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Received for review February 21, 1978. Accepted October 16, 1978. Research was undertaken while the author was a Divisional Research Fellow in the Division of Geological and Planetary Sciences, California Institute of Technology, and with ship time provided by the San Francisco Bay project of the U.S. Geological Survey. Additional financial support was provided by Department of Energy Contract No. EY-76-S-02-3292 to the Chesapeake Bay Institute, Johns Hopkins University. CBI Contribution No. 265. Contribution No. 2784 of the Division of Geological and Planetary Sciences, California Institute of Technology.

Sources of Metals in Municipal Incinerator Emissions

Stephen L. Law*

Department of the Interior, Bureau of Mines, Avondale, Md. 20782

Glen E. Gordon

Department of Chemistry, University of Maryland, College Park, Md. 20742

■ Data from the U.S. Department of the Interior, Bureau of Mines, and the University of Maryland on metal concentrations in municipal solid waste and in incinerator residues have been examined in three different ways to distinguish between combustible and noncombustible sources of the metals in the bottom ash, fly ash, and atmospheric particles from a municipal incinerator. Silver, Cd, Cr, Mn, Pb, Sn, and Zn were found to be derived from the noncombustible components of refuse as well as from the combustibles. Eight of the other 13 metals examined may also have significant noncombustible sources. Separation of the combustible components of municipal solid waste prior to use as a fuel should reduce the concentrations of these metals in the effluent streams from combustion processes.

Suspended-particle emissions to the atmosphere from municipal incinerators have been shown to be significant contributors to the Cd, Sb, Zn, and, possibly, Ag, In, and Sn in the aerosols of urban areas (*1, 2*). Stack particles from a municipal power plant were found to contain higher concentrations of Be, Cd, Pb, and Zn when a mixture of 50% refuse-derived fuel (RDF) and 50% coal was burned in place of coal only (*3*). Emissions of Hg and Se, however, were observed to decrease during these same studies (*3*). In a similar study, Jackson and Ledbetter (*4*) found that Pb emissions on stack particles increased about 20- and 40-fold relative to pure coal when 1:1 and 2:1 RDF/coal mixtures were burned in a stoker-fired boiler. The ultimate source of metals in the atmospheric and aqueous emissions and in the ash materials of any municipal refuse combustion process is the urban refuse being burned. With the current trend toward energy recovery from municipal solid waste (MSW), the identification of possible sources of pollutants will be an important first step in achieving pollution control and environmental acceptance. The interests of the Nuclear and Atmospheric Chemistry group of the University of Maryland in environmental pollutants and of the Department of the Interior, Bureau of Mines, in resource recovery from waste materials were combined in this study of municipal incinerator residues to arrive at some insights into the sources of the observed metals.

Urban refuse can be divided into two major components: a combustible fraction (paper, cardboards, plastics, fabrics, etc.) and a noncombustible fraction (ferrous metals, nonferrous metals, glass, ceramics, etc.). Most energy recovery systems will include the capability of separating MSW into the two components prior to burning the combustible fraction. A system of shredders, magnetic separators, trommels, screens, air classifiers, and cyclones not only can separate the combustibles from the noncombustibles, but will also result in the recovery of valuable iron, aluminum, and other nonferrous metals, glass, and perhaps other recyclable components (*5*).

Data are available on concentrations of various elements typically found in the combustible fraction of municipal solid waste (*6, 7*). Data have also been reported for the concentrations of metals in the ash materials being discharged after incineration as bottom ash and fly ash (*1, 2, 8, 9*), as airborne particles (*1, 2*), and dissolved in the aqueous effluents (*9, 10*). Although the data averages obtained from these references were not originally designed for source identification, they are used in this study to estimate the contribution of incinerated noncombustible sources to the concentration of several individual metals observed in the emissions of municipal incinerators, and to discover which elements warrant more specific study. Many of the metals of higher concentration observed in incinerator atmospheric emissions, e.g., Ag, Cr, Pb, Sn, and Zn, are metals that are used in surface coatings, galvanizing, solders, and similar surface applications where high temper-

