million (dry weight): Minnesota, 8.1; Montana, 4.4; North Dakota (Center), 17; North Dakota (Stanton), 7.6; Texas, 19; and Poland, 0.7. No significant correlations were found between soluble and total concentrations of the other elements in either the soft coal or lignite ashes. Dreesen et al. (1977) reported a positive correlation between the concentrations of boron, molybdenum, and selenium extracted from coal fly ash by water and the levels of these elements in effluent waters from the respective coal-fired power generating plant.

Differences in concentration of elements in aqueous equilibrates of fly ash may be due to the original element concentration in the parent coal and differences in operating conditions during coal combustion. Also the predominant particle sizes of the ash studied is extremely important, finer particles being notably higher in surface area and total concentration of many elements (Davison et al., 1974).

LITERATURE CITED

- Adriano, D. C., Woodford, T. A., Ciravolo, T. G., *J Environ. Qual.* 7, 416 (1978).
- Ash At Work, Vol. IX No. 3, National Ash Association, Washington DC, 1977, p 4.
- Barber, G., in "Ash Utilization", Proceedings of the Third International Ash Utilization Symposium, Pittsburgh, PA, U.S. Bur. Mines Cir. 8640, 1974, pp 246-253.
- Cherry, D. S., Guthrie, R. K., Rodgers, J. J., Jr., Cairns, J., Jr., Dickson, K. L., *Trans. Am. Fish. Soc.* 105, 686 (1976).
- Cox, J. A., Lundquist, G. L., Przyjazny, A., Schmulback, C. D., *Environ. Sci. Technol.* 12, 722 (1978).
- Davison, R. L., Natusch, D. F. S., Wallace, J. R., Evans, C. A., Jr., *Environ. Sci. Technol.* 8, 1107 (1974).
- Dreesen, D. R., Gladney, E. S., Owens, J. W., Perkins, B. L., Wienke, C. L., Wagen, L. E., *Environ. Sci. Technol.* 11, 1017 (1977).
- Erdman, J. A., Ebens, R. J., Case, A. A., *J. Range Manage.* 31, 34 (1978).
- Fine, L., Jensen, W., *Crops Soils* 29, 18 (1976).
- Fisher Scientific Co., "Reagents of Choice for Arsenic in Parts per Billion", Tech. Data Bull. TD-142, Nov 1960.
- Furr, A. K., Kelly, W. C., Bache, C. A., Gutenmann, W. H., Lisk, D. J., *J. Agric. Food Chem.* 24, 885 (1976).
- Furr, A. K., Parkinson, R. G., Hinrichs, R. A., Van Campen, D. R., Bache, C. A., Gutenmann, W. H., St. John, L. E., Jr., Pakkala, I. S., Lisk, D. J., *Environ. Sci. Technol.* 11, 1194 (1977).
- Furr, A. K., Parkinson, T. F., Gutenmann, W. H., Pakkala, I. S., Lisk, D. J., *J. Agric. Food Chem.* 26, 357 (1978a).
- Furr, A. K., Parkinson, T. F., Heffron, C. L., Reid, J. T., Haschek, W. M., Gutenmann, W. H., Bache, C. A., St. John, L. E., Jr., Lisk, D. J., *J. Agric. Food Chem.* 26, 847 (1978b).
- Greweling, H. T., "The Chemical Analysis of Plant Tissue", Mimeo No. 6622, Agronomy Department, Cornell University, Ithaca, NY, 1966.
- Gutenmann, W. H., Bache, C. A., Youngs, W. D., Lisk, D. J., *Science* 191, 966 (1976).
- Higgins, B. P. J., Mohleji, S. C., Irvine, R. L., *J. Water Pollut. Control Fed.* 48, 2153 (1976).
- Martin, J. B., Doty, D. M., *Anal. Chem.* 21, 965 (1949).
- Olson, O. E., *J. Assoc. Off. Anal. Chem.* 52, 627 (1969).
- Plank, C. O., Martens, D. C., *Soil Sci. Soc. Am. Proc.* 38, (1974).
- Sandell, E. B., "Colorimetric Metal Analysis", Interscience, New York, 1959.
- Stoewsand, G. S., Gutenmann, W. H., Lisk, D. J., *J. Agric. Food Chem.* 26, 757 (1978).

Dorothy J. Churey¹
 Walter H. Gutenmann¹
 Alina Kabata-Pendias²
 Donald J. Lisk^{*1}

¹Pesticide Residue Laboratory
 Department of Food Science
 New York State College of Agriculture and Life
 Sciences
 Cornell University
 Ithaca, New York 14853
²Institute of Soil Science and Cultivation of Plants
 Pulawy, Poland

Received for review October 13, 1978. Accepted January 8, 1979.