METALS IN MSW:
WHERE ARE THEY AND WHERE
DO THEY GO IN AN INCINERATOR?

H. GREGOR RIGO
Rigo & Rigo Associates, Inc.
Berea, Ohio

A. JOHN CHANDLER
A. J. Chandler & Associates Ltd.
Willowdale, Ontario, Canada

Discussion by:

Marjorie A. Franklin
Franklin Associates, Ltd.
Prairie Village, Kansas

This paper is an important contribution to the literature in an area where there has been much speculation but too little solid investigation. Like all good research, this study raises as many questions as it answers. I will confine my discussion to the section on metal partitioning between MSW components.

The observation that mercury contamination occurs naturally even without human (anthropogenic) activity is worthy of mention. The natural atmospheric sources come from volatilization of gaseous mercury from soils, vegetation, oceans, and other water bodies. A report prepared for the U.S. EPA in 1992 (Franklin, 1992) noted that while total mercury generation by human activity is probably greater than that from natural causes, natural atmospheric emissions are probably higher than anthropogenic atmospheric emissions. Finding mercury in organic materials, such as yard trimmings and untreated wood, tends to substantiate this phenomenon.

The findings of mercury in newsprint and other paper surprises me. Mercury or mercury compounds are not allowed for use as a fungicide in the U.S., and the Bureau of Mines reported no mercury use for this purpose after 1972. Some limited samplings of newsprint for uses such as animal bedding have not found significant levels of heavy metals. Is it possible that mercury is still allowed as a fungicide for paper-making in Canada? Or is the mercury inherent in the wood used to make paper pulp?

This points up another area of concern for municipal solid waste managers in the U.S. We have been working to reduce toxics in products in MSW, but perhaps we need to scrutinize products imported into the U.S. For example, large quantities of newsprint used here are imported from Canada. As Rigo and Chandler point out, the presence of an imported solder may account for increased heavy metals content. (Very few cans are still soldered in the U.S.)

These comments are not intended as criticisms, but rather as the kind of questions we should be asking as we continue to consider these issues.

REFERENCE


AUTHORS' REPLY

The authors heartily endorse Marge Franklin highlighting that The WASTE Program's Burnaby, B.C., field exercise is only the beginning. Further field work is needed to confirm or deny these findings. Extramural investigations are needed to answer the questions she raised as well as the much longer list contained in the final Burnaby report. The Burnaby results, coupled with the emergence of a "world economy," emphasizes the importance of global initiatives if individual societies are to avoid simply wasting money. We must consider natural as well as anthropogenic sources to maximize the return on our environmental expenditures. Absent such considerations and we may spend lots of money removing some metals, but not enough to make any measurable difference.

We were aware that mercury fungicides are no longer used to preserve the wet lath in the United States and under-
stand they are also phased out in Canada. A portion of the paper we found was probably recycled pacific-rim product and may have been treated with a mercury fungicide there. It is also possible that both the mixed paper samples analyzed were contaminated by dirt or other broken mercury containing MSW constituents. Given the level of mercury in the sorted wood and the analyzed "blanks" for new kiln dry wood used to clean the mills, we do not believe environmental uptake is a likely explanation. But, we cannot rule it out.

Discussion by:

Ben Levie
R. W. Beck
Denver, Colorado

INTRODUCTION

This paper and the work completed at Burnaby is a good contribution to the understanding of metal sources and partitioning in MWCs. R. W. Beck is currently performing two enhanced waste composition studies for Palm Beach and Hennepin Counties. Results for these will extend our knowledge base on this subject and the potential effect of removing selected components prior to incineration.

QUESTIONS AND COMMENTS

- To the extent that mercury is in its elemental form and not held by surface (capillary) forces, the drying process used in the sorting/analysis protocol will result in volatilization of this mercury. This may bias mercury distribution towards non-elemental sources.
- Tables would be easier to digest and fewer needed if mercury were shown by itself rather than in combination with other metals.
- The small variation in mercury emissions makes it difficult to draw strong conclusions from the contributions of metals from specific sources. However, perhaps one could say that lower numbers of mercury emissions suggest a MSW composition which does not contain components with high contributions of mercury, such as batteries or florescent tubes.
- It would be nice to see factor analysis plots.
- Why are diapers and batteries defined as HHW?
- Have you done additional analyses to discern the origin of mercury in newsprint?
- How is dental waste disposed of in Burnaby?