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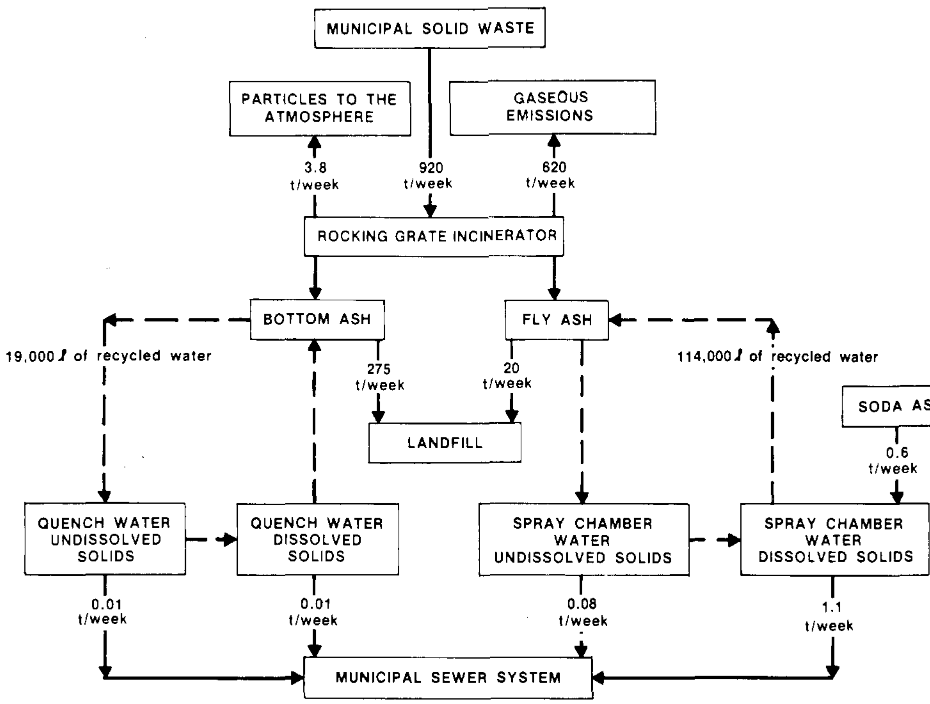

Figure 1. Flow diagram of a municipal incinerator. Flow rates of solids are given in tons/week on a dry-weight basis

atures could cause flaking and volatilization from bulk metal scrap (*1*).

Data Compilation

Incinerator Description. The principal emphasis of this study was on a local municipal incinerator designed to incinerate 270 metric tons (t) of solid waste daily in two 135-t/day rocking-grate, continuous-flow stoker furnaces. The three rocking grates of the primary combustion chamber in each furnace are fed through a large hopper. After the combustion process, the hot residues are dropped into a water-quench tank. Following quenching, the residues are carried by drag conveyor to a chute for loading onto disposal trucks.

Upon leaving the primary combustion chamber, the hot gases pass through a flue into a secondary combustion chamber and then into the fly-ash spray-baffle scrubber. Pressurized nozzles spray water down the baffle walls. The combustion gases pass through the two 90° turns in the baffle, causing some of the larger fly-ash particles to impinge upon the walls and become entrained in the flowing water. This water is pumped to a holding tank where the heavy solids are allowed to settle for removal by drag conveyor to trucks for landfill disposal.

The recycled fly-ash scrubber water becomes highly acidic during the incineration process because of the acidic gases formed: HCl, H_2SO_4, SO_2, and HF (*11, 12*). Soda ash is added continuously and automatically throughout the operating week at an average rate of 135 kg/day to neutralize this acidity to a pH of 4 to 7. The pH is checked every hour, and the rate of soda ash addition is adjusted as needed.

Disposition of Incinerated Solid Waste. Enough information was obtained to make an estimated mass-balance flow sheet for the disposition of the MSW being put into the incinerator system (*9*), as shown in Figure 1 (where flow rates of solids are given in dry weight/week). The input of MSW to the incinerator averages about 1230 t/week (*13*) less about 25% moisture (*14*). Solids leaving the incinerator each week are estimated at 410 t as bottom ash (*13*), containing about 33% moisture (*15*); 64 t as fly ash (*13*) less an estimated 70% moisture (*16*); 3.8 t (dry weight) as stack-emitted particles (*1*); 1.1 t (dry weight) as spray-chamber dissolved solids (0.6 t of which comes from the added soda ash) (*10*); 0.08 t (dry weight) as undissolved solids in the spray-chamber waters (*9*); and 0.01 t (dry weight) as dissolved solids in the quench waters (*9*). The estimate for total undissolved solids discharged each week in the spray-chamber and quench waters is based on the total volume of water discharged to the sewer system at the end of the week and the measured undissolved solids content of about 0.5 g/L in both waters at the time of discharge. The total dissolved solids content of the spray-chamber waters averaged 10 g/L at the time of discharge. The dissolved solids in the quench waters averaged 0.7 g/L at the time of discharge to the sewer. Based on the preceding approximations, a total of about 300 t/week (dry weight) of the initial refuse leaves the incinerator in some solid form. This leaves 620 t/week of the dry weight refuse unaccounted for. It is assumed in Figure 1 that this amount of material is emitted as gaseous products of the combustion process.

