Elemental Content of Vegetables and Apple Trees Grown on Syracuse Sludge-Amended Soils

A. Keith Furr, Thomas F. Parkinson, Don C. Elfving, Carl A. Bache, Walter H. Gutenmann, G. James Doss, and Donald J. Lisk*

Two successive crops of peppers, kohlrabi, lettuce, peas, spinach, sweet potatoes, and turnips were grown in pots of control and municipal sludge-amended acid and neutral soils. Two commerical apple cultivars were also cultured. Cadmium, copper, nickel, and zinc were higher in the sludge-grown crops. Cadmium, nickel, and zinc were usually higher in vegetable crops grown on the sludge-fortified acid soil. Copper was higher in the vegetables grown on the neutral soil–sludge mixture. Nickel and zinc generally decreased in concentration in sludge-grown vegetable crops and apple trees during the second year of growth. There was not a consistent varietal or soil pH effect as regards heavy metals in apple trees. Copper and zinc tended to concentrate in apple twigs while nickel and lead concentrated in apple leaves. Metal residues in apple fruit were comparatively low.

It is estimated that ~7 million metric tons of sewage sludge will be produced annually in the United States by 1985 (Walsh, 1976). Present means of sludge disposal includes ocean dumping or incineration which can cause water and air pollution or burying in sanitary landfills.

Much research is presently under way to study the possible use of sludge as a soil conditioner or fertilizer amendment in agriculture. Whereas sludges contain essential plant nutrient elements, the content of toxic heavy metals such as Cd, Ni, and Pb especially in municipal sludges (Furr et al., 1976c) is well-known. Cadmium is of most concern owing to its uptake by plants from soil, its efficient deposition in foraging animal tissues, and its known toxicity (Browning, 1969).

The magnitude of uptake of such elements by plants grown on sludge-amended soils has been extensively studied by using agronomic crops. Much less attention has been given to vegetable and especially fruit crops. The need for such research is important since it is presently common for growers or householders to voluntarily haul sludge from sewage treatment plants for use on soil used for ornamentals, turf, agronomic, and sometimes garden crops since legislation regulating such practices are diffuse or nonexistent.

A number of researchers have studied the absorption of heavy metals by vegetables grown on sludge-fortified soils and the factors affecting the extent of absorption. Leafy vegetables have been found to absorb among the highest concentrations of Cd when grown on sludge-amended soils (Chaney and Giordano, 1977). The concentrations of Cd and Zn in Swiss chard leaves have been found to approximate the concentrations of these elements extractable from sludge-amended soil by using diethylenetriaminepentaacetic acid (Hornick et al., 1976). The effect of soil pH is an important factor. Cadmium in Swiss chard (Chaney et al., 1976) and Zn in several vegetables (Chaney, 1973) attained higher concentrations when grown on sludge-fortified soils which were more acidic. The ratio of Cd to Zn in sludge has also been shown to affect Cd absorption by vegetables. As the ratio increased, Swiss chard (Page, 1976) and other vegetables (Giordano and Mays, 1976) were shown to accumulate proportionately more Cd. Cadmium has been shown to accumulate in a number of sludge-grown vegetables to very high levels such that the crop yields were reduced 25%. Yet the crops showed no outward signs of phytotoxicity (Bingham et al., 1975). Cu, Ni, and Pb have also been shown to increase in certain instances when vegetables were grown on a sludge-fortified soil (pH 6.4) but less consistently than in the case of Cd and Zn (Giordano and Mays, 1976). However, when a sludge several-fold higher in Ni was used to fortify a soil (pH 5.3), the resultant vegetables were consistently higher in Ni than control vegetables (Furr et al., 1976a). In general, the availability of Cu, Ni, and Pb in soils increases as soil pH decreases.

Little has been reported on the extent of uptake of heavy metals by vegetables grown repeatedly on the same sludge–soil mixture at different pH values. Little is known about the uptake of heavy metals by fruit trees under these conditions. In a study of the absorption of metals by vegetables grown on a soil fortified with sludge from Ithaca, NY, at pH 7.1, Cu, Ni, and in some instances Cd concentrations decreased in specific crops grown the second year on the same sludge–soil mixture (Furr et al., 1976b) as compared to the levels of these elements in the crops grown the first year. In the work reported, the magnitude of uptake of Cd, Cu, Ni, Pb, and Zn by a variety of vegetables and apple trees grown successively for 2 years in potted soils amended with municipal sludge at pH values of 6.4 and 6.9 was studied.

