SILVER ANNIVERSARY

International Conference on Heavy Metals in the Environment

Final Program

Susanna
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6-10 August, 2000
University of Michigan
Ann Arbor, Michigan, USA

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trum, Environmental Biology, Universitaire Campus,
ronomie-BGETA, France)

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N-Instituto Tecnológico e Nuclear, Portugal)

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nces, Purdue University, Indiana)

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itute for Lake Research, Russian Academy of Sciences)

POSTER SESSION I
15:50 Monday (August 7) and 10:30 Tuesday (August 8)
Location: Alumni Center, University of Michigan

Mercury in the Atmosphere

I-1. Mercury species in smelter and power plant plumes
J. Lu, C.M. Banic, and W.H. Schroeder (Meteorological Service of Canada, Environment Canada, 4 Ontario)

I-2. Measurement of particulate and reactive gaseous mercury, RGM, in the ambient air: Methods development
M. Lynam, J. Dvonch, and G. Keeler (University of Michigan Air Quality Laboratory), M. Landis (US EPA National Exposure Research Laboratory, North Carolina) and R. Stevens (Florida Department of Environmental Protection)

I-3. Heavy metals quantification on alkaline batteries incineration emission
S. Xará, M. Almeida, C. Costa (Laboratório de Engenharia de Processos, Universidade do Porto, Portugal), M. Silva (Escola Superior de Biotecnologia, Universidade Católica Portuguesa, Portugal)

I-4. Measurements of total gaseous mercury in Alberta, Canada: effects of meteorology and local emissions
M. Kellerhals and K. McDonald (Environment Canada)

I-5. Vertical distribution of mercury compounds in the atmosphere
K. Kvietkus and J. Sakalys (Atmospheric Pollution Research Laboratory, Institute of Physics, Lithuania)

I-6. Evaluation of mercury atmospheric contamination in a dental office using the transplanted Spanish moss (*Tillandsia usneoides, L.*): Establishing background levels
C. Calasans, C. Carvalho, W. Primo, M. Cavalcante, C. Souza (Laboratório de Ciências Ambientais, Universidade Estadual do Norte Fluminense, Brazil), C. Castanheira (Prefeitura Municipal de Campos dos Goytacazes, Brazil)

I-7. Total gaseous mercury (T.G.M.) in Champ/Drac, France from January 12, 2000 to January 24, 2000: Correlation with other pollutant levels and meteorological parameters
C. Ferrari, A. Dommergue, A. Veysseyre, F. Planchon (Laboratoire de Glaciologie et Géophysique de l'environment du CNRS, France), C. Boutron (Laboratoire de Glaciology et Géophysique de l'environment du CNRS, France)

I-8. Determination of current and historic loads of atmospheric deposition in the Czech Republic using analyses of moss and forest floor humus
J. Sucharová and I. Suchara (Research Institute of Ornamental Gardening, Czech Republic)

I-9. Atmospheric mercury measurements in Guiyang, P. R. China
X. Feng, J. Sommar, O. Lindqvist (Department of Inorganic Chemistry, Göteborg University, Sweden), Y. Hong, Y. Zhu (State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences)

I-10. Inventory of Hg emission in Chongqing China today
C. Qing (Southwest Agricultural University, China) and S. Mu (UNMC, USA)

I-11. Mercury absorbed by different plants in acid precipitation area in Chongqing
S. Mou (Southwest Agricultural University, China) and L. Mu (National Institute of Health, Maryland)

I-12. Factors controlling short-term variability of total gaseous mercury distribution in urban air
K. Kim (Department of Earth Sciences, Sejong University/Sejong Institution, South Korea) and M. Kim (Seoul Metropolitan Institute of Environment and Health, South Korea)

I-13. Study on the accumulation and transformation of atmospheric mercury in soil
D. Wang (College of Resources and Environment, Southwest Agricultural University, China)

HEAVY METALS QUANTIFICATION ON ALKALINE BATTERIES INCINERATION EMISSIONS

Susana Xará* (1,2), Manuel Fonseca Almeida(1), Carlos Costa(1), Margarida Silva(2)

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ABSTRACT

Heavy metals emissions associated with municipal solid waste (MSW) incineration is a point of discussion and care due to the known harmful effects of these metals on humans and environment. Batteries are appointed as one of the main contributors for those emissions, particularly for mercury, cadmium, zinc and lead. In this paper, results for heavy metals emissions from alkaline batteries obtained in a laboratorial incinerator are presented. The incineration process took place in a tubular oven where batteries were heated at 1000°C with a constant airflow. Heavy metals on released gas were collected with concentration by absorption on a set of serial bubblers, and, following, quantified by atomic absorption spectroscopy. The results obtained estimate the potential contribution of alkaline batteries to heavy metals emissions in a municipal solid waste incinerator.