AUTHORS’ REPLY

We are also very pleased that Dr. Levie is performing enhanced waste composition studies. From discussions with him, we know that our study helped focus his efforts. We look forward to having the Hennepin and Palm Beach results added to the literature.

While we agree that the drying process could loose elemental mercury, we doubt that this is significant for many MSW components. For example, even though elemental mercury is present in working fluorescent light bulbs, it is the reaction of mercury with phosphorous that causes the bulbs to burn out. Nevertheless, controlled experiments to determine the loss of elemental mercury at the 40-60°C temperatures we used to "air-dry" the samples should be performed. We suggest that losses during screening, coarse grinding, and fine milling also be evaluated as part of a comprehensive effort.

We agree that a paper covering more metals than just mercury necessarily makes the tables more complex. Mercury-only tables are available in the mercury focused papers the authors published in the Ash VI Proceedings (Rigo, 1993; Chandler, 1993).

We also agree that there was little variation in mercury loadings between runs. Hence, failing to find relationships between specific components and mercury emissions may be the result of either too little variability in this test or no relationship. Additional studies like the Burnaby field exercise are needed to confirm or deny the tentative conclusions presented.

Since five factors were used to characterize the simultaneous composition/residue/stack emissions data collected at Burnaby, 60 paired factor analysis plots are needed to graphically display the results for one element, since more than the two principal factors need to be displayed. Factor loading tables that provide the same information in a more concise format can be found in Volume II, Annex 9 of the final report.

We included diapers in household hazardous waste [HHW] because of the potential for bacterial and viral contamination. Batteries were included in the HHW category because some types of batteries exceed TCLP limits for mercury, lead, or cadmium and it seemed imprudent to split the category.

Waste amalgam and potentially blood-borne pathogen-contaminated wastes are handled as special wastes and "red-bag" materials in British Columbia. The materials we would consider RCRA non-hazardous are managed like any other non-hazardous waste.
The extensive, detailed research which the authors have carried out at the Burnaby WTE facility is a landmark in that for the first time the sources of metals in MSW are identified down to the last item, and the fates of the metals of concern within the boiler and in the flyash, bottom ash, and emissions are determined.

The data that was collected during the various tests, and shown in Table 3, provides some information on the variance of the metals concentrations in the waste which was analyzed. It is interesting to compare these variances with corresponding variances which are found in the emissions and the ash residues. The mean and standard deviations which can be derived from this table are shown below.

<table>
<thead>
<tr>
<th></th>
<th>Arithmetic Mean</th>
<th>Standard Deviation</th>
<th>Relative Std. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead (lb/million Btu)</td>
<td>3.7 E-4</td>
<td>1.34 E-4</td>
<td>35.8%</td>
</tr>
<tr>
<td>Cadmium (lb/mm Btu)</td>
<td>13.9 E-6</td>
<td>7.4 E-6</td>
<td>53.3%</td>
</tr>
<tr>
<td>TCDD TEQ (ng/Nm³)</td>
<td>1.4</td>
<td>0.96</td>
<td>68.8%</td>
</tr>
<tr>
<td>Particulate (gr/dscf)</td>
<td>0.0055</td>
<td>0.003</td>
<td>54.5%</td>
</tr>
</tbody>
</table>

Note that the cadmium data in Table 3 has an extremely wide range, indicating more than one population. The four points which are more consistent with lead and chromium may be considered to be of similar populations. Almost all of the data plotted as a straight line on log coordinates, as seen in Fig. 1, which shows only the 4-point cadmium data. I find that data from waste, emissions, a single facility, and groups of facilities also plot close to straight lines on log coordinates, through most of the range of the data, but tail off below and above that. See Fig. 14, presented in my paper on ash testing in this Proceedings (page 115). When the data is plotted on log probability paper, however, the points stay on the line. The line can be extrapolated in 90% or 99% of the scale to reflect these probabilities. This finding is in agreement with the findings below relating to the Statistical Tolerance Limit procedure proposed for MACT determination.

Since the Clean Air Act requires that the Maximum Achievable Control Technology (MACT) be determined for various classes of facilities, it is interesting to apply the proposed procedure for determining the "MACT Floor" to this data.