EXPERIMENTAL SECTION

The sludge used was obtained from the Ley Creek Treatment Plant serving the northern portion of Syracuse, NY. This plant receives domestic wastes and that from ~100 industrial concerns. The industrial activities represented include plating, welding, foundry, printing, laundering, fat rendering, and manufacture of bearings, die castings, gears, tools, steel and electrical products, china, paper board, chemicals, wood preservatives, beverage, dairy, and other food products. Wastewater entering this plant is treated to yield an anaerobically digested, waste-activated sludge.

About a ton of the sludge was sampled, air-dried, sieved through a 6.4-mm mesh screen, and thoroughly mixed. The sludge had been produced a year earilier and remained outdoors, thus allowing time to leach out excess salts and for further microbiological decomposition of phytotoxic

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, and Departments of Pomology (D.C.E) and Vegetable Crops, Toxic Chemicals Laboratory (C.A.B., W.H.G., G.J.D., and D.J.L.), New York State College of Agriculture and Life Scienes, Cornell University, Ithaca, New York 14853.

0021-8561/81/1429-0156$01.00/0

constituents (industrial cutting oil, for instance). The sludge had a fertilizer equivalent of 0.88–1.12–0.12% N–P–K, a pH of 6.8, and an ash content of 52.4%. The soils used were Hinckley gravelly loamy sand (sandy-skeletal, mixed, mesic typic udorthents) (pH 4.9; cation-exchange capacity (CEC) 12.8 mequiv/100 g) and Teel silt loam (coarse-silty mixed mesic fluvaquentic eutrochrepts) (pH 7.1; CEC 13.9 mequiv/100 g). The bulk density of each soil was 1.04 g/cm^3. The soils were air-dried, sifted through a 2-mm screen, and thoroughly mixed. Ten percent (w/w) of the dry sludge was thoroughly mixed with each soil in a cement mixer. This would be approximately equivalent to 100 dry tons of sludge/acre (224 metric tons/hectare) assuming that the acre furrow slice (upper 20 cm of soil) weighs two million pounds (909 091 kg). Soil alone was used as the control. The pH values of the final sludge–soil mixtures as determined by the method of Peech et al. (1953) were 6.4 and 6.9 for the Hinckley and Teel soils, respectively.

The crops grown were McIntosh and Empire apple trees (*Malus domestica Borkh.*) grafted on MM. 106 rootstock, 680 Staddons Select green pepper (*Capsicum annuum*), White Vienna kohlrabi (*Brassica oleracea*), 506 Buttercrunch leaf lettuce (*Lactuca sativa*), 158 Frosty pea (*Pisum sativum*), 769 Winter Bloomsdale spinach (*Spinacia oleracea*), Jewel sweet potato (*Ipomoea patatas*), and American Purple Top turnip (*Brassica rapa*). All of the crops were grown in 2-gal plastic pots containing 7.5 kg of soil except apple trees and sweet potatoes which were planted in 3-gal pots containing 11.4 kg. The number of plants grown in each pot were as follows: apple tree, 1; green pepper, 1; kohlrabi, 5; lettuce, 20; pea, 6; spinach, 20; sweet potato, 1; turnip, 5. All treatments were replicated 4 times. All plants were watered daily, care being taken to avoid splashing soil on aerial portions of plants. All plants were fertilized weekly with a solution containing reagent grade KH_2PO_4 (0.001 M) and KNO_3 (0.005 M) (Hoagland and Arnon, 1950); 500 mL was added to the 2-gal pots and 1000 mL to the 3-gal pots.

At maturity the crops were harvested. Only the edible plant portions of the vegetables were sampled for analysis. The leaf lettuce was harvested at ~2-week intervals throughout the growth period and the successive portions combined before subsampling for analysis. Fruit, seeds, twigs, and leaves of apple were sampled. No fruit was produced by the McIntosh trees during the second year, only by the Empire variety. Prior to analysis all crop protions were thoroughly rinsed with distilled water to remove adhering dust. Sweet potatoes and turnips 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 with stainless steel surfaces. The sample material was then freeze-dried in polystyrene containers, mixed, and subsampled for analysis.