Table I. Composition of Typical Refuse [a]

product	% (by wt)	product	% (by wt)
ferrous metal	7.6	corrugated board	3.5
aluminum	1.1	paper	51.7
copper-base metal	0.06	putrescibles	4.4
zinc-base metal	0.14	glass	10.5
plastics	5.0	miscellaneous	0.9
leather and rubber	0.7	fine glass, grit, dirt, and ceramics	10.0
fabrics	1.8		
wood	2.6		

[a] Based on ref *11*.

Input Metals. Table I gives a breakdown of representative municipal refuse compositions as determined in a Bureau of Mines study (*11*). Urban refuse has a typical composition of ferrous metal, 7.6%; Al, 1.1%; Cu-base metal, 0.06%; Zn-base metal, 0.14%; glass, 10.5%; and fine glass, grit, dirt, and ceramics, 10.0%. The remaining 70.6% of the refuse shown in Table I is classified as combustible, but contains metals in the pigments, inks, stabilizers for plastics, clay fillers, whiteners, photosensitizers, and various other chemical compounds in addition to the natural metal concentrations in the raw ma-

Table II. Metals in the Combustible Fraction of Municipal Solid Waste [a]

element	concn, ppm average	concn, ppm range
Ag	3	<3–7
Al	9000	5400–12 000
Ba	170	47–450
Ca	9800	5900–17 000
Cd	9	2–22
Co	3	<3–5
Cr	55	20–100
Cu	350	80–900
Fe	2300	1000–3500
Hg	1.2	0.66–1.9
K	1300	920–1900
Li	2	<2–7
Mg	1600	880–2100
Mn	130	50–240
Na	4500	1800–7400
Ni	22	9–90
Pb	330	110–1500
Sb	45	20–80
Sn	20	<20–40
Zn	780	200–2500

[a] References *6* and *7*.

Table III. Pilot Plant Products Obtained from Typical Incinerator Residues [a]

product	% (by wt)
large ferrous metal	15.0
fine ferrous	5.0
aluminum	1.75
heavy nonferrous metal	0.75
clean glass	30.0
slag	25.0
fine ash and tailings from mineral jig and flotation cells	22.5

[a] Based on ref *11*.

terials used in the final commercial product.

The Bureau of Mines, at its Avondale Metallurgy Research Center in Maryland, is operating a pilot plant for the separation of the various components of MSW (*5*). This 4.5 t/h plant consists of shredders, magnetic separators, trommels, screens, air classifiers, cyclones, mineral jigs, and froth flotation cells. The combustible products collected in the three cyclones consist primarily of light paper and packaging materials together with plastic film and light fabrics. The heavier combustibles such as wood, leather, rubber, and heavy-gage plastics are concentrated in a heavy organic product from the secondary air classifier. Most of the food wastes and yard wastes are concentrated in the organic wastes separated out by the mineral jig. Elemental analyses of the separated combustibles from the cyclones, classifier, and mineral jig have been performed on MSW from Washington, D.C., Baltimore, Howard, and Montgomery Counties, Md., Tampa, Fla., and Tulsa, Okla. (*6, 7*). Average concentrations for 20 elements are shown in Table II. Concentration ranges for different batches of refuse are also shown, providing an indication of the caution that should be taken in arriving at conclusions based on the averages.

Metals in Incinerator Emissions. Solid waste residues discharged from an incinerator as "bottom ash" generally contain product components similar to those shown in Table III, which were obtained from another Bureau of Mines pilot plant at Avondale, Md., designed for the recovery of products from incinerator residues (*11*). Some residues used for the averaged composite data in Table III actually came from the incinerator used as a model for this study, and it is assumed that the percentages shown are typical for our model. Metal concentrations in the various products of incineration from the model incinerator are compiled in Table IV. The fine bottom ash data of Table IV represent the composition of the 22.5% fine ash fraction in Table III. Approximately 30% of the fine bottom ash material in Tables III and IV does not come from the combustible components of the refuse, but is probably slag, fine glass, dirt, etc. The average concentration for each element in each type of emission listed in Table IV includes a large standard deviation or range of concentrations. These uncertainties generally represent the standard deviations of sample variation and not analytical error.

Results

Metals Balance. The ideal experimental design for obtaining a metals balance would be to characterize several tons of refuse before incineration, followed by careful characterization of the combustion products of the same refuse after incineration. However, the use of available data averages will serve to "flag" those elements leaving an incinerator in quantities greater than could be expected from just the combustible components of refuse.