The U.S. EPA proposes in the Combustion Emissions Technical Resource Document (CETRED), "Statistical Tolerance Limit Values" to determine the number of which 99% of the facilities could meet with a 95% confidence limit. For eight tests, the factor K is 4.353. The MACT Floor is calculated as follows:

\[ \text{MACT floor} = (\text{Mean}) + K \times (\text{standard deviation}) \]

For Lead:
\[ 3.7 \times 10^{-4} + 4.353 \times 1.34 \times 10^{-4} = 9.5 \times 10^{-4} \text{ lb/mmBtu} \]

For Cadmium:
\[ 13.9 \times 10^{-6} + 4.353 \times 7.4 \times 10^{-6} = 46 \times 10^{-6} \text{ lb/mmBtu} \]

For TCDD TEQ:
\[ 1.4 + 4.353 \times 0.96 = 5.8 \text{ ng/Nm³} \]

For Particulate:
\[ 0.0055 + 4.353 \times 0.003 = 0.0186 \text{ gr/dscf} \]

The comparison between the variance of actual emissions over a period of years with the variance of one week of waste sampling is of great interest. The standard deviation increased from roughly 12% to roughly 50% when the four-year test period was used.

I have analyzed data from two other facilities, one having refractory furnaces and a dry-injection baghouse, and one having water-wall furnaces with spray-dry scrubber and fabric filter: the four-year standard deviations are similar, indicating that the above illustration is probably typical.

The comments of Dr. Rigo on these statistical matters would be of great interest to the reader. Is there some statistical method which could be used to extrapolate a week's data to a year's data?

**AUTHORS’ REPLY**

Mr. Hasselriis raises a number of interesting points and questions that are really outside the scope of the original paper.

In Mr. Hasselriis' first table, some of the cadmium data are excluded as outliers. This is a questionable and unnecessary procedure since the data are lognormally distributed and the geometric mean and standard deviation correctly lower emissions. (See Zakaria and Sutin, The SEMASS Shred-and-Burn Technology, page 293 of this Proceedings.)
characterizes the data. I do not know how to use plots like Mr. Hasselriis' Fig. 1 in these comments and Fig. 14 in his paper to establish distribution form. The methods the authors use are presented in "Selecting Statistically Meaningful Emission Rates," (Rigo, 1993) and "Estimating Stack Gas Emission Rates," (Rigo, 1992).

I also do not know how to relate percentage points on plots like these or probability plots to tolerance limits since tolerance limits consider both the uncertainty with which the mean is known and the variability of the data. Clearly, however, once the "K factor" referenced by Mr. Hasselriis is known, it corresponds to the number of standard deviations by which the tolerance limit is located above the mean. So, an appropriate percentage can be determined by referencing a cumulative normal probability table. The tolerance limit corresponds to the K-factor's distribution percentage, not 99% or 95%.

Regarding the development of MACT floors, the analytic approach presented in CETRED (EPA 530-R-94-014) was heartily endorsed by many reviewers, but must be applied to an appropriate database to produce the intended results. Since data from one plant (not the best performing 12% of all units) is considered here and the summary statistics smears the between-unit and within-unit variabilities, the results represent emission limits likely to be met in 99% of future testing of the two original SEMASS boilers, not a MACT floor applicable to other plants or the legal definition of the MACT pool.

Mr. Hasselriis correctly uses the same units to establish his emissions levels for all pollutants. CETRED uses a different group of "best performing units" for each pollutant. This can result in the development of limits that cannot be simultaneously achieved by any real plant.

The increase in standard deviation noted by Mr. Hasselriis between a single test series and tests spread out over a four-year period is typical. Within a single series, the unit is operating in a like manner. Over time, even if set up the same, performance will change to some extent. A single test series is really repeated measurements. Different test series include between-test variability. For example, if there is a waste composition effect, that will be included over time. So will differences between different units being tested at a single plant and the effect of different sampling times and methods.

The authors want to emphasize that the foregoing discussion of the sources of variability must not be taken out of context. We do not believe that wasting money frequently testing all units in a plant is appropriate. We are simply pointing out that there is too much going on to validly assign cause or do more than make an observation that should be tested or otherwise confirmed. Examining lots of data convinces us that MWC emissions are describable and predictable.

As a final note, if the week's worth of data are stable and representative, then extrapolation to any other time period can be done as described in "Selecting Statistically Meaningful Emission Rates." Absent these two key requirements and statistics will not help. Application of statistics is, in fact, harmful, since it creates an inappropriate aura of scientific validity.

REFERENCES


FIG. 1 ATTACHMENT TO COMMENTS BY FLOYD HASSELRIIS

FIG. 2 ATTACHMENT TO COMMENTS BY FLOYD HASSELRIIS