A second planting of the vegetables was made in the same pots of soil. After harvesting at the end of the first summer, the pots of soil or sludge–soil were emptied, all remaining nonedible plant parts and soil lumps were broken up, and the entire mass was repotted. The contents were kept moist for 2 months and then stored in an unheated greenhouse during the following 6 winter months. The following spring the potted contents were again emptied, broken up, repotted, and planted with the same crop as in the previous year. The plants were similarly watered and fertilized during culture the second year.

A subsample of the sludge was analyzed for 38 elements by using nondestructive neutron activation analysis as previously described (Furr et al., 1975). In addition, B, Cd, Cu, K, N, Ni, P, Pb, Se, and Zn were determined by other methods. The determination of Cd, Pb, Zn, and Cu 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, Ni was determined by furnace atomic absorption using a Perkin-Elmer Model 303 spectrophotometer equipped with an HGA-2000 furnace. Selenium was determined by a modification of the fluorometric method of Olson (1969). Boron and phosphorus were determined respectively by the curcumin and molybdivanadophosphoric acid spectrophotometric procedures (Greweling, 1966). Potassium was determined by flame emission spectrometry and nitrogen by the Kjeldahl method.

Table I. Total Elemental Content of Sludge

element	ppm (dry wt)	element	ppm (dry wt)
Ag	33	Mg	8881
Al	31340	Mn	395
As	116	Mo	7.2
Au	0.3	N	8800
B	12	Na	8701
Ba	266	Ni	169
Br	9.3	P	11200
Ca	62580	Pb	653
Cd	81	Rb	54
Ce	67	Sb	6.5
Cl	2173	Sc	1.3
Co	5.1	Se	1.1
Cr	111	Sm	12
Cs	1.8	Sn	870
Cu	1112	Sr	1479
Dy	6.3	Ta	0.9
Eu	2.7	Th	13
Fe	10710	Ti	1376
Hf	5.2	U	2.1
Hg	4.9	V	42
I	35	W	18
In	2.0	Yb	1.0
K	1200	Zn	4127
La	19		
Lu	13		

Table II. Total Content of Selected Heavy Metals in Soils

	ppm (dry wt) in	
element	Hinckley soil (pH 4.9)	Teel soil (pH 7.1)
Cd	0.2	0.3
Cu	9.9	16
Ni	2.8	23
Pb	7.2	14
Zn	44	70

RESULTS AND DISCUSSION

The results of elemental analysis of the sludge is shown in Table I. In Table II are listed total concentrations of selected heavy metals in the soils which are typically found at elevated levels and are of concern in municipal sludges.

Tables III and IV list concentrations of Cd, Cu, Ni, Pb, and Zn, found in the edible portions of the vegetables when grown successively for 2 years in control or sludge-amended soil in pots. Without exception, all of the vegetables grown during both years on either the acid or neutral soil amended with sludge showed higher concentrations of Cd, Cu, Ni, and Zn than the corresponding control soil. The results for lead were variable. When comparing crops, lettuce and spinach absorbed the highest concentrations of Cd, Cu, and Zn during both years when grown on either

Table III. Heavy Metal Concentrations in Edible Portions of Vegetables Grown in Pots on Sludge-Amended Acid Soil[a]

	concn, ppm (dry wt)													
	green pepper		kohlrabi		lettuce		peas		spinach		sweet potato		turnips	
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
							First Year Crops							
Cd	0.3	1.5	0.3	2.0	1.0	47	0.1	0.3	2.0	32	0.1	0.2	0.2	1.7
Cu	3.8	8.1	0.9	4.5	3.3	9.6	3.4	5.7	8.0	17	2.4	5.4	0.8	3.3
Ni	0.4	2.3	0.9	5.3	0.6	3.0	1.7	5.3	1.0	3.9	0.3	1.2	0.7	3.0
Pb	0.6	0.5	0.7	0.7	2.0	1.3	0.1	0.1	1.9	1.5	0.2	0.2	2.3	0.8
Zn	12	18	45	86	34	363	42	55	318	724	8.5	19	66	74
							Second Year Crops							
Cd	0.2	2.0	0.2	1.6	3.8	27	0.04	0.2	1.3	11	0.1	0.4	0.3	3.1
Cu	5.8	11	1.5	6.5	6.7	8.7	4.6	8.2	4.2	12	3.4	5.2	2.7	7.2
Ni	0.3	1.3	1.0	1.7	2.1	2.1	4.1	6.0	1.2	2.3	0.2	0.7	0.7	1.5
Pb	0.4	0.4	0.5	0.5	1.3	1.5			0.9	1.7	0.9	0.5	0.9	0.7
Zn	11	19	22	53	65	195	49	59	113	294	4.9	9.9	26	69

[a] Hinckley gravelly loamy sand.