Using the information in Figure 1 and Table IV, an average weekly output of metals is estimated in Tables V and VI for each effluent from the incinerator. The output in the recycled waters of the incinerator used as a model is negligible for all elements except Ca, K, and Na, as shown in Table V. Table VI shows the total output including the data in Table V. No actual measurements of Hg emissions to the atmosphere were made on the model incinerator; however, a few limited measurements have been reported for other incinerators (*17*). Based on these very sparse data for Hg in MSW, an estimate was also made for the maximum Hg output that could come from the incinerator.

The total mass of each metal going into the incinerator in the combustible fraction of municipal solid waste is also listed in Table VI for comparison with total outputs. This estimate is based on the data in Table II and an average of 920 t (dry weight) of refuse being processed by the incinerator per week, of which 70% is assumed to be combustible. The input of Hg from the combustible fraction data (*6*) is seen to be equivalent to the total estimated atmospheric output derived from an independent data source (*17*). The combustible fraction also contains sufficient amounts of Al, Ca, Cu, Fe, K, Mg, Na, and Sb to account for the fine bottom ash, fly ash, atmospheric particles, and aqueous emissions of these metals. The metals not completely accounted for in the combustibles are Ag, Co, Cr, Mn, Ni, Pb, Sn, Zn, and, possibly, Ba, Cd, and Li, although the range of concentrations in combustibles for the latter three elements could adequately account for the emission concentrations. Some elements, notably Ca, Cu, and Na, have an average input from the combustibles that is a factor of 2 or more higher than the total output observed in the emissions listed in Table VI. These elements may be leaving the incinerator with the bulk scraps and slags comprising the approximately 77.5% of the bottom ash residues not included in Table VI. The value of Table VI is the indication of metal emissions in excess of amounts that could reasonably be expected from the combustible components alone.

Metals from Noncombustibles. The source of the metals in excess of the amounts in the combustible materials is postulated to be in the noncombustible materials. Except for Ba (9%), the noncombustible contribution appears to range from

Table IV. Metals in the Products of Incineration from a Municipal Incinerator

element	concentration, ppm				
				dissolved in aq effluents	
	fine bottom ash [a]	fly ash [b]	atmospheric particles [c]	quench water [d]	fly ash scrubber water [d]
Ag	38 ± 8	130 ± 30	390 ± 360	<0.1	<0.1–0.2 [e]
Al	49 000 ± 800	121 000 ± 12 000	16 000 ± 8000	<3	28 ± 24
Ba	1 400 ± 600	1 500 ± 400	890 ± 570	<4	<4
Ca	40 000 ± 18 000	23 000 ± 10 000	23 000 ± 1100	103 ± 34	840 ± 250
Cd	41 ± 15	64 ± 16	1 100 ± 400	<0.04	1.7 ± 0.9
Co	70 ± 10	100 ± 30	12 ± 7	<0.2	<0.2–0.5 [e]
Cr	520 ± 240	1 160 ± 720	490 ± 350	<0.2	<0.2
Cu	450 ± 190	510 ± 180	2 000 ± 1200	<0.1	<0.1–1.6 [e]
Fe	16 000 ± 6000	24 000 ± 8000	9 000 ± 3300	<0.3	<0.3
Hg	0.4	0.9 ± 1.7		<0.0002	<0.0002–0.005 [e]
K	6 300 ± 1400	12 200 ± 1800		32 ± 11	305 ± 97
Li	19 ± 3	34 ± 4		<0.1	0.31 ± 1.13
Mg	12 800 ± 2600	9 700 ± 1700	6 800 ± 2500	1.6 ± 2.4	115 ± 47
Mn	3 100 ± 1700	1 500 ± 600	1 500 ± 1400	<0.1	3.8 ± 2.8
Na	8 200 ± 1400	16 000 ± 2000	98 000 ± 28 000	72 ± 16	2320 ± 950
Ni	210 ± 250	1 800 ± 2800	200 ± 80	<0.4	<0.4
Pb	1 700 ± 800	7 200 ± 3200	97 000 ± 26 000	<1	15 ± 10
Sb	120 ± 90	340 ± 290	2400 ± 2400	<1.4	0.54 ± 0.37
Sn	400	1 250 ± 650	10 700 ± 1500	<4	<4
Zn	5 500 ± 1500	10 000 ± 2000	120 000 ± 60 000	<0.05–0.4 [e]	63 ± 35

[a] Does not include the bulk metal, glass, and other objects larger than about 3-mm diameter; based on ref *8*. [b] Reference *8*. [c] Reference *1*. [d] Reference *10*. [e] Range is given instead of standard deviation when concentrations of some samples were below detection.

