

Multielement and Chlorinated Hydrocarbon Analysis of Municipal Sewage Sludges of American Cities

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■ An analytical survey of 68 elements, dieldrin, and polychlorinated biphenyls (PCB's) was conducted in municipal sewage sludges sampled during 1972-73 from 16 American cities using several instrumental methods. Unusually elevated concentrations of certain toxic elements were found in sludges

from specific cities. Relatively high levels of gold and mercury in sludge from San Francisco possibly derived from geochemical sources. Fluorine was high in several cities which fluoridate their water. PCB's were highest in sludge from Schenectady.

Municipal sewage sludges result from the treatment of city sewage wastes containing human excreta, residues from food, and sometimes lumber processing, and a galaxy of industrial chemicals. These latter chemicals may derive from the manufacture of paper, textiles, rubber, plastics, leather, paints, detergents, drugs, agricultural chemicals and electrical

equipment, processes such as printing, engraving and petroleum refining, operation of blast furnaces, foundries, smelters, plating processes and laundries, and a host of other human activities. Upward of 100 million tons of this material are produced annually in this country. Disposal of it has included ocean dumping, burning, disposal in landfills, and limited use on lawns, ornamentals, forests, and agricultural land. Since these latter methods may cause environmental pollution, other approaches have included studies of its possible conversion to fuels such as methane or oil or as a soil conditioner and fertilizer in horticulture and agriculture. In addition to its content of industrial organics, chlorinated insecticides and pathogens (1), toxic elements in it confound its safe use as a soil amendment for plant growth.

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Table I. Data Pertinent to Municipal Sludges Studied

City	Sewage plant	Wastewater treatment scheme	Sludge handling scheme	Chemicals added	Ultimate sludge disposal method
Atlanta, Ga.	Intranchment Creek	Trickling filter	Digestion, drying beds		Landfill, fertilizer-soil conditioner
Cayuga Heights, N.Y.	Cayuga Heights	Sedimentation	Digestion	Lime	Land disposal
Chicago, Ill.	Several	Activated sludge	Aerobic and anaerobic digestion, heat drying		"Vertigreen" fertilizer-soil conditioner
Denver, Colo.	Metropolitan Denver, District #1	Activated sludge	Aerobic and anaerobic digestion, concentration and filtration	Ferric chloride, lime	Land disposal
Houston, Tex.	Southwest and Northside	Activated sludge	Aerobic and anaerobic digestion, dehydration		"Hou-actinite" fertilizer-soil conditioner
Ithaca, N.Y.	Ithaca	Trickling filter	Digestion, vacuum filtration	Ferric chloride, lime	Landfill, soil conditioner
Los Angeles, Calif.	Joint Water Pollution Control	Sedimentation	Digestion, centrifugation, drying beds	None	Fertilizer-soil conditioner
Miami, Fla.	Virginia Key	Aeration, sedimentation	Concentration, digestion, shallow lagoons	None	Fertilizer-soil conditioner
Milwaukee, Wis.	Several	Activated sludge	Aerobic and anaerobic digestion, heat drying		"Milorganite" fertilizer-soil conditioner
New York, N.Y.	Newtown Creek	Activated sludge	Thickening tanks, digestion	None	Ocean disposal
Philadelphia, Pa.	Northeast	Activated sludge	Digestion lagooning	None	Ocean disposal
San Francisco, Calif.	Richmond-Sunset	Sedimentation	Thickening tanks, digestion, elutriation, vacuum filtration	Ferric chloride	Parks, gardens
Schenectady, N.Y.	Anthony Street	Sedimentation	Digestion, vacuum filtration, heat drying	Ferric chloride, lime	"Orgro" fertilizer-soil conditioner
Seattle, Wash.	West Point	Sedimentation	Digestion, vacuum filtration or centrifuging		Landfill or soil conditioner
Syracuse, N.Y.	Metropolitan	Sedimentation, Activated sludge	Digestion	None	Pumped to Solvay Process waste beds
Washington, D.C.	Blue Plains	Sedimentation	Digestion	None	Land disposal

Table II. Concentrations of Elements and Chlorinated Hydrocarbons Found in Various Municipal Sludges