Table IV. Heavy Metal Concentrations in Edible Portions of Vegetables Grown in Pots on Sludge-Amended Neutral Soil[a]

	concn, ppm (dry wt)													
	green pepper		kohlrabi		lettuce		peas		spinach		sweet potato		turnips	
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
							First Year Crops							
Cd	0.1	0.5	0.04	1.6	0.6	42	0.01	0.1	1.0	20	0.02	0.1	0.1	1.0
Cu	7.4	12	1.3	11	6.8	17	3.8	13	7.9	17	2.5	6.1	1.3	7.0
Ni	0.4	1.5	0.2	1.1	0.8	1.7	1.3	2.4	0.7	3.0	0.1	0.5	0.2	0.9
Pb	2.9	0.5	0.5	0.4	1.2	1.2	0.3	0.1	1.3	1.3	0.3	0.3	0.6	0.7
Zn	14	20	10	51	37	281	33	60	149	405	6.3	9.0	8.4	30
							Second Year Crops							
Cd	0.1	1.9	0.1	1.5	0.6	14	0.02	0.1	0.6	7.8	0.02	0.3	0.2	2.4
Cu	7.1	9.6	1.3	4.3	6.5	9.3	6.1	9.1	5.3	11.1	4.6	5.9	1.8	7.8
Ni	0.5	0.8	0.3	1.3	0.8	1.4	2.5	2.8	1.0	2.6	0.1	0.4	0.1	1.2
Pb	0.6	0.4	0.5	0.6	1.3	1.2			0.8	0.9	0.3	0.4	0.6	0.6
Zn	12	15	7.5	28	47	125	36	56	64	273	5.4	8.0	9.0	57

[a] Teel silt loam.

soil containing sludge. The concentrations of these elements in lettuce and spinach when grown on sludge diminished appreciably during the second year.

In nearly all instances Cd, Ni, and Zn were higher in the crops grown on the sludge-amended acid soil than the corresponding crops grown in the sludge-containing neutral soil. This trend continued during both years. Cd, Ni, and Zn are known to be more available to plants as soil pH decreases. Conversely, Cu was generally higher in crops grown in the sludge-amended neutral soil than the acid soil containing sludge, particularly during the first year. Since copper is known to be strongly complexed by organic matter, it is possible that the more rapid microbial decomposition of organic material at the more neutral soil pH released the element for plant absorption. In general, Ni and Zn in the crops decreased in concentration during the second year of growth on sludge as compared to the corresponding crops during the first year. This was true in the case of both soils. Since dietary Zn has a protective effect against Cd deposition in animal tissues, it has been proposed that the Cd/Zn ratio in crops in this study would exceed this ratio.

Table V lists the concentrations of heavy metals found in apple tree tissues. With the exception of Pb, growth of the trees on sludge resulted in an increased concentration of heavy metals in the various tree parts. The absorption of metals such as Cd, Cu, and Ni by white spruce and sycamore trees grown on soil receiving sludge or municipal wastewater has been reported (Lepp and Eardley, 1978; Sidle and Sopper, 1976). In general, crops grown in pots where the roots are confined to the growth medium under study would expectedly absorb higher concentrations of metals than in the field where roots would typically penetrate untreated subsoil. This might be particularly true of deep-rooted trees but would depend on the depth of sludge incorporation since the bulk of a tree's root surface is located in the upper 1–2 ft of soil. In general, there did not appear to be outstanding varietal differences between Empire and McIntosh apple seedlings as regards metal absorption when comparing corresponding treatments.

