Multielement Absorption by Crops Grown on Ithaca Sludge-Amended Soil

A. K. Furr,[1] W. C. Kelly,[2] C. A. Bache,[3] W. H. Gutenmann,[3] and D. J. Lisk[3]

[1]Nuclear Reactor Laboratory, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061

[2,3]Departments of Vegetable Crops and Food Science, respectively, New York State College of Agriculture and Life Sciences, Cornell University, Ithaca, N.Y. 14853

About 50 million tons of municipal sewage sludge is produced annually in this country (HUDSON, 1968). It consists of a heterogenous mixture of solid wastes from domestic and industrial activities. Present means of disposal include ocean dumping and burning which can cause water and air pollution or burying in sanitary landfills. Its use as a soil conditioner and source of nutrients in agriculture has been studied.

Since municipal sludges may typically contain elevated concentrations of Zn, Cu, Cd, Pb, Cr and other elements largely from industrial wastes, edible crops growing on sludge-amended soils may absorb these elements. The extent of absorption depends on many factors (CHANEY, 1973). Previous investigations of this problem have been largely confined to a few of the most common elements as listed above in mainly forage plants (PAGE, 1974). However, depending on the spectrum of industries served, sludge may contain virtually any element and a galaxy of organic compounds. Furthermore, it is common practice for suburban home owners and farmers to load and haul away sludge from sewage treatment plants for use on lawns, ornamentals and edible garden crops. The purpose of the work reported here was to study the extent of absorption of 42 elements by plants representing major classes of edible garden crops grown on sludge-amended soil.

EXPERIMENTAL

Sludge from the city of Ithaca, NY was used. The Ithaca sludge process includes primary settling, trickle filtration, anaerobic digestion and finally vacuum filtration with the addition of lime. It had a pH of 7.2. The Ithaca sludge had remained in a pile outside for about one year prior to use. (Amending soil with freshly processed sludge and planting immediately may typically cause phytotoxicity or inhibition of seed germination owing to elevated salt concentrations and the presence of toxic elements such as B, Cu, Ni and Zn or organic constituents such as industrial cutting oils. Salts must therefore first be leached out and time allowed for decomposition of phytotoxic organic constituents.) The sludge was air-dried on a sheet of polyethylene, pulverized in a hammer mill through an 1/8 inch mesh screen and thoroughly mixed by quartering. It had a fertilizer equivalent of 2.0-9.2-0.17% (N-P_2O_5-K_2O) and an ash content of 58.9%.

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The soil was an Arkport fine sandy loam, pH 5.3 sampled near Ithaca, NY. It was air-dried and sifted through a 2-mm screen and mixed by quartering. Ten percent (w/w) of the dry sludge was thoroughly mixed with the soil (or 100 dry tons of sludge per acre) in a cement mixer. Soil mixed with 10% Canadian peat moss was used as the control. The pH of the final mixtures were: Ithaca sludge-amended soil, 7.1, and control soil 5.3.

The crops planted 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-inch plastic pots containing 6 kg. of the soil mixtures except potatoes which were grown in 12-inch pots containing 12 kg. The number of plants grown in each pot was; bean, 2; cabbage, 1; carrot, 3; millet, 5; onion, 3; potato, 1; and tomato, 1. All treatments were replicated twice.

At the time of planting, four grams of 0-20-0 (as P_2O_5) and 1 gram of 0-0-60 (as K_2O) was thoroughly mixed into the top 3 inches of growth media in the 9-inch pots. Twice these weights of fertilizers were used in the 12-inch pots. All plants were fertilized once each week during the 11th, 12th and 13th week of growth with a solution containing reagent grade KH_2PO_4 (0.001M), KNO_3 (0.005 M) and $Ca(NO_3)_2$ (0.005 M), 250 ml added to the 9-inch pots and 500 ml to the 12-inch 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. After harvesting the pots of soil and sludge-soil were kept moist in an unheated greenhouse during the fall and winter to simulate field practice. In the spring a second planting of the crops was made in the same pots. At the time of the second planting the contents of each pot were dumped out, lumps broken up and the material (plus partially decomposed roots) again placed in the respective pots fertilized as before and seeded.

At harvest 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 the soil, peat moss, sludge and crop material were analyzed for 33 elements using nondestructive neutron activation analysis as previously described (FURR, et al. 1975).