INTRODUCTION

In Portugal, Municipal Solid Waste (MSW) destinations are landfilling and incineration, except materials collected separately or separated after collection that are recycled. Presently, there are two incineration plants in the two major urban centers. For some material streams as small spent domestic batteries, recycling processes are not foreseen, thus they are included in global MSW stream or collected and stored until an environmental acceptable option is available.

The goal of the project where the work presented on this paper is included is assessing the environmental impact resulting from incineration and landfilling of domestic spent alkaline batteries (AA format), the most representative ones in terms of market share not only in Portugal but also in most of countries (Xará et al, 1999). This evaluation is based on Life Cycle Assessment (LCA) technique, an objective technique for environmental impact evaluation of systems (product, process or activity) by: (i) compiling an inventory of relevant inputs and outputs of the system; (ii) evaluating the potential environmental impacts associated with those inputs and outputs; (iii) interpreting the results of the inventory analysis and impact assessment phases in relation to the objectives of the study (ISO 14040, 1997).

Inventory step involves data collection and calculation procedures to quantify relevant inputs and outputs of the system in terms of materials and energy consumption and emissions produced. Concerning the incineration emissions, a distinction can be made between product-derived emissions and process-derived emissions (Lindfors et al, 1995). Product-derived emissions are derived from the products being incinerated and examples of them are heavy metals. However, as required data is not available for batteries, it must be obtained by simulating the burning process on laboratory scale. With this objective, incineration takes place in a set including a tubular oven where batteries are heated. Particles and gases are collected for heavy metals determination.

The work done in the scope of this project intends to be a small contribution for creation a database to support this kind of environmental analysis with domestic alkaline batteries, not only for evaluating management options, but also for studies including production, use and discard of batteries.

METHODS

In the experiments carried out under the subject of this work, an incineration process was simulated in a laboratory tubular oven made with refractory steel where each battery was loaded and heated at 1000°C for 1 hour under a constant flow of air. The batteries tested were AA alkaline batteries. Before loading them, both the plastic jacket and the paper disc under the anodic collector were removed. Batteries were opened, too, to avoid explosions due to inner part vaporization during burning. Gases produced, after passing through a 0,45μm filter are collected by concentration on a series of 2 bubblers with 100ml of 10% nitric acid solution. Following 10 batteries combustion experiments, fitting tubes, filter support, tubular oven and bubblers, all were washed with fresh acid nitric solution. Using the solutions obtained, heavy metals as zinc, copper, cadmium, manganese and lead were quantified by flame atomic absorption spectroscopy. Mercury was determined by cold vapor atomic absorption spectroscopy.

A prior blank experiment was also performed in order to evaluate the heavy metals at the solutions obtained with the same conditions used at the further burning experiments.

thermore, in order to evaluate the environmental impact of batteries after combustion when landfilled, a leachate test was arried out using distilled water in a proportion of 100g of burned batteries for 1liter of water, in a flask continuously mixed in up to bottom rotational movement with a speed of 21rpm for 24 hours. The resulting solution was filtered and heavy metals etermined. Similar tests with non-burned batteries, either entire or transversally opened were also carried out to assess its omparative pollutant potential.

ESULTS AND DISCUSSION

he results obtained for heavy metals quantification on gases in batteries incineration are presented on Table 1, expressed as nilligrams per battery (mg/bat.) for all metals except for mercury that is expressed as micrograms per battery (µ g/bat.). ilter+tubular oven solution includes all the solution used to wash filter and filter support (50ml) and oven (100 ml) following urning process. Bubblers solutions include solution used in gas collection (100 ml) and washing solution (50 ml). esults from leaching tests are presented in Table 2.

n both tables, the results expressed as less than a given amount were obtained using the detection limit of the equipment for ach metal.