There did not appear to be a consistent effect of soil pH on the uptake of the metals by the trees. As with the vegetables, Ni and Zn tended to show a decrease in concentration in the sludge-grown trees during the second year. In the case of the sludge-grown trees, Cu and Zn tended to concentrate in the twigs while Ni and Pb concentrated in the leaves. The concentration of metals appeared comparatively low in the Empire apple fruit. None of the plants exhibited symptoms of phytotoxicity. Wilcoxon's signed rank test (Steel and Torrie, 1960) was used to detect real differences in metal concentrations between paired treatments (Table VI).

The data obtained further support previous findings that leafy vegetables such as lettuce or spinach absorb inordinately high concentrations of heavy metals such as Cd,

Table V. Heavy Metal Concentrations in Apple Tree Parts When Grown in Pots of Control or Sludge-Amended Acid or Neutral Soils

	concn, ppm (dry wt)									
	Emp[a] leaves		Emp twigs		Emp fruit[b]		Mc[c] leaves		Mc twigs[d]	
element	control soil	sludge soil	control soil	sludge soil	control soil	sludge soil	control soil	sludge soil	control soil	sludge soil
	First Year Crop (Acid Soil)									
Cd	0.1	0.1	0.05	0.1			0.1	0.1	0.08	0.2
Cu	5.0	7.5	4.0	17			4.0	7.3	5.3	15
Ni	1.1	2.3	0.3	1.5			0.9	2.2	0.9	2.0
Pb	3.1	3.7	1.2	3.3			3.2	3.4	1.6	2.4
Zn	15	59	19	65			24	44	22	61
	Second Year Crop (Acid Soil)									
Cd	0.1	0.1	0.05	0.1	0.01	0.03	0.1	0.1	0.1	0.1
Cu	4.0	5.3	4.3	15	2.8	4.1	3.1	6.8	4.5	16
Ni	0.9	2.2	0.7	1.0	0.2	0.1	1.0	2.1	0.9	0.7
Pb	7.3	6.4	0.8	1.3	2.0	2.5	9.6	6.9	1.1	1.2
Zn	11	42	16	70	1.6	1.6	12	26	21	54
	First Year Crop (Neutral Soil)									
Cd	0.1	0.1	0.02	0.1			0.05	0.1	0.02	0.1
Cu	5.4	6.2	6.0	12			5.9	7.0	6.8	13
Ni	0.9	2.7	0.3	2.5			1.1	2.3	0.7	1.2
Pb	3.9	3.2	0.9	2.3			3.7	4.2	1.7	2.8
Zn	16	54	13	55			17	54	18	54
	Second Year Crop (Neutral Soil)									
Cd	0.1	0.1	0.02	0.1	0.03	0.02	0.1	0.1	0.03	0.1
Cu	3.5	5.6	5.7	15	1.2	2.5	4.0	6.4	7.4	15
Ni	0.8	2.4	0.6	0.9	0.1	0.4	0.8	1.8	0.7	1.0
Pb	6.7	8.0	1.1	1.2	0.3	1.5	6.8	6.3	0.9	1.2
Zn	12	23	12	61	0.7	0.9	10.2	22	16	45

[a] Empire. [b] Fruit was produced during second year only. [c] McIntosh. [d] No McIntosh apple fruit resulted.

Table VI. Metals Which Were Significantly Different ($p < 0.01$) in Concentration in the Plants When Comparing Specific Treatments

	metals			
	first year		second year	
treatment comparison	vegetables	apple trees	vegetables	apple trees
metals higher in plants grown on sludge–acid soil vs. control	Cd, Cu, Ni, Zn	Cu, Ni, Pb, Zn	Cd, Cu, Ni, Zn	Cu
metals higher in plants grown on sludge-neutral soil vs. control	Cd, Cu, Ni, Zn	Cu, Ni, Zn	Cd, Cu, Ni, Zn	Cu, Ni, Zn
metals higher in plants grown on sludge-acid soil vs. sludge–neutral soil	Cd, Ni[a]	Cu	Cd, Zn	Zn
metals higher in plants grown on sludge-acid soil in either year	none	Cu, Ni	none	none
metals higher in plants grown on sludge-neutral soil in either year	none	Ni	Cu	none

[a] Cu was significantly higher in vegetables grown on the sludge–neutral soil mixture as compared to the sludge–acid soil during the first year.