Cadmium, Pb, Zn, Cu, Ni, Cr, Se, B and As were determined by other methods. The determination of Cd, Pb and Zn was performed by dry ashing the samples 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, Cu, Cr and Ni 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 fluorescence of piazselenol resulting from reaction of Se with 2,3-diaminonaphthalene. Boron was determined in the growth medias and Swiss chard samples 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

The concentrations of 42 elements determined in the soil, peat moss and sludge are listed in Table 1. Twenty-seven elements were higher in total concentration in the sludge than in the soil. Even though Ithaca is a relatively small city the sludge showed relatively high levels of Cd, Cr, Cu, Mo, Ni, Pb, Ti and Zn. Several large industries are located in Ithaca which manufacture guns, gears, drive chains, and other miscellaneous metal products, however. Also a major portion of the Cu, Cd, Cr, Ni and Zn in wastewater can derive from domestic uses (KLEIN et al., 1974). Based on the concentrations of elements found in the peat moss it would not appear to have contributed significantly to element accumulation in the control plants. B, Br, Ca, Cd, Cl, Cr, Cu, Fe, Hg, I, Mo, Ni, Sb, Sc, Se, Ta, V, W and Yb were found higher in at least 3 of the crops grown during the first year on sludge-amended soil as compared to the control (Table 2). Ca, Cd, Cl, Cu, Fe, I, Mo, Ni, W and Yb were most consistently high, their plant concentrations in the sludge-soil treatment exceeding those of the controls in 5 or more of the crops studied. Plant absorption of the elements B, Br, Cd, Cl, Cu, I and Ni would probably not be greatly affected by the higher pH (7.1) of the sludge-soil mixture as compared to the soil alone (5.3). Absorption of Ca, Mo and Se would be favored by the rise in pH while absorption of iron would tend to be decreased. The effect of factors such as chelate formation in sludge amended-soil may, of course, alter the influence of pH per se.

The elements listed in Table 3 were found higher in at least 3 of the crops grown during the second year on the sludge-soil mixture as compared to their concentrations in the second year control crops. Al, B, Br, Ca, Cd, Cu, Fe, and K were most consistently high (in 5 or more of the 7 crops). Cr and Cu were notably lower in concentration in both the control and sludge grown crops during the second year than in the corresponding first year crops. The concentrations of the remaining elements in Table 1 were also determined in the crops but have not been included in Table 2 either because the sludge treatment did not result in an increase in absorption in more than two of the crops or analytical interferences prevented their accurate analysis.

Several elements in the sludge which considerably exceeded in concentration that in the soil were Ba, Hf, Hg, Mn, Pb, Sn and Zn. Yet this did not result in greatly enhanced absorption by the respective plants. Barium may well be fixed as the insoluble sulfate in soils as was recently shown to be true of lead (OLSEN and SKOGERBOE, 1975). Mercury is bound tightly by humic substances especially those with sulfur and sulfhydryl functions (PAGE, 1974). Mn and Zn would expectedly be less available in soils at pH 7.1 than at 5.3. It is also possible that plant parts other than the edible portions analyzed may have concentrated certain of these elements.

Considering toxic elements, Ni in beans, Cd and Sb in onions and Hg in millet attained concentrations of some concern in the first year crops. The oral LD_{50} in rats (mg/kg) are $Ni(NO_3)_2$ (1620), $Cd(Cl)_2$ (88), $SbCl_5$ (1115) and $HgCl_2$ (37) (CHRISTENSEN et al., 1975). Both Cd and Ni are believed to be carcinogenic.

CHANEY (1973) has reviewed factors which control the uptake of elements in sludges by plants. The nature, concentration and valence of the element, the pH of the soil, its organic matter and phosphate content, cation exchange capacity and the nature and condition of the plant are among these. Other factors such as the nature of soil clays, redox potential, ionic competition and chelate formation may also affect the availability of these elements in sludge-fortified soils.

Virtually any element may be present in municipal sludges. Depending on the spectrum of industries served, population changes and industrial relocation these sludges expectedly vary widely in elemental composition and concentration as a function of sampling location and time. Plant absorption of the more common elements and their animal toxicity can be roughly predicted based on the results of past research. Conversely little is known about the soil chemistry or animal toxicity of many other elements which are known to be present in sludges. Recommendations for the safe use of sludge in agriculture will therefore require element uptake studies with many plants, animal feeding studies with the harvested crops and analysis of as many elements as possible with existing analytical techniques in plants and animals for correlation with possible phytotoxic and pathologic effects.

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TABLE I

Total elemental analysis of soil and amendment materials.

