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Element Composition of Municipal Refuse Ashes and Their Aqueous Extracts from 18 Incinerators

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There are approximately 70 operating municipal refuse incinerators in the United States presently and about 250 more in the planning or construction phase. Paper, wood, plastics, rubber, leather, textiles, food and yard wastes comprise the bulk of the combustible refuse burned. Non combustible materials also introduced into incinerators include glass, ceramics, ferrous and non ferrous metals, ash, dirt and rock. Toxic elements and organics in stack emissions as well as in collected fly ash and bottom ash are the main environmental concerns.

Depending on factors such as water temperature, the pH of the ash and the chemical nature of the compounds present, a portion of the elements in the ash dissolves in the spray and quench water used in incinerators. This can affect the concentration of such elements in wastewater reaching sewage treatment plants. Also, since most refuse incinerator ash is disposed in landfills, resultant downward leachates can contaminate groundwater. It was of interest therefore to determine the solubility of elements in such ashes. In the work reported here, ashes from about one fourth of the operating incinerators in the United States were obtained, extracted with water and the quantity of 20 elements and nitrate was determined in the ashes and the aqueous extracts.

MATERIALS AND METHODS

During 1987, about 15 kg of ash were obtained from each of 18 municipal refuse incinerators throughout the United States. The samples included fly ash, bottom ash and mixtures of both. (Fly ashes and bottom ashes are mixed after collection in some incinerator plants to lower the concentration of specific toxicants usually in the fly ash and thereby permit its disposal in landfills). The total material was air-dried at room temperature. Fly ashes were mixed by tumbling. In the case of bottom ashes or fly ash-bottom ash mixtures, stones, metal, glass or ceramic objects were removed and the remaining material was pulverized to pass through a 5-mesh (4 mm openings) screen and then reduced to a fine powdery consistency in a hammermill. This material was then mixed by tumbling.

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Depending on their bulk density, 5 to 15 grams of each ash was Soxhlet-extracted for 8 hours with 100 ml of distilled, deionized water. The aqueous extract was evaporated to 1 ml in a Kjeldahl flask, 2 ml of 70% perchloric acid was added and the solution was refluxed for 90 minutes to oxidize soluble organic matter. The digest was made to a volume of 10 ml of water and analyzed for 19 elements by inductively coupled plasma emission spectrometry. Similarlty, 1 gram of each of the ashes was wet ashed with nitric and perchloric acids and the same 19 elements were determined in the digests. The instrument used was a model 975 Jarrell Ash inductively-coupled plasma spectrometer equipped with a nonadjustable cross-flow nebulizer. The limits of detection of the method in units of element weight per gram of ash extracted are given in Table 1. Total nitrogen was determined by the Kjeldahl method. Nitrate was determined by the hydrazine reduction and phenoldisulfonic acid colorimetric method (Methods of Soil Analysis, 1965).

Table 1. Limits of detection of the ICP emission spectrometric method for elements in the ash samples.

Weight of element per gram of ash extracted									
Al	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn
γ[a]	mg[b]	γ	γ	γ	γ	γ	mg	mg	γ
0.2	0.0005	0.01	0.01	0.01	0.06	0.02	0.01	0.00003	0.006

Table 1 (continued)

Weight of element per gram of ash extracted							
Na	Ni	P	Pb	S	Si	Y	Zn
mg	γ	γ	γ	mg	γ	γ	γ
0.00006	0.03	0.05	0.10	0.10	0.50	0.01	0.006

[a] Micrograms
[b] Milligrams

RESULTS AND DISCUSSION

The total concentrations of elements found in the refuse ashes are listed in Table 2. Aluminum, Ca, Fe, K, Mg, Na and S are consistently major elements in these ashes. There does not appear to be any consistent relation between the type of ash and the content of specific elements. The great variability in element composition among the ashes attests mainly to the wide variety of material which comprises municipal refuse as a function of time and probably to some extent the variation in operating parameters among incinerators. The pH of the ashes are mainly alkaline which has also been reported by Vogg (1987).