Zn, and Cu when grown on municipal sludge amended soils and are particularly to be avoided for growth if sludges high in these elements are used on horticultural land. The data also showed that elements such as Cd, Ni, and Zn were more available for absorption by the sludge-grown vegetables as soil pH decreased. Liming sludge-amended soils to a more neutral pH is thus to be recommended. The effect of soil pH on the magnitude of absorption of these elements by the control vegetables was variable. Nickel and Zn most consistently decreased in concentration in the vegetables and apple tree tissue during the second year of growth. In some crops Cd appeared to be less available during the second year. Data obtained by Baker et al. (1976) and Bates et al. (1975) with corn and ryegrass, respectively, grown on the same soils receiving repeated annual sludge applications indicated that plant absorption of Cd was more dependent on the equivalent amount of the element applied during a specific year than on the cumulative quantity applied. This implies that Cd is undergoing continual conversion to less available forms in the soil.

ACKNOWLEDGMENT

We thank I. S. Pakkala, R. D. Lahr, R. Sheldrake, H. G. Knight, R. Gunnip, J. C. Civiletto, and H. J. Arnold for their assistance during this investigation.

LITERATURE CITED

Baker, D. E.; Amacher, M. C.; Doty, W. T. *Proc. Annu. Waste Management Conf., 8th* **1976**.

Bates, T. E.; Haq, A.; Soon, Y. K.; Moyer, J. A. *Proc. Int. Conf. Heavy Metals Environ.* **1975**.

Bingham, F. T.; Page, A. L.; Mahler, R. J.; Ganje, T. J. *J. Environ. Qual.* **1976**, *5*, 57.

Browning, E. "Toxicity of Industrial Metals"; Butterworths: London, 1969; Chapter 9, pp 98–108.

Chaney, R. L. *Proc. Jt. Conf. Natl. Assoc. State Univ. Land Grant Coll.* **1973**, 129–141.

Chaney, R. L.; Giordano, P. M. In "Soils for Management and Utilization of Organic Wastes and Wastewaters"; Elliott, L.

F.; Stevenson, F. J.; Eds.; American Society of Agronomy: Madison, WI, 1977.
Chaney, R. L.; Hornick, S. B.; Simon, P. W. *Proc. Annu. Waste Management Conf., 8th* **1976**.
Furr, A. K.; Kelly, W. C.; Bache, C. A.; Gutenmann, W. H.; Lisk, D. J. *J. Agric. Food Chem.* **1976a**, *24*, 889.
Furr, A. K.; Kelly, W. C.; Bache, C. A.; Gutenmann, W. H.; Lisk, D. J. *Bull. Environ. Contam. Toxicol.* **1976b**, *16*, 756.
Furr, A. K.; Lawrence, A. W.; Tong, S. S. C.; Grandolfo, M. C.; Hofstader, R. A.; Bache, C. A.; Gutenmann, W. H.; Lisk, D. J. *Environ. Sci. Technol.* **1976c**, *10*, 683.
Furr. A. K.; Stoewsand, G. S.; Bache, C. A.; Gutenmann, W. H.; Lisk, D. J. *Arch Environ. Health* **1975**, *30*, 244.
Gajan, R. J.; Larry, D. *J. Assoc. Off. Anal. Chem.* **1972**, *55*, 727.
Giordano, P. M.; Mays, D. A. *Annu. Hanford Life Sci. Symp., 15th* **1976**.
Greweling, H. T. "The Chemical Analysis of Plant Tissue", Agronomy Department, Cornell University, Ithaca, NY, 1966, Mimeo No. 6622.
Hoagland, D. R.; Arnon, D. I. *Bull.—Calif. Agric. Exp. Stn.* **1950**, *No. 347*.
Hornick, S. B.; Chaney, R. L.; Simon, P. W., Agricultural Research Service, U.S. Department of Agriculture, Beltsville, MD, unpublished data, 1976.
Lepp, N. W.; Eardley, G. T. *J. Environ. Qual.* **1978**, *7*, 413.
Olson, O. E. *J. Assoc. Off. Anal. Chem.* **1969**, *52*, 627.
Page, A. L., Department of Soil Science and Agricultural Engineering, University of California, Riverside, CA, unpublished data, 1976.
Peech, M.; Olsen, R. A.; Bolt, G. H. *Soil Sci. Soc. Am. Proc.* **1953**, *17*, 214.
Sidle, R. C.; Sopper, W. E. *J. Environ. Qual.* **1976**, *5*, 419.
Steel, R. G. D.; Torrie, J. H. "Principles and Procedures of Statistics"; McGraw-Hill: New York, 1960; pp 402–3.
Walsh, L. M. "Application of Sewage Sludge to Cropland; Appraisal of Potential Hazards of the Heavy Metals to Plants and Animals", Agronomy Department, Iowa State University, Ames, IA 50011, Nov 22, 1976, Council for Agricultural Science and Technology, Report No. 64.