Table V. Element Emissions in the Recycled Waters of a Municipal Incinerator

element	output, kg/week				
	dissolved solids		undissolved solids		
	spray waters	quench waters	spray waters	quench waters	total
Ag	0.01	<0.002	0.01	0.000 4	0.02
Al	3	<0.06	10	0.5	14
Ba	<0.5	<0.08	0.1	0.01	0.1
Ca	96	2	2	0.4	100 ± 30
Cd	0.2	<0.000 8	0.005	0.000 4	0.2
Co	0.02	<0.004	0.008	0.000 7	0.02
Cr	<0.02	<0.004	0.09	0.005	0.1
Cu	0.08	<0.002	0.04	0.005	0.1
Fe	<0.03	<0.006	2	0.2	2
Hg	0.0001	<0.000 04	0.000 07	0.000 004	0.0001
K	35	0.6	1	0.06	37 ± 11
Li	0.04	0.002	0.003	0.000 2	0.04
Mg	13	0.03	0.8	0.1	14
Mn	0.4	<0.002	0.1	0.03	0.5
Na	264	1	1	0.1	270 ± 110
Ni	<0.05	<0.008	0.1	0.002	0.1
Pb	2	<0.02	0.6	0.02	3
Sb	0.06	<0.03	0.03	0.001	0.1
Sn	<0.5	<0.08	0.1	0.004	0.1
Zn	7	0.002	0.8	0.06	8

a possible 25% for Cd to 89% for Sn. Sullivan and Makar, in their studies of the aggregate heavy nonferrous metal from both raw refuse and incinerator residues (*11*), made the following observation: "... the raw refuse product contains at least three times the amount of lead found in the incinerated product. A significant part of the lead apparently is oxidized during incineration and reports in the fine ash of the residues and the fly ash. Another difference is noted in the ratio of copper to zinc in materials from the two sources. In all probability, during incineration some of the zinc volatilizes and oxidizes, resulting in a significantly higher ratio of copper to zinc in the metal from incinerator residues."

Taking the percentage data given in the same report by Sullivan and Makar for raw refuse and for incinerator residues (*11*), and the flow rates given in Figure 1, the weekly exchange of metals in the noncombustible fractions during municipal refuse processing by the model incinerator has been estimated in Table VII. Any conclusions drawn from the data in Table VII are very tenuous; a definitive study would involve before and after measurements in the same batch of refuse being processed by an incinerator. Table VII uses averages, or the higher values where only ranges are given, from different incinerators. Nevertheless, the totals before and after incineration shown in Table VII give support to the probability of metals losses from the ferrous, the aluminum, and the heavy nonferrous fractions of refuse. Tables VI and VII both show

Table VI. Elemental Input-Output during One Week's Operation of a Municipal Incinerator

element	output, kg/week [a] fine bottom ash [b]	fly ash	atmospheric particles	total output [c]	input, kg/week from combustibles [d] average	range	not accounted for by combustibles [e]
Ag	2 ± 0.5	3 ± 0.6	1 ± 0.1	6 ± 1	2	<2–5	4
Al	3000 ± 50	2400 ± 240	60 ± 30	5500 ± 300	5800	3500–7700	
Ba	90 ± 40	30 ± 10	3 ± 2	120 ± 50	110	30–290	(10)[f]
Ca	2500 ± 1100	460 ± 200	90 ± 4	3200 ± 1300	6300	3800–11 000	
Cd	3 ± 1	1 ± 0.3	4 ± 2	8 ± 3	6	1–14	(2)[f]
Co	4 ± 1	2 ± 0.6	0.05 ± 0.03	6 ± 2	2	<2–3	4
Cr	32 ± 15	23 ± 14	2 ± 1	60 ± 30	35	13–64	25
Cu	28 ± 12	10 ± 4	8 ± 5	50 ± 20	230	50–580	
Fe	990 ± 370	480 ± 160	34 ± 13	1500 ± 540	1500	600–2300	
Hg	0.02	0.02 ± 0.03	~1[g]	1 ± 0.1	1	0.4–1.2	
K	390 ± 90	240 ± 40	~50[h]	720 ± 150	840	590–1200	
Li	1 ± 0.2	1 ± 0.1	~0.1[h]	2 ± 0.3	1	<1–5	(1)[f]
Mg	790 ± 160	190 ± 30	26 ± 6	1000 ± 200	1000	570–1400	
Mn	190 ± 110	30 ± 10	6 ± 2	230 ± 120	80	30–150	150
Na	510 ± 90	320 ± 40	370 ± 110	1500 ± 350	2900	1200–5000	
Ni	13 ± 15	36 ± 56	1 ± 0.3	50 ± 70	10	6–60	40
Pb	110 ± 50	140 ± 60	370 ± 100	620 ± 210	210	70–970	410
Sb	7 ± 6	7 ± 6	9 ± 9	20 ± 20	30	10–50	
Sn	25	25 ± 13	40 ± 6	90 ± 30	10	<10–30	80
Zn	340 ± 90	200 ± 40	460 ± 230	1000 ± 360	500	130–1600	500