Element	Element concentration (ppm, dry wt.) in: Soil	Peat Moss	Ithaca Sludge
Al	39,400	252	41,600
As	2.9	0.1	3.0
Au	0.004	0.02	0.6
B	14	5	63
Ba	331	36	1220
Br	3.5	37	10
Ca	3410	5600	71,200
Cd	0.1	0.01	44
Ce	77	---	31
Cl	82	346	5670
Co	9.3	1.4	10.5
Cr	17.3	0.3	302
Cs	2.6	0.5	1.1
Cu	47	0.5	734
Eu	---	0.03	0.2
Fe	24,900	468	60,900
Hf	9	---	72
Hg	0.1	0.1	11.7
I	1.2	9.1	---
K	14,000	336	2180
La	25	0.3	8.8
Lu	0.4	0.01	0.4
Mg	7470	1190	8570
Mn	278	4.3	652
Mo	----	----	21
Na	6210	258	863
Ni	17	0.1	191
Pb	13	0.3	104
Rb	115	----	42
Sb	0.8	3.5	2.9
Sc	8.7	0.1	3.2
Se	0.3	0.2	1.4
Sm	5.0	0.02	1.2
Sn	12	----	70
Ta	0.6	0.1	0.6
Th	15	0.2	18
Ti	3292	39	2270
U	1.4	0.2	7.9
V	67	0.7	29
W	2.1	0.7	4
Yb	2.0	0.2	0.2
Zn	180	2.3	1826

TABLE II

Element concentrations (ppm, dry wt.) in edible portions of crops grown in pots on Ithaca sludge-amended soil during the first year.

	BEANS		CABBAGE		CARROTS		MILLET		ONIONS		POTATOES		TOMATOES	
Element	control soil	sludge soil	control soil	sludge soil	control soil	sludge soil	control soil	sludge soil	control soil	sludge soil	control soil	sludge soil	control soil	sludge soil
B	16	28	23	25	19	--	17	9	--	--	6	9	4	9
Br	5.5	6.2	6.5	11	4.9	4.5	13	10	5.0	11.7	1.8	5.4	6.2	6.1
Ca	2670	7050	4500	7630	1650	2430	3700	2650	4210	13200	237	426	780	600
Cd	0.1	0.1	0.2	0.7	1.1	0.5	0.2	0.4	0.6	2.2	0.3	0.5	0.1	0.3
Cl	2270	2460	3210	3220	3220	2040	5260	5780	1650	4280	870	2750	3200	3160
Cr	3.5	0.6	0.2	3.5	2.8	0.9	0.5	0.2	1.1	5.9	0.07	0.11	0.2	0.2
Cu	3.2	3.4	3.0	4.2	2.0	---	2.4	3.9	3.4	1.7	3.1	5.7	2.2	2.5
Fe	108	97	78	177	143	146	49	100	100	264	49	70	173	170
Hg	0.2	0.1	0.1	0.4	0.1	0.1	0.7	1.0	0.3	0.5	0.1	0.1	0.1	0.4
I	0.7	0.7	0.3	2.9	0.9	1.0	---	11.7	0.7	1.3	0.04	0.5	0.4	1.7
Mo	1.0	13	1.0	0.4	0.2	0.2	0.3	2.3	0.7	1.8	0.2	0.8	0.5	0.9
Ni	3.9	6.7	1.9	4.8	2.7	---	1.4	3.1	2.2	---	0.6	1.1	0.5	1.4
Sb	0.4	1.0	1.4	0.9	0.9	0.9	1.1	0.3	0.8	11.5	0.4	0.7	2.5	0.5
Sc	0.01	0.02	0.03	0.01	0.01	0.00	0.00	0.02	0.01	0.02	0.004	0.01	0.03	0.01
Se	0.02	0.04	0.01	0.03	0.00	0.01	0.02	0.02	0.00	0.00	0.01	0.02	0.01	0.01
Ta	0.03	---	0.03	0.06	0.07	0.06	0.07	0.03	0.3	0.6	0.04	0.06	0.12	0.02
V	0.06	0.1	0.4	0.3	0.4	0.1	0.04	0.2	0.2	0.4	4.8	0.04	0.12	0.03
W	0.2	0.5	0.4	1.0	0.4	0.4	0.3	0.3	0.2	0.4	0.04	0.4	0.4	0.5
Yb	0.04	0.1	0.01	0.1	0.01	0.1	0.1	0.1	0.2	0.2	---	0.1	0.1	0.2

TABLE III

Element concentrations (ppm, dry wt.) in edible portions of crops grown in the same pots of Ithaca sludge-amended soil during the second year.