Constituent	Analytical method used	Parts per million (dry weight) in sludge from:																
		Atlanta	Cayuga Hgts.	Chicago	Denver	Houston	Ithaca	Los Angeles	Miami	Millwaukee	New York	Philadelphia	San Francisco	Schenectady	Seattle	Syracuse	Washington, D.C.	Cow manure
Dieldrin	EC ^a	0.26	<0.03	0.24	0.16	0.28	0.06	0.44	0.43	0.05	...	2.2	0.06	0.04	0.10	0.05	...	<0.01
PCB ^b	EC	3.80	0.79	11.60	1.60	0.35	4.30	4.00	8.50	2.20	...	4.80	<0.01	23.10	0.50	6.60	...	<0.01
As	S ^c	3.6	3.0	29	14	20.4	4.8	26.0	10.0	3.3	8.0	16.2	∞6.4	21.9	30.0	26.0	...	4.0
Au	NA ^d	0.90	1.00	0.77	0.25	1.04	0.50	0.99	5.65	0.21	1.46	0.48	7.00	2.00	1.10	0.34	...	0.0002
B	S	22	30	44	30	36	40	90	33	30	50	44	22	33	40	32	...	23.5
Ba	NA	535	272	623	632	485	1004	1066	938	344	417	533	542	828	504	322	...	268
Be	ES ^e	<15	<7	<6	<10	<4	<7	<11	<5	<4	<12	<7	<5	<15	<7	<13	...	0.10
Bi	SSMS ^f	13.3	8.7	55.8	17.4	49.0	15.2	10.8	31.0	14.0	7.6	10.2	4.5	0.03	8.2	6.6	...	16.0
Br	NA	37.1	13.7	41.3	15.3	30.2	20.0	53.2	165	16.4	123	35.9	48.2	33.2	44.1	24.8	...	31.0
Cd	ASV ^g	104.2	6.8	14.8	46.1	111.8	66.7	171.4	149.6	443.7	29.7	192.4	8.5	22.4	64.0	200.0	...	0.8
Ce	NA	92.8	12.4	34.9	43.9	26.3	18.6	272	63.1	26.2	70.7	30.5	14.2	15.8	37.0	48.6	...	55.0
Co	NA	9.4	3.9	3.7	8.8	6.3	10.5	16.8	17.6	4.3	6.2	15.6	5.3	15.6	9.4	5.1	...	5.9
Cr	FAA ^h	1320	169	207	936	3480	640	4925	1430	14000	646	2320	1500	458	1320	1000	...	56
Cs	NA	1.40	1.00	0.91	1.23	0.76	0.98	0.99	0.56	0.45	0.85	1.60	0.99	0.66	0.90	1.01	...	1.48
Cu	FAA	1463	821	578	1370	1560	1300	2890	1200	1288	1890	2680	900	900	1170	1060	...	62
Dy	SSMS	4.3	1.5	3.5	0.8	2.6	19.8	17.0	0.6	7.2	1.7	1.2	3.9	0.7	1.3	4.2	...	1.0
Er	SSMS	1.3	0.4	0.2	1.2	0.6	2.3	4.5	0.7	2.0	0.5	0.6	0.9	0.4	0.4	1.4	...	0.7
Eu	SSMS	4.4	0.7	2.5	2.4	9.4	0.8	9.9	1.9	12.2	2.0	0.7	3.7	0.8	1.0	3.4	...	0.7
F	SSMS	370.5	314.9	297.6	48.0	13.8	88.2	198.8	86.4	49.5	5.1	281.2	738.7	5.2	2.2	9.1	...	6.6
Ga	SSMS	17.1	8.7	9.2	8.9	24.1	51.7	54.0	0.9	27.9	12.3	12.4	3.3	5.7	10.2	6.6	...	16.5
Gd	SSMS	7.0	1.1	3.4	2.7	4.5	19.8	22.7	2.8	17.5	6.5	1.5	4.1	1.8	2.5	4.0	...	1.5