The quantities of elements and nitrate extracted from the ashes with water are given in Table 3. There appears to be little

Table 2. Total concentrations of elements in the refuse ashes.

Ash			Cd	Co	Cr	Ni	Y	Al	Ca	Cu	Fe
Code	Type	pH	ppm					per cent			
A	FA[a]	7.3	159	73.3	272	101	10.8	9.54	7.48	0.05	1.54
B	FA	12.5	10.0	nd[b]	111	139	50.8	9.00	9.16	0.02	7.98
C	FA	4.2	2.42	nd	328	166	51.9	10.0	3.11	0.22	12.7
D	FA	8.4	600	55.9	305	52.7	6.54	6.53	7.37	0.09	1.26
E	FA	10.6	16.5	nd	127	130	70.7	11.0	1.75	0.02	9.32
F	BA[c]	11.3	2.56	44.7	443	223	9.51	5.80	7.86	0.11	2.34
G	BA	7.9	13.1	55.7	628	362	5.54	4.71	5.52	0.14	2.96
H	BA	12.5	3.80	5.77	362	189	8.23	4.73	8.58	0.18	4.91
I	BA	9.5	1.78	6.14	367	169	9.88	5.38	6.06	0.14	4.78
J	BA	7.4	513	44.3	308	154	6.30	4.17	5.76	0.08	2.69
K	BA	9.5	0.57	nd	489	333	5.40	4.67	7.23	0.15	7.53
L	BA	7.9	105	33.1	621	246	15.0	7.18	7.94	0.12	4.74
M	FA-BA[d]	8.2	17.3	52.4	354	51.4	3.08	2.52	2.04	0.03	0.80
N	FA-BA	8.4	6.57	14.9	132	28.4	2.06	1.60	2.08	0.03	0.40
O	FA-BA	8.7	28.3	31.6	339	147	4.67	5.40	3.64	0.10	2.50
P	FA-BA	9.3	19.8	10.6	442	408	8.38	5.17	7.15	0.14	5.22
Q	FA-BA	9.1	32.0	48.1	515	222	5.96	5.12	4.69	0.09	4.26
R	FA-BA	9.7	3.00	nd	547	235	4.85	4.94	7.22	0.21	11.7
S	FA-BA	10.2	2.15	69.6	221	66.2	9.57	15.2	7.34	0.09	1.55
T	FA-BA	9.8	33.5	30.2	350	150	4.61	5.37	8.03	0.34	3.15

Table 2 (continued)

Ash	K	Mg	Mn	N	Na	P	Pb	S	Si	Zn
code	per cent									
A	2.71	1.29	0.15	nd[e]	4.92	0.53	0.89	1.78	0.09	1.01
B	1.01	1.41	0.06	nd	1.33	0.34	0.19	1.57	0.14	0.15
C	1.71	0.67	0.03	nd	1.09	0.37	0.09	2.09	0.11	0.14
D	7.83	1.04	0.09	nd	5.09	0.77	0.49	2.32	0.16	1.31
E	2.21	0.66	0.02	nd	0.36	0.03	0.01	0.85	0.09	0.02
F	1.14	1.35	0.07	nd	4.44	0.32	0.20	1.04	0.10	0.16
G	0.78	0.72	0.06	0.38	2.52	0.31	0.37	1.15	0.32	0.44
H	1.24	0.86	0.13	nd	1.68	0.35	0.62	1.68	0.08	0.33
I	1.42	1.08	0.13	0.25	2.10	0.48	0.12	1.12	0.32	0.34
J	2.24	0.81	0.08	0.10	3.20	0.42	1.62	2.10	0.09	2.59
K	0.79	0.86	0.11	0.14	2.87	0.44	0.11	1.27	0.52	0.42
L	1.92	1.26	0.15	nd	2.31	0.60	0.91	1.72	0.15	0.88
M	0.42	0.39	0.04	0.89	0.62	0.15	0.07	0.82	0.07	0.66
N	0.53	0.25	0.03	0.45	0.80	0.15	0.04	0.55	0.01	0.23
O	0.57	0.46	0.07	0.16	2.60	0.22	0.08	0.72	0.11	0.19
P	0.87	1.11	0.09	0.17	3.70	0.45	0.40	1.32	0.25	0.31
Q	0.89	0.96	0.08	0.24	2.07	0.31	0.20	1.18	0.05	0.38
R	0.74	0.91	0.08	0.03	3.37	0.40	0.10	1.40	0.79	0.23
S	1.62	1.66	0.10	nd	3.07	0.44	0.01	1.15	0.97	0.05
T	0.54	0.64	0.09	nd	2.80	0.24	0.24	1.44	0.69	0.39