	BEANS		CABBAGE		CARROTS		MILLET		ONIONS		POTATOES		TOMATOES	
Element	control soil	sludge soil	control soil	sludge soil	control soil	sludge soil	control soil	sludge soil	control soil	sludge soil	control soil	sludge soil	control soil	sludge soil
Al	17	19	24	24	14	35	---	28	7	18	10	11	13	15
B	18	41	35	35	1.1	22	10	12	15	24	6	10	9	12
Br	5.1	3.5	8.4	11.1	4.0	6.0	8.8	8.2	2.9	3.0	3.3	5.2	3.7	5.6
Ca	4610	6000	7700	19500	2060	2710	3780	3950	1920	6360	83	342	786	1780
Cd	0.1	0.1	0.3	0.9	1.9	0.8	0.2	0.4	0.3	0.9	0.3	0.3	0.1	0.3
Cl	1980	1970	4000	4400	1880	2500	4100	6230	1260	1120	2800	2620	2390	2470
Cr	0.2	0.2	0.2	0.2	0.1	0.4	0.3	0.2	0.1	0.2	0.2	0.3	0.1	0.3
Cu	1.8	2.2	0.6	2.2	1.3	2.6	1.2	2.0	1.0	1.5	2.5	4.6	1.6	1.7
Fe	84	111	136	90	71	34	74	164	40	86	35	56	20	85
Hg	0.3	0.1	0.3	0.2	0.1	0.04	0.4	0.5	0.1	0.2	0.1	0.1	0.1	0.2
K	24600	20600	17400	28400	18400	19300	13100	15500	14000	11000	20000	31400	17000	21900
Mg	2360	1670	2850	1050	1260	880	2100	4650	720	630	640	870	900	960
Mo	2.0	30	0.8	4.9	0.2	0.6	0.9	---	---	---	0.6	---	---	---
Ni	4.4	5.5	2.1	1.9	1.2	1.1	1.8	2.3	0.6	1.4	1.0	0.9	0.4	0.9
Se	0.01	0.02	0.02	0.04	0.01	0.04	0.03	0.03	0.02	0.02	0.02	0.03	0.02	0.02
Ti	12	1.6	3.2	6.7	---	6.1	---	2.0	0.5	3.9	3.0	2.5	2.0	3.1

REFERENCES

CHANEY, R.L.: Proc. Joint Conf., National Assoc. State Univer. & Land-Grant Colleges, pp. 129-141 (1973).

CHRISTENSEN, H. E., T.T. LUGINBYHL and B. S. CARROLL: Registry of Toxic Effects of Chemical Substances, US Dept. H. E. W., National Inst. Occupat. Safety Health, Rockville, MD (1975).

EVANS, R. J. and S. L. BANDEMER: Anal. Chem. 26, 595 (1954).

FISHER SCIENTIFIC CO.: "Reagents of Choice for Arsenic in Parts per Billion", Tech. Data Bull. TD-142 (1960).

FURR, A. K., G. S. STOEWSAND, C. A. BACHE, W. H. GUTENMANN, and D. J. LISK: Arch. Environ. Health 30, 244 (1975).

GAJAN, R. J. and D. LARRY: J. A. O. A. C. 55, 727 (1972).

GREWELING, H. T.: "The Chemical Analysis of Plant Tissue", mimeo No. 6622, Agronomy Dept., Cornell University, Ithaca, NY, pp. 74-76 (1966).

HUDSON, H. E., JR.: "How Serious is the Problem?", Proc. 10th San. Eng. Conf., Univ. Illinois Bull. 65, 115-120 (1968).

KLEIN, L. A., M. LANG, N. NASH and S. L. KIRSCHNER: "Sources of metals in New York City Wastewater", J. Water Poll. Contr. Fed. 46, 2653 (1974).

OLSEN, O. E.: J. A. O. A. C. 52, 627 (1969).

OLSON, K. W. and R. K. SKOGERBOE: Environ. Sci. & Tech. 9, 227 (1975).

PAGE, A. L.: "Fate and Effects of Trace Elements in Sewage Sludge When Applied to Agricultural Lnads", U. S. E. P. A. Pub. No. EPA-670/2-74-005, Cinncinati, Ohio (1974).

PEECH, M., R. A. OLSEN and G. H. BOLT: Soil Sci. Soc. Amer. Proc. 17, 214 (1953).