Ge	SSMS	1.3	2.0	1.6	10.5	4.2	6.2	6.4	2.6	5.4	4.3	1.5	1.5	1.1	1.7	3.6	...	19.1
Hf	NA	3.0	1.6	2.2	3.7	2.0	10.7	2.7	1.0	1.8	1.5	2.9	1.3	7.0	3.7	3.3	...	4.9
Hg	FL ⁱ	6.9	10.8	6.1	3.6	3.8	13.6	7.1	15.5	3.4	15.0	4.7	18.0	9.1	8.2	6.4	...	0.2
Ho	SSMS	0.48	0.13	0.07	0.41	0.21	0.46	0.51	0.67	0.38	0.53	0.18	0.28	0.14	0.09	0.31	...	0.36
I	NA	3.1	8.2	14.8	14.3	7.6	7.4	17.1	7.7	10.3	11.8	10.8	3.6	1.0	2.0	4.0	...	4.6
In	NA	0.08	0.23	0.10	0.18	3.7	0.26	0.17	1.30	0.07	0.16	0.58	0.08	0.12	0.20	0.48	...	1.40
Ir	SSMS	0.10	0.21	0.03	0.13	0.10	0.46	0.16	0.26	0.20	0.05	0.07	0.18	0.04	0.05	0.20	...	0.14
La	NA	29.6	6.4	11.5	9.3	10.9	11.9	380	7.1	33.9	14.1	13.4	5.1	7.6	9.7	12.8	...	23.7
Lu	NA	0.25	0.06	0.09	0.06	0.08	0.15	0.09	0.04	0.04	0.24	0.14	0.08	0.11	0.14	0.12	...	0.60
Mn	NA	267	128	95	224	102	527	116	32	134	152	95	113	235	350	216	...	286
Mo	NA	6.0	1.2	10.8	18.1	9.8	21	40	37	32.9	5.0	8.1	2.2	25.5	2.3	4.5	...	13.9
Nd	SSMS	2.0	1.1	3.4	2.6	2.2	3.2	3.3	1.4	8.6	1.1	1.5	2.0	0.6	0.6	3.8	...	2.5
Ni	FAA	169	36.4	51.2	562	102	166	402	453	360	140	432	223	72	153	211	...	29
Os	SSMS	0.29	0.19	0.07	0.20	3.18	1.35	0.47	0.15	0.59	0.08	0.09	0.17	0.06	0.06	0.22	...	0.10
Pb	ASV	1445	136	605	1011	2236	329	3065	1467	2253	1976	7627	2521	598	2411	1412	...	16.2
Pd	SSMS	5.2	0.5	11.7	5.6	11.2	5.2	13.5	2.6	16.2	1.1	0.8	3.9	0.32	0.9	2.1	...	3.8
Pr	SSMS	3.7	4.9	3.1	3.3	2.7	3.5	119	5.3	15.8	4.2	1.4	2.5	1.6	1.1	7.1	...	10.7
Pt	SSMS	0.10	0.23	0.07	0.25	0.20	0.64	0.44	0.12	0.38	0.11	0.74	0.18	0.08	0.05	0.18	...	0.14
Rb	NA	46.2	28.7	31.1	46.4	18.3	25.7	19.3	4.5	4.3	32.7	30.9	25.1	43.0	24.3	46.1	...	88.9
Re	SSMS	0.05	0.12	0.03	0.12	0.09	0.21	0.98	0.07	0.19	0.05	0.04	0.09	0.04	0.03	0.10	...	0.06
Ru	SSMS	0.58	0.52	0.21	1.31	7.05	3.19	0.87	0.94	0.27	0.30	1.01	2.08	0.22	0.27	0.51	...	0.38
Sb	NA	14.6	2.6	4.4	3.5	9.9	5.9	14.3	14.8	4.2	10.6	44.4	5.2	9.1	10.8	5.4	...	10.6
Sc	NA	7.1	1.5	2.0	1.6	1.2	1.7	1.1	0.5	0.8	3.1	2.8	2.2	2.1	5.2	2.1	...	5.7
Se	F ^j	1.7	1.7	1.7	3.5	...	4.6	8.7	2.9	1.7	2.7	3.4	3.0	4.7	2.7	2.1	...	2.4