[a] Fly ash

[b] Not detectable

[c] Bottom ash

[d] Fly ash-bottom ash mixture

[e] Less than 0.03%

Table 3. Quantities of elements and nitrate extracted from the refuse incinerator ashes.

		Weight of element per gram of ash extracted								
Ash	Al	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn
Code	γ^{a}	mg^{b}	γ	γ	γ	γ	γ	mg	mg	γ
A	50.1	7.76	35.3	2.17	1.49	1.40	nd	1.80	0.59	1.54
B	17.8	4.54	nd	0.32	0.25	0.29	nd	0.32	nd	nd
C	6.09	1.18	1.28	1.76	0.34	0.66	94.3	0.07	0.79	23.8
D	15.1	1.56	221.6	1.20	0.80	2.06	0.50	1.07	0.55	0.74
E	29.9	0.90	nd	nd	0.22	0.19	nd	0.37	nd	0.04
F	58.0	0.68	0.01	0.10	0.08	0.95	nd	0.10	nd	nd
G	8.27	1.88	nd	nd	0.06	0.30	nd	0.35	0.15	0.99
H	69.7	1.50	0.01	0.03	0.08	0.09	0.15	0.28	nd	nd
I	33.2	1.50	0.05	0.12	0.13	0.32	nd	0.46	0.01	0.01
J	24.2	2.71	87.5	0.59	0.55	1.34	0.32	1.05	1.12	8.67
K	19.9	1.36	0.63	0.01	0.11	0.22	0.16	0.40	0.01	0.04
L	6.63	1.22	0.46	0.02	0.11	0.27	0.17	0.30	0.07	1.39
M	21.8	1.53	nd	nd	0.20	0.70	nd	0.85	0.12	4.55
N	38.0	3.59	nd	nd	0.35	1.31	nd	3.08	0.06	0.21
O	78.4	0.60	nd	nd	nd	0.23	nd	1.07	0.01	nd
P	13.8	0.79	nd	nd	0.10	0.62	0.93	0.35	0.11	0.17
Q	83.3	2.69	0.03	nd	0.01	0.67	nd	1.00	0.06	0.09
R	171.7	1.18	nd	0.01	0.10	0.44	nd	0.38	nd	nd
S	281.9	1.02	0.05	0.09	0.33	0.38	nd	0.20	nd	nd
T	315.8	1.60	nd	0.09	0.12	0.74	nd	0.32	nd	nd

Table 3 (continued)