Table 1. Heavy metal contents on gases resulting from alkaline batteries (AA) incineration in a tubular laboratorial oven at 1000ϒC

	Zn (mg/bat.)	**Cu (mg/bat.)**	**Cd (mg/bat.)**	**Mn (mg/bat.)**	**Pb (mg/bat.)**	**Hg (µg/bat.)**
Filter+tubular oven	256.8	0.08	0.01	2.8	0.4	0.3
Bubbler 1	4.1	<0.06	<0.0005	0.002	0.06	0.4
Bubbler 2	0.01	<0.06	<0.0005	0.0008	<0.001	0.07
Total	260.9	0.08	0.01	2.8	0.46	0.77

Table 2. Heavy metals contents on leachate obtained with burned, entire and transversally opened alkaline batteries (AA) leaching tests.

Metal		**Batteries**	
	Burned	**Entire**	**Opened**
Zn (mg/bat.)	1.3	0.8	1.7
Cu (mg/bat.)	0.01	<0.01	<0.009
Cd (mg/bat.)	<0.006	<0.007	<0.007
Mn (mg/bat.)	2.4	0.06	0.4
Pb (mg/bat.)	<0.018	<0.023	<0.023
Hg (µg/bat.)	<0.21	<0.28	0.8

inc powder is the main anode constituent on alkaline batteries, contributing to about 14% per weight on AA batteries format Xará et al, 1999). Since the boiling point of this metal is about 908ϒC it has a great ability to vaporize and be present at nci[illegible]ation released gases. However it will not be there as a metal, since it easily combines with oxygen to form ZnO. These xperiments shown zinc mainly at the filter and tubular oven, despite it was also transported to the first bubbler. These results re meaningful since at preliminary blank experiment, zinc is only detected at the washing solution of stainless refractory tube nder an insignificant amount, i.e., as traces. Zinc is also present at the burned, entire and open batteries solutions resulting rom leaching tests.

ooper is present on alkaline batteries both on cathode and anode. On the blank experiment, copper was detected as trace at he stainless refractory tube washing solution. Copper at the filter and stainless refractory tube solution referred in Table 1 is ooked as not significant, since it has the same order of magnitude than with the blank test. As metal and oxide, Copper is not ignificantly vaporized at the temperature of the tests that explaining to be not found at the bubblers solutions. admium is present on the anode of alkaline batteries. At the blank test this metal was not detected in any of the solutions. In he burning batteries experiments only traces of cadmium were found at filter+stainless refractory tube washing solution. anganese dioxide is the main cathodic constituent on alkaline batteries, with a total percentage of about 22% per weight on A format (Xará et al, 1999). Despite that, manganese is only significantly present at filter+stainless refractory tube washing olution.

ead is present on anodic material composition of alkaline batteries. In consequence of batteries burning, lead is found at ilter+stainless refractory tube washing solution and at the first bubbler solution. Probably, it results from metal vaporization nuch more volatile than its oxide form.

ercury is present on the anode material of alkaline batteries at very low levels. These experiments found it at the ilter+stainless refractory tube washing solution in a total amount of about 0,77 µ g/bat.

.EFERENCES

Lindfors, L.-G., Christiansen, K., Hoffman, L., Virtanen, Y., Juntilla, V., Hanssen, O.-J., Rønning, A., Ekvall, T. and Finnveden, G. (1995) In: Nordic Guideline on Life Cycle assessment, Nord 1995:20, Nordic Council of Ministers, Copenhagen.

Xará, S., Almeida, M., Silva, M. and Costa, C. (1999) "Life cycle analysis and solid waste management: household batteries", 7th International Waste Management and Landfill Symposium (Sardinia´99), T. Christensen, R. Cossu and R. Stegmann, vol. V, pg 651-656.

International Organisation for Standardisation, ISO 14040 (1997) Environmental management - Life cycle assessment - Principles and framework, Switzerland.

HEAVY METALS QUANTIFICATION ON ALKALINE BATTERIES INCINERATION

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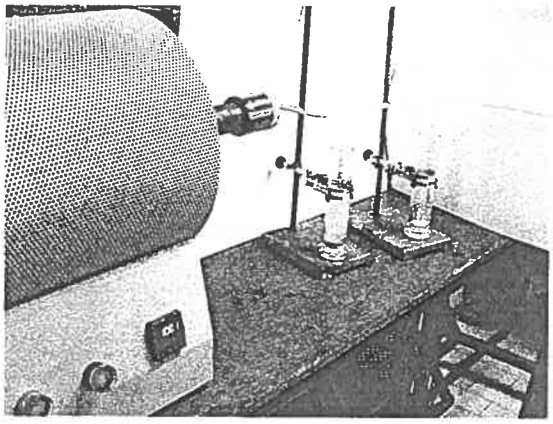
2 College of Biotechnology, Portuguese Catholic University, Rua Dr. António Bernardino de Almeida, 4200 Porto, Portugal