Element	NA	5.0	1.0	3.1	2.0	2.2	1.4	14.2	1.4	1.5	6.7	2.6	1.1	1.5	2.0	2.0	8.3	5.2	
Sm	NA	146	128	166	161	234	111	209	289	133	202	492	133	189	373	191	291	3.8	
Sn	NA	42	68	259	262	138	67	360	259	94	334	322	176	224	186	210	...	81	
Sr	NA	0.53	0.18	0.20	0.35	0.36	0.43	1.2	0.33	0.11	0.49	0.66	0.31	1.45	0.41	0.92	0.58	0.38	
Ta	SSMS	0.89	0.40	0.73	1.20	0.49	4.26	4.83	2.23	3.65	0.50	0.34	0.91	0.38	0.27	0.44	...	0.29	
Tb	SSMS	0.09	0.22	0.11	0.45	0.37	1.52	0.54	0.12	0.36	0.10	0.25	0.05	0.07	0.21	0.17	...	0.22	
Te	NA	12.8	3.1	5.6	4.6	...	11.1	7.0	2.3	2.6	7.8	6.5	3.5	4.4	3.9	5.6	16.3	...	
Th	NA	4580	1080	2380	1340	1680	2160	3170	2360	1580	2050	2680	1910	1960	2560	1550	4260	2800	
Ti	SSMS	0.49	0.13	0.07	0.65	0.11	0.78	0.78	3.31	0.68	0.11	0.37	1.0	0.08	0.06	0.32	...	0.14	
Tm	NA	0.8	1.2	6.4	6.4	2.9	4.8	3.4	3.7	2.1	1.0	0.9	2.0	3.3	3.2	3.0	1.6	2.4	
U	NA	50.4	18.8	48.7	34.1	26.6	14.8	35.7	34.8	22.9	53.9	38.4	35.4	36.7	57.3	50.1	91.5	43.2	
V	NA	5.1	0.9	4.2	5.6	41.1	17.7	14.7	22.9	9.5	10.5	32.1	5.1	99.6	21.1	15.3	3.3	2.5	
W	SSMS	3.7	10.1	1.5	4.9	4.1	4.3	5.5	0.9	7.7	4.2	2.1	3.7	0.8	1.1	3.6	...	2.8	
Y	NA	1.30	0.40	0.61	0.33	0.36	0.42	0.57	0.17	0.29	0.74	0.64	0.62	0.61	0.52	0.40	1.6	1.78	
Yb	NA	2838	560	1160	2860	2560	1700	4590	1400	1370	1340	6890	601	1090	1830	1840	1475	71	
Zn	SSMS	18.1	12.7	22.3	31.6	39.6	319	86.6	16.6	14.4	5.4	11.1	15.8	92.1	4.8	37.1	...	5.5	
Zr	...	3.47	0.97	1.36	1.34	0.81	1.83	1.74	0.91	0.81	1.29	2.34	1.44	1.21	2.70	1.91	5.12	2.88	
Al	NA	2.70	11.64	2.53	1.55	0.77	5.45	4.01	4.28	0.86	1.61	1.99	1.07	7.93	2.64	6.55	2.40	26.4	
Ca	NA	0.05	0.29	0.10	0.39	0.66	0.20	0.39	1.02	0.22	0.85	0.11	0.61	0.39	0.22	0.28	0.34	0.18	
Cl	NA	2.42	1.74	0.88	8.28	3.23	5.74	2.07	0.95	4.30	2.12	1.99	3.05	3.46	2.71	1.44	4.50	1.59	
Fe	NA	0.56	0.29	0.72	3.87	0.27	0.38	0.47	0.29	0.84	3.30	1.39	2.80	0.42	1.56	1.59	0.71	3.29	
K	NA	1.13	0.50	0.54	0.33	0.20	0.32	0.57	0.75	0.50	0.60	0.61	0.63	0.81	0.82	0.67	0.55	0.73	
Mg	NA	2.45	1.48	3.99	3.14	5.43	1.62	2.19	3.34	5.80	...	2.30	2.16	1.81	2.62	2.07	1.25	1.25	
N	K ^a	0.15	0.17	0.36	0.18	0.11	0.08	0.68	1.19	0.16	1.54	0.27	0.30	0.20	0.88	0.60	0.11	4.92	
Na	NA	1.40	0.96	1.60	1.32	1.60	2.72	2.08	1.66	1.84	...	1.92	1.16	1.02	1.80	1.40	...	0.90	
P	S	57.3	57.7	49.5	37.8	31.5	58.9	43.2	39.7	30.9	46.7	53.2	41.4	59.4	56.7	51.8	...	63.5	
Ash