Received for review March 14, 1980. Accepted September 2, 1980.

Solubilities in the System Magnesium Oxide–Ammonia–Orthophosphoric Acid–Pyrophosphoric Acid–Water at 25 °C

A. William Frazier* and Ewell F. Dillard

Measurements were made of solubilities in the system $MgO-NH_3-H_3PO_4-H_4P_2O_7-H_2O$ at 25 °C. The maximum solubility of MgO was 0.16% at pH 5.30 but only 0.01% at pH 6.11. The addition of ammonium tripolyphosphate corresponding to 13% of the total P_2O_5 (40–42%) had a negligible effect on the solubility of magnesium in the system. However, the solubility of MgO in ammonium polyphosphate solutions will increase from 0.02 to 1.2% when the fluorine level increases from 0 to 2.7%. thus, magnesium contents above 0.02% MgO which can be obtained in liquid fertilizers appear to be mainly due to a fluoride complex; the presence of adequate fluorine can effectively increase the "saturation" limit of the MgO impurity above the level that is likely to be encountered in commercial wet-process phosphoric acids.

The most troublesome impurity in ammonium polyphosphate fluid fertilizers prepared from wet-process phosphoric acid is magnesium. It precipitates both as complex phosphate salts (Frazier et al., 1972, 1966) in otherwise clear liquid fertilizers and as gels and crystalline solids in suspensions, thereby altering grade and increasing the viscosity to unacceptably high values. Whereas the solubility of magnesium in ammonium polyphosphate liquids is significant in the absence of fluoride, liquids containing a limited quantity of fluoride ions have been shown to solubilize only ~0.01% MgO (Frazier et al., 1972). Consequently, a trend in liquid fertilizer research has been toward reducing the fluoride content to a very low level in wet-process acid prior to production of the liquid fertilizers. However, in the absence of fluorine, no quantitative limits have been determined for the solubility of magnesium in ammonium polyphosphate liquids. The results obtained from experimental and commercial fertilizer solutions in which $Mg(NH_4)_2P_2O_7{\cdot}4H_2O$ had precipitated are erratic because of the variable fluoride values encountered. Also, it has been theorized that tripolyphosphate will sequester magnesium, but the content of tripolyphoshate varies so greatly in high polyphosphate liquid fertilizers that if the effect is real, the saturation limit of magnesium would be governed more by this component than by any other factor. The answers to these questions required a study of the ammonium portion of the phase system $MgO-NH_3-H_3PO_4-H_4P_2O_7-H_2O$ at 25 °C. The significant results are now available for presenting the solubility diagram in the region of interest in fluid fertilizer technology.

Division of Chemical Development, National Fertilizer Development Center, Tennessee Valley Authority, Muscle Shoals, Alabama 35660.

EXPERIMENTAL SECTION

For the study of this five-component system, $MgO-NH_3-H_3PO_4-H_4P_2O_7-H_2O$, equilibrium mixtures were prepared from recrystallized $(NH_4)_3HP_2O_7{\cdot}H_2O$, reagent $NH_4H_2PO_4$, NH_4OH, and H_3PO_4. The water-soluble salt, $Mg(NH_4)_6(P_2O_7)_2{\cdot}6H_2O$, was prepared as the magnesium source. The initial solutions were adjusted to obtain the invariant-point solutions with which three ammonium phosphates and one magnesium ammonium phosphate, or two ammonium phosphates and two magnesium ammonium phosphates, were in equilibrium. The solutions were readjusted periodically so that the desired solid phases finally persisted in well-crystallized euhedral form, after which the mixtures were rotated in a water bath at 25.0 ± 0.1 °C for 3 weeks to ensure equilibrium. The equilibrated liquid phases then were sampled for analysis, and the solid phases were examined microscopically to confirm that the desired phases (Frazier et al., 1972, 1966) had been present throughout the entire equilibration period. The