[a] Based on the dry-weight flow rates of Figure 1. [b] The fine bottom ash is assumed to be 22.5% of the total quenched residues from incineration (Table III). Bulk scrap, cans, bottles, etc., are not included in the analyses. [c] Includes output from Table V. [d] Based on data from Table II. The combustibles are assumed to be 70% of the total 920 t shown in Figure 1. [e] Obtained by difference between the total output from the incinerator and the input from combustibles. [f] The range of concentration in the combustibles could easily account for these values. [g] Not actually measured. The gas-phase Hg and the Hg particles emitted to the atmosphere are estimated assuming 0.7 ppm Hg in MSW (*17*) and a maximum input to the incinerator of 920 t of refuse per week. [h] Not measured. The concentrations of K and Li in the atmospheric particles are assumed to be the same as in fly ash.

Table VII. Metals Estimated in the Noncombustible Fractions of Municipal Refuse before and after Incineration

metals in the separated fraction	estimated incinerator input-output, kg/week [a] before incineration: ferrous fraction	aluminum fraction [c]	heavy non-ferrous fraction	total	after incineration [b]: total	ferrous fraction [d]	aluminum fraction	heavy non-ferrous fraction
Al	1 100	7200	30	8 300	4 900	2	4800	50
Cr	20	20	NR[e]	40	20	20	2	NR[e]
Cu	260	70	710	1 000	1 300	140	30	1100
Fe	68 000	70	10	68 000	55 000	55 000	50	20
Mn	270	100	NR[e]	400	20	4	20	NR[e]
Ni	20	20	10	50	60	40	2	20
Pb	320	20	310	650	130	30	10	90
Sn	260	20	30	310	70	60	1	10
Zn	NR[e]	70	730	800	760	10	10	740

[a] Based on percentage data reported in ref *11* and the flow rates shown in Figure 1. [b] Bottom residues only. The 22.5% fine ash in Table III is not included. [c] The percentages for metals in this Al fraction are specifications for recovered aluminum; see Table 9 of ref *18*. [d] The estimated average percentages for metals in this ferrous fraction come from data in ref *19*. [e] NR, not reported.

the probability of a high percentage of the Cr, Mn, Pb, and Sn in the incinerator emissions coming from noncombustible materials. A noncombustible source for a portion of the Al, Fe, and Zn is also indicated by both sets of data. Table VI indicates that some of the Ag, Ba, Cd, Co, and Ni may also come from noncombustible sources. Table VII does not provide information for Ag, Ba, Cd, and Co and does not indicate any loss of Ni during incineration. In fact, Table VII indicates a gain of Ni and also of Cu during incineration, providing additional warning to users of these data that discretion is advised in establishing conclusions until experiments specifically designed to monitor noncombustible sources of metals in incinerator effluents have given more definitive results.

Concentration Ratios. A third approach to the identification of metals introduced into incinerator effluents by both noncombustible and combustible sources is to consider the ratios of the metal concentrations before and after burning. Absolute concentrations in incinerator residues will obviously be different from the concentrations in the unburned MSW, but the ratios of metal concentrations will often remain similar. If the ratio of one metal to another in the combustible fraction of MSW is observed to be significantly increased in the combustion products, the increase may be the result of additions from the noncombustible components of the MSW. This is especially true if the metal used for the normalized comparison is relatively unaffected by the combustion process, e.g., iron or aluminum. A similar technique has been in use for several years in attempts to determine the sources of particles in the atmosphere (*20*).

Calling this ratio of normalized metal concentrations an enrichment by noncombustibles factor (ENF), the ratio can be described by the following expression:

$$\mathrm{ENF} = \frac{(C_X/C_{Fe})_i}{(C_X/C_{Fe})_{\mathrm{combustibles}}}$$

where the Cs represent concentrations of element X and Fe in the combustion product i (bottom ash, fly ash, or particles emitted to the atmosphere) and in the average combustibles prior to incineration.