^a Electron capture gas chromatography. ^b Determined as Aracor 1254. ^c Spectrophotometric. ^d Neutron activation. ^e Emission spectroscopy. ^f Spark source mass spectrometry. ^g Anodic stripping voltammetry. ^h Furnace atomic absorption. ⁱ Flameless atomic absorption. ^j Fluorescence. ^k Kjeldahl.

Municipal sludges may contain virtually any element depending on the spectrum of industries served, their changing rates of production, and periodic relocation. Analytical surveys of a few to several toxic elements in sludges have been conducted in England (2), Canada (3), and the United States (4-6). In the work reported, an analytical survey of 68 elements, dieldrin, and polychlorinated biphenyls (PCB's) was conducted of sewage sludges from various American cities.

Experimental

In 1972 and 1973 a description of our proposed study was sent to 35 cities with a request that they participate and return a representative sample of their sludge to us for analysis. The cities which responded and the data they provided pertaining to their sludge treatment are listed in Table I. Cayuga Heights is a small village just north of Ithaca. Its sludge is almost entirely composed of domestic waste. The cow manure sample was obtained as a dehydrated bagged commercial product of Agway, Inc. It was considered pertinent to compare the element composition of cow manure as an accepted soil amendment with that of municipal sludges. The sludge samples were air-dried, mixed in a Lucite twin shell blender, and subsampled for analysis.

The determination of dieldrin and PCB's was performed by Soxhlet extraction, isolation using acetonitrile partitioning and column chromatography on Florisil (7). Final determination was made by electron affinity gas chromatography using a column 6 ft long containing 10% OV-17 on 80-100 mesh Gas Chrom Q operated at 220 °C.

Analysis for elements by nondestructive neutron activation was carried out. Weighed samples were placed in 0.4-dram polyethylene vials (1.5 cm i.d. × 2 cm high). The samples were irradiated three times, once for a short period in a pure thermal flux to eliminate induced Si activity leading to ²⁸Al (which varied depending on Na and Cl content but on the order of 1 min) and again in a mixed fast and thermal flux for a comparably brief period, and finally for a period of approximately 8 h. The neutron fluxes to which the samples were exposed were respectively 4 × 10¹⁰ n/m²-s, 1.2 × 10¹² n/cm²-s, and 1.3 × 10¹² n/cm²-s for the long irradiation. After the short irradiations, the samples were counted within a few minutes on a Ge(Li) counting system for a period of 8 min. Data were acquired using a Nuclear Data Model 4420 multichannel analyzer and stored on magnetic tape for later processing. For the long irradiations, the samples were first counted as soon as practical, considering the level of the activity due to sodium. This period of time varied from 2 to 5 days after the end of the irradiation. The samples were counted again after a period of 15-20 days. Each sample, therefore, was irradiated three times and counted four times.

The counts stored were in the form of gamma spectra containing peaks which could be attributed to the gamma emissions from the radioactive constituents in the samples. For some elements, only a single peak represents the element, whereas in other cases two or more isotopes with possibly several gammas could be employed for quantitative measurements. Repeated tests have demonstrated the capability of the computer program to accurately fit the peaks with a gaussian curve, or in some cases overlapping gaussian curves, situated on a background usually represented by a quadratic polynomial, although for very narrow peaks the background can be represented by a linear function. For quantitative measurements, peak areas are compared to results obtained with known standards, usually well-known chemical compounds or pure elements, but on other occasions to documented samples.

Recently, for example, well-known geologic materials and coal samples obtained from the Bureau of Standards have

been processed with agreement well within the accepted range of variability being found for nearly every element detected. To ascertain that continued quality be maintained, groups of three compounds of selected elements are periodically processed with the identity of the elements being changed each time. In the group of test elements processed, nearest to the experiments reported here (Na, Mg, Al, Ti, Cr, Mn, Cu, Mo, Cd, Sn, Ta, W, U, Zn, Se, and Sb), no net variance exceeding 5% compared to the previous standard values was found, and most were within 1–2%. However, in a few cases, individual compounds or specimens were unsuitable for use as standards.