Heavy metals emissions associated with municipal solid waste (MSW) incineration is a point of discussion and care due to the known harmful effects of these metals on humans and environment. Batteries are appointed as one of the main contributors for those emissions, particularly for mercury, cadmium, zinc and lead. In this paper, results for heavy metals emissions from alkaline batteries obtained in a laboratorial incinerator are presented. The incineration process took place in a tubular oven where batteries were heated at 1000°C with a constant airflow. Heavy metals on released gas were collected with concentration by absorption on a set of serial bubblers, and, following, quantified by atomic absorption spectroscopy. The results obtained estimate the potential contribution of alkaline batteries to heavy metals emissions in a municipal solid waste incinerator.

METHODS

- **Batteries**
  - AA alkaline batteries (set of 10) opened
  - plastic jacket and paper disc under the anodic collector were removed
- **Incineration process simulation**
  - laboratory tubular oven made with refractory steel
  - each battery was loaded and heated at *1000°C* for *1 hour* under a constant flow of air
- **Sampling and quantification**
  - gases produced, after passing through a 0,45μm filter are collected by concentration on a series of 2 bubblers with 100ml of 10% nitric acid solution
  - following combustion experiments, fitting tubes, filter support, tubular oven and bubblers, all were washed with fresh acid nitric solution
  - using the solutions obtained, heavy metals as zinc, copper, cadmium, manganese and lead were quantified by flame atomic absorption spectroscopy, mercury was determined by cold vapor atomic absorption spectroscopy
  - a prior blank experiment was also performed
- **Leaching test**
  - to evaluate the relative environmental impact of batteries after combustion when landfilled
  - 100 grams of burned batteries for 1liter of distilled water
  - flask continuously mixed in a up to bottom rotational movement with a speed of 21rpm for 24 hours
  - the resulting solution was filtered and heavy metals determined
  - similar tests with non-burned batteries, either entire or transversally opened were also carried out to assess its comparative pollutant potential.



RESULTS

The results obtained for heavy metals quantification on gases from batteries incineration are presented on Table 1, expressed as milligrams per battery (mg/bat.) for all metals except for mercury that is expressed as micrograms per battery (μg/bat.). Filter+tubular oven solution includes all the solution used to wash filter and filter support (50ml) and oven (100 ml) following burning process. Bubblers solutions include solution used in gas collection (100 ml) and washing solution (50 ml). Results from leaching tests are presented in Table 2. In both tables, the results expressed as less than a given amount were obtained using the detection limit of the equipment for each metal.

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	Zn (mg/bat.)	Cu (mg/bat.)	Cd (mg/bat.)	Mn (mg/bat.)	Pb (mg/bat.)	Hg (μg/bat.)
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	Zn (mg/bat.)	Cu (mg/bat.)	Cd (mg/bat.)	Mn (mg/bat.)	Pb (mg/bat.)	Hg (μg/bat.)
Burned	1.3	0.01	< 0.006	2.4	< 0.018	< 0.21
Entire	0.8	< 0.01	< 0.007	0.06	< 0.023	< 0.28
Opened	1.7	< 0.009	< 0.007	0.4	< 0.023	0.8

These experiments shown **zinc** mainly at the filter and tubular oven, despite it was also transported to the first bubbler. These results are meaningful since at preliminary blank experiment, zinc is only detected at the washing solution of stainless refractory tube under an insignificant amount, i.e., as traces.

Copper at the filter and stainless refractory tube solution referred in Table 1 is looked as not significant, since it has the same order of magnitude than with the blank test. As metal and oxide, Copper is not significantly vaporized at the temperature of the tests that explaining to be not found at the bubblers solutions.

In the burning batteries experiments only traces of **cadmium** were found at filter+stainless refractory tube washing solution.

Manganese is only significantly present at filter+stainless refractory tube washing solution.

In consequence of batteries burning, **lead** is found at filter+stainless refractory tube washing solution and at the first bubbler solution. Probably, it results from metal vaporization much more volatile than its oxide form.

These experiments found **mercury**at the filter+stainless refractory tube washing solution in a total amount of about 0,77 μg/bat.

ACKNOWLEDGEMENTS

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