To obtain the data in Table VIII, the concentrations from Table IV of each element in the fine bottom ash, the fly ash, and the atmospheric particles were divided by the corresponding concentration of Fe in each residue. The same normalization to iron was made with the data for the combustible fraction of MSW using the data in Table II. The results (Table VIII) show the ratios of the two Fe-normalized concentrations and the magnitude of the differences between the unburned combustibles and the resulting residues from combustion. For elements for which ratios are close to or less than unity, e.g., Al, Ba, Ca, Cu, K, Li, and Mg, the contribution from noncombustible components is probably not significant. Mercury is a special case, as it is so volatile that it is undoubtedly vaporized out of all the fractions. It has been found that most of the Hg in coal entering coal-fired power plants leaves the stack in the vapor phase (*21*), which probably occurs also in incinerators. In cases of elements for which the ratios are high in all incinerator products, e.g., Ag, Cr, Mn, Ni, Sn, and Zn, the additional amount required to increase the ratio must come from the noncombustible components of the MSW. Some of the more volatile elements, e.g., Cd, Na, Pb, and Sb, show a slight depletion of concentration in the fine bottom ash and fly ash (except for Pb), but a very marked increase in the atmospheric particles. These elements may also be partially, or in the case of Pb significantly, derived from the noncombustibles. A decision regarding the contribution of noncombustibles to the concentration of an element showing ENF values both above and below unity must be made by examining the ENF values for all incineration residues and the relative amounts of each residue. For example, the ratio of Cd leaving the incinerator in each type of residue to Cd entering in the combustibles can be assumed to approximately equal the ENF values in Table VIII. The ENF value of 31 for Cd in the atmospheric particles (representing only 4% of the total mass of residues) is high enough to bring the overall Cd estimated output-to-input ratio to almost 2 even though the ENF is 0.7 for the fine bottom ash (72% of the total residue mass) and 0.7 for the fly ash (23%). Performing the same operations for the other elements, Pb is obviously coming from noncombustibles with an overall output-to-input ratio of 4, Sb must remain undecided with a ratio of 1, and Na has an overall ratio of only 0.5. Actual input–output numbers are given in Table VI, but Table VIII provides a means of arriving at the same conclusions using only concentration data rather than requiring total amounts.

Although volatility can be used to explain the depletion of some elements, e.g., Sb, Cd, and, especially, Hg, from the fine bottom ash and in the fly ash, solubility in the quench waters (pH 6–12) and in the fly-ash scrubber waters (pH 3–6) may explain the low ratios in Table VIII for other elements such as Ca, K, and Na. Copper may possibly be lost to the bulk slag not included in the fine bottom ash analyses.

Cobalt shows some addition from noncombustibles in the fine bottom ash and in the fly ash, but not in the atmospheric particles. A comparison of Al-normalized data gave results similar to those for the Fe-normalized data shown in Table VIII except that cobalt was also enriched (2.3) in the atmospheric particles.

Table VIII. Ratio of Iron-Normalized Elemental Concentrations in Incinerator Effluents to Iron-Normalized Concentrations in Input Combustibles

element	fine bottom ash	fly ash	atmos particles
Ag	1.8	4.2	33
Al	0.8	1.3	0.5
Ba	1.2	0.9	1.3
Ca	0.6	0.2	0.6
Cd	0.7	0.7	31
Co	3.4	3.2	1.0
Cr	1.4	2.0	2.3
Cu	0.2	0.1	1.5
Fe	1.0	1.0	1.0
Hg	0.1	0.1	
K	0.7	0.9	
Li	1.4	1.6	
Mg	1.1	0.6	1.1
Mn	3.3	1.1	3.3
Na	0.3	0.3	5.6
Ni	1.4	7.8	2.3
Pb	0.8	2.1	77
Sb	0.4	0.7	14
Sn	2.9	6.0	140
Zn	1.9	1.2	39

Conclusions

Three approaches have been used with existing data to determine if metals reporting in the ash materials of municipal incinerators are coming primarily from the combustible portion of the refuse input, or from noncombustible sources as well. The data analyses include comparison of the metal concentrations remaining in the residues after incineration, comparison of the scrap metal components of refuse with the resulting metal components after incineration, and comparison of the metal concentration ratios, normalized to Fe, for the combustible fraction and for the incinerator ash residues. These studies indicate that Ag, Cd, Cr, Mn, Pb, Sn, and Zn in incinerator effluents come from noncombustible sources in addition to the contribution from combustible materials. Therefore, removal of the noncombustible components of MSW by some recycling operation prior to burning the combustible components for their energy content should reduce the emissions of these seven metals. The studies also indicate the possibility that emissions of Al, Ba, Co, Fe, Li, Na, Ni, and Sb may be reduced by separating the combustibles from the noncombustibles prior to use as a fuel. The other elements studied (Ca, Cu, Hg, K, and Mg) are probably coming primarily from the combustible components of refuse.