Since the comparison library has been run under exactly comparable conditions, for all the elements, using the same reactor operated at the same power or flux levels and counted under the same geometric conditions at closely similar levels of activities, the quality of the data should be essentially limited only by the statistical variance introduced by the relative size of the peaks employed and the background on which the peaks are superimposed. However, in a few cases not enough data on possible interference peaks can be derived from the sample data and in such cases (e.g., for Ni), the interference potential is considered so great that no reliable values can be quoted.

Other methods of analysis which were employed required preliminary ashing of the samples. Up to 1 g of sample was dry ashed at 475 °C by the method of Gajan and Larry (8).

Spark source mass spectrometric analysis was performed using a subsample of the ash. The ash was thoroughly mixed with an equal weight of high-purity graphite (Ultra Carbon Corp., 1M-VSP outgassed ultra superior purity) by the usual method (9). The electrodes were sparked against each other under the following conditions: repetition rate: 100 pulses/s; pulse length: 100 μ s; source pressure: 1×10^{-7} torr while sparking with cryosorption pumping; ion accelerating voltage: 22 kV. Ilford Q-2 photoplates were used as an ion detector. Results were calculated and corrected by the method of Owens and Giardino (10). The lead content of the sludges (as determined by anodic stripping voltammetry) was used as an internal standard for the method.

Emission spectroscopy was performed using a Bausch and Lomb dual grating spectrograph with a Model RC-2 Baird atomic microphotometer. The standards consisted of high-purity (99.999%) oxides of Si, Al, Ca, Fe, and Mg spiked with 12.7, 25.4, 63.5, and 127 μ g/g of the 49 element Spex Mix (1.27% each element). Unspiked matrix served as a blank. The standards and the ashed samples were mixed 1:9 with UCP-2 graphite containing 0.01% GeO₂. These were fired in duplicate using a DC arc. A Stallwood Jet with 70% argon and 30% oxygen atmosphere surrounded the crater electrode.

Cadmium and lead were determined by conventional stripping voltammetry using a Princeton Applied Research Corp. Model 174 polarographic analyzer (8). Chromium, copper, and nickel were determined by furnace atomic absorption using a Perkin Elmer Model 303 spectrophotometer equipped with an HGA-2000 furnace. Mercury was determined by flameless atomic absorption analysis following combustion of the dry sample using an oxygen flask (11).

The determination of selenium was accomplished by a modification of the method of Olsen (12) employing wet digestion of the sample and measurement of the fluorescence of piaszelenol resulting from reaction of selenium with 2,3-diaminonaphthalene. Boron was determined by the curcumin spectrophotometric procedure (13). Arsenic was determined by distillation of arsine and determination using the silver diethylthiocarbamate spectrophotometric procedure (14, 15). Phosphorus was determined by the molybdivanadophosphoric acid spectrophotometric method (13). Nitrogen was determined by the Kjeldahl method.

Results and Discussion

The results of analysis of the sludge samples are listed in Table II. Except for potassium which appears elevated (above 2%) in several of the sludges, the range of concentrations of boron, cadmium, copper, chromium, lead, mercury, nickel, nitrogen, phosphorus, and zinc reported here agrees with those for these elements in typical municipal sludges (16).

Some interesting observations are also apparent. The relatively high level of PCB's in sludge from Schenectady may derive from the predominant manufacture of electrical equipment there. Gold is especially high in the Miami and San Francisco sludges. The San Francisco sludge was produced at the Richmond-Sunset Treatment Plant receiving mainly domestic wastes. The gold may in part originate from its presence as colloidal gold in the natural waters of the cities' watershed area. Notably, mercury is also high in these same two sludges. Mercury and gold are often found in association (17), and gold and mercury mining has abounded in the San Francisco area. Of course, mercury in sludge also results from its many industrial applications.

Several cities' sludges are also high in fluorine. As well as industrial contributions of the element, its presence in sludges could also derive from municipal fluoridation of water and elevated natural levels of the element in various geographical areas. Cities such as Chicago, Denver, Miami, Milwaukee, Philadelphia, and San Francisco fluoridate the water supply (18). The natural fluoride concentrations in city water supplies along the northeastern seaboard average from 0.02 to 0.1 ppm (19), whereas in midwestern, western, and southern states the average is above 0.2 ppm (20, 21).