	Weight of element per gram of ash extracted								
Ash	Na	Ni	NO_3^-	P	Pb	S	Si	Y	Zn
code	mg	γ	γ	γ	γ	mg	γ	γ	γ
A	34.3	0.49	41.2	10.0	0.36	3.18	1.49	0.20	5.11
B	1.32	0.09	16.7	4.5	0.14	1.21	13.6	0.03	0.29
C	1.94	7.66	21.9	4.7	nd	0.72	0.87	0.11	59.0
D	22.5	0.10	30.5	4.3	3.13	7.49	17.1	0.06	7.69
E	0.19	nd	14.1	1.0	nd	0.83	3.77	0.01	0.21
F	0.28	0.06	7.7	0.0	0.10	0.26	0.59	0.02	0.11
G	0.73	0.36	20.8	3.4	nd	0.18	11.3	0.03	0.79
H	1.71	nd	15.4	2.5	nd	0.68	2.77	0.01	0.14
I	3.37	0.13	18.0	3.2	0.27	1.17	4.78	0.03	0.23
J	19.0	0.21	21.8	8.8	4.89	5.67	18.6	0.05	2.60
K	1.85	0.03	17.3	2.8	0.33	0.57	1.63	0.02	0.41
L	0.35	nd	8.4	1.9	0.58	1.13	5.00	0.02	0.51
M	1.55	nd	16.5	10.0	nd	0.72	27.1	0.06	1.35
N	10.9	nd	24.6	5.4	nd	1.59	31.4	0.10	1.63
O	4.54	nd	20.7	3.1	nd	0.28	9.87	0.03	0.48
P	0.66	0.16	16.4	11.0	nd	0.86	3.83	0.01	0.47
Q	2.75	0.13	30.7	1.6	1.27	1.92	9.03	0.02	0.11
R	2.04	nd	15.3	0.0	nd	1.16	1.69	0.02	0.14
S	0.64	nd	18.3	1.3	nd	1.02	3.07	0.02	0.29
T	1.50	nd	17.1	0.9	0.20	1.04	1.37	0.01	0.16

[a] Micrograms [b] Milligrams [c] Not detectable (see Table 1)

relation between the total concentration of specific elements in the ashes or their pH and the quantities of elements extracted from them by water. Some observations are noteworthy. Iron, Mn, Ni and Zn were all relatively high in the water extract of ash C which was the most acidic ash and dissolution of these elements would be favored by low pH. Sodium and K were relatively high in both total concentration in ashes A, D and J and in their respective aqueous extracts. Likewise, Cd in ashes D and J and Zn in ash J were high in concentration both in the ashes and the corresponding extracts.

The forms of elements in refuse ashes may include soluble salts, metal oxides, precipitates and many other complex inorganic and organic forms varying greatly in solubility. They may also be adsorbed in exchangeable and nonexchangeable forms to particiculate surfaces or associated with mineral lattices. Wadge and Hutton (1987), using specific extractants showed that Cd and Pb in refuse fly ash were mainly associated with the exchangeable fraction whereas in coal fly ash they were mostly present in mineral lattices. Cadmium and Pb are typically much higher and more water-soluble in refuse fly ash than coal fly ash. Austin and Newland (1985) showed that Cd, a surface-adsorbed element and Mn associated with the fly ash matrix, were more easily dissolved from refuse fly ash than from lignite fly ash. Therefore observations of possible relationships between total and water extractable elements in such ashes may be entirely fortuitous.

The metals and other elements present in the spray and quench waters of municipal refuse incinerators (Law 1977; Law and Gordon 1979) may be removed (Reimann 1987) or discharged to wastewater treatment plants. A knowledge of chemical composition of aqueous leachates of municipal incinerator refuse ashes is most pertinent to their disposal in landfills. The quantities of metals and elements extracted from the ashes in this study by Soxhlet extraction with distilled water would most closely simulate continuous leaching by rain of refuse ash disposed in a shallow layer in a landfill reserved exclusively for such ash disposal. The typically high pH of refuse incinerator ashes tends to inhibit the dissolution of metals contained in it. It has been shown that leaching refuse ashes with leachate that has already passed through municipal waste dissolves more metals than when distilled water is used which becomes rapidly alkaline (Francis and White 1987). The municipal waste leachate extractant at pH 6.0 - 6.5 and probably buffered, would therefore more closely simulate conditions in an actual landfill where both refuse and refuse incinerator ash are codisposed. Leachates from a landfill where the refuse ash alone is disposed being higher in pH would expectedly contain much lower concentrations of metals. The effect of increasing and decreasing metal solubility in ashes by respectively lowering and raising the pH of the leachate has been reported by others (Riemann 1987; Behel et al. 1986).

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