The conclusions reached in this study are based on data averages taken from research not originally intended to identify the sources of metals in effluents from the combustion of municipal refuse. More conclusive data should be obtained from studies designed to determine the disposition of specific elements during the burning of well-characterized batches of municipal refuse.

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Received for review April 24, 1978. Accepted October 27, 1978. The University of Maryland portion of this study was in part supported by the National Science Foundation RANN Program under Grant No. ENV 75-02667. Portions of this research were performed in partial completion of the requirements for a Ph.D. in Chemistry from the University of Maryland, College Park, Md.

Inactivation by Chlorine of Single Poliovirus Particles in Water

Roger Floyd and D. Gordon Sharp

Department of Bacteriology and Immunology, School of Medicine, University of North Carolina, Chapel Hill, N.C. 27514

J. Donald Johnson*

Department of Environmental Sciences and Engineering, School of Public Health, University of North Carolina, Chapel Hill, N.C. 27514

■ Some kinetic aspects of the inactivation of poliovirus by chlorine in water have been observed in experiments with both HOCl and OCl^- using virus preparations in which no less than 99% of the virions were free single particles. In this manner any influence of virion aggregation on the reaction rates observed was minimized. Under these conditions HOCl was clearly superior to OCl^- as a disinfecting agent for this virus. Inactivation rates for both agents increased with increasing concentration, but in neither case did this increase continue in a linear fashion. Both forms of free chlorine became less efficient as the concentration was increased. While the decline in log plaque titer was not strictly linear with time for either HOCl or OCl^-, HOCl was nearly linear below 0.6 log survival ratio. However, the OCl^- inactivation rate slowed significantly below a 10^{-2} survival level. These observations suggest that the mechanisms of viral inactivation by these two agents were not the same. Physical evidence of change has been detected by electron microscopy in negatively stained preparations of HOCl-treated poliovirions, even though inactivation occurred first. Some of the virions appeared to retain physical integrity after plaque titer indicated that they must have been inactive.

There is some evidence from laboratory viral inactivation studies (*1*) as well as field studies of viral contamination of water (*2*) that concentrations of chlorine that will inactivate bacteria to acceptable levels for drinking water will not always reduce virus concentrations to the same level. There is also evidence that aggregates or clumps of virions survive exposure to both radiation and chemical disinfecting agents which will inactivate singly dispersed particles (*3–6*). Direct observation by electron microscopy (*7, 8*) and differential centrifugation (*7, 9*) has demonstrated that suspensions of viruses, as they are usually prepared in the laboratory, are very rarely free of aggregation, particularly when the virus particle counts are $\geq 10^9$ particles/mL. Furthermore, the degree of aggregation observed varies greatly with different viruses (*9*), as well as with the pH and concentration of salts in the virus suspension. We have found it difficult to produce suspensions of viruses without aggregation, although the data in this paper indicate that poliovirus can be prepared with only a very small amount of aggregation (approximately 10^{-3} of the particles in small aggregates), but as yet it has not been possible to produce routinely a virus suspension with a given degree of aggregation. However, in those reports of studies of inactivation of viruses with chlorine (*1, 10, 11*), whether as HOCl or OCl^-, no real attempt to control or even to characterize the aggregation has been made. Therefore, in the work to be reported in this paper, we have utilized a suspension of poliovirus as free from aggregation as possible in order to obtain kinetics of inactivation of the virus uncomplicated by aggregation effects. Evidence is presented that the methods of virus preparation used here, as well as in the earlier work with bromine (*12, 13*), do achieve the required freedom from aggregation. This evidence, as well as a direct view of the changes produced by the chlorine, was supplied by electron microscopy. The evidence indicates an unexpected complexity in the inactivation of single virus particles.

Materials and Methods

Virus. The Mahoney strain of poliovirus type 1 was grown and plaqued in human epidermoid carcinoma cells (HEp-2). Concentration, purification, and storage of virus stocks for these experiments were the same as those for the earlier poliovirus work with bromine (*12, 13*).

Physical assay of virus suspensions was made for virion count and aggregation analysis by quantitative methods of electron microscopy as previously described (*8, 9*).

Inasmuch as some of the experiments required exposure of the virus to chlorine solutions for time intervals as short as 1 s, the fast-flow apparatus was used (*14*) in all experiments. When exposures of 30 s or more were required, the virus–chlorine mixture emerging from the fast-flow apparatus was

0013-936X/79/0913-0438$01.00/0