A number of elements are notably high in sludges from specific cities. These include antimony (Philadelphia), barium (Ithaca and Los Angeles), cadmium and chromium (Milwaukee), copper and lead (Philadelphia), nickel (Denver, Los Angeles, Miami, Milwaukee, and Philadelphia), tin (Philadelphia), uranium (Chicago and Denver), zinc (Los Angeles and Philadelphia), and zirconium (Ithaca). The sources of some of the rarer elements such as cerium, gallium, germanium, hafnium, lanthanum, praseodymium, scandium, samarium, and others are speculative. Industrial uses are one source. Shacklette et al. (22) in an extensive national survey reported soils in the United States to contain the following concentrations of elements: gallium (<5–70), lanthanum (<30–200), and scandium (<5–50). Relatively high concentrations of rare earth elements have been reported in many plants (23–26). Complexation of rare earth ions by organic chelates in soils has been suggested as a mechanism leading to their availability to plants (27). A large number of rare earth elements were recently reported at surprisingly high concentrations in aquatic plants (28). Germanium found at a concentration of 19.1 ppm in the cow manure sample in this study has been reported to be absorbed from soils by cereal crops and to be rapidly excreted by animals (29).

When considering the application of municipal sludges to agricultural soils, availability of specific elements to edible plants must be considered. Of the elements which have been studied, arsenic, barium, chromium, fluorine, lead, and mercury tend to be excluded by plants. Boron, cadmium, cobalt, copper, manganese, molybdenum, nickel, selenium, zinc, and possibly antimony tend to be absorbed (30, 31). Many factors control ion uptake, however, such as soil type, pH, organic matter, redox potential, and plant species. It is also important to remember that municipal sludge from largely domestic sources may also be unsafe for agricultural uses since a major portion of copper, cadmium, chromium, nickel, and zinc in wastewater can derive from domestic uses (32).

In summary, interpretation of the data presented here would be obviated if specific municipal sludges could be

monitored periodically rather than just once. As pointed out in the introduction, municipal sludges are highly variable in composition with time and location of sampling for the reasons given. If we assume a sludge sample is representative, a broad-range multielement analysis can be quite revealing, and the data obtained are crucial in deciding what the ultimate means of safe and hopefully useful sludge disposal is to be.

Acknowledgment

The authors thank Corning Glass Works and Exxon Research and Engineering Co. for the use of their facilities and instrumentation.

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Received for review October 2, 1975. Accepted January 27, 1976.

Industrial Waste Disposal. Excess Sulfuric Acid Neutralization with Copper Smelter Slag

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■ An economic process for the disposal of two industrial waste products, sulfuric acid and copper reverberatory slag, has been developed. Metal values are effectively extracted from the slag, and acid is consumed in a nonpolluting way. The

process is a leach lime roast procedure that consumes 1 ton of acid per ton of slag while permitting extraction of 85% of the copper and zinc. Ninety percent of the sulfur is retained, and a solid storable product is produced.

Production of sulfuric acid is the most important method for removing sulfur oxides from copper, lead, and zinc smelter gases. The requirement to meet emission standards, which in some states is being established at 90% removal of input sulfur to the smelter, has necessitated expansions of the contact acid plants at many nonferrous sulfide smelters. It appears, therefore, that sulfuric acid production from smelters will be significant for some years. There are several new potential

processes under development and evaluation (1-4), but the present significant investment in acid plants under construction denotes a tremendous growth in sulfuric acid production from nonferrous smelters in the future (5).

Of the sulfur entering the smelters in 1960, 387 000 tons (20%) were removed as sulfuric acid; in 1970, 600 000 tons (26%) of sulfur from smelter feed were recovered as acid (5). If growth continues as expected and the 90% sulfur recovery criteria are met, 2 598 000 tons of sulfur as sulfuric acid, or other forms of by-product sulfur, are anticipated by 1980 from smelters alone. Furthermore, as more sulfur and its compounds are recovered in the future from coal and petroleum

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