Technical note 11/97

Heavy Metal Analysis of Municipal Solid Waste Incinerator Ash and Slag, Palma de Mallorca, 1996.

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Introduction

Two samples, one of ash and one of slag, were collected from the Municipal Solid Waste incinerator, Palma de Mallorca on August 23, 1996. They were transported to the Greenpeace Research Laboratory, University of Exeter, UK for heavy metal analysis. At present 5000 tonnes of ash are being stored, on-site, in plastic bags, as no permit for landfill disposal has been awarded.

Analytical Methodology

Both samples were dried in an oven for 48 hours, until dry weight reading became constant. Although already homogenous, they were crushed using a pestle and mortar and 0.5g was weighed out into a 120ml microwave Teflon vessel (fitted with a screw cap and pressure relief valve). To this 10ml of deionised water was added, followed by 7.5ml of concentrated hydrochloric acid and 2.5ml of concentrated nitric acid (both of analytical grade, Merck Ltd. UK). The vessels were sealed, placed on a rotating table in a microwave (model MDS-2000. CEM Corp.), and allowed to digest for one hour at full power (630W). After cooling to ambient temperature, the digests were filtered into grade-A volumetric flasks, diluted with deionised water, made up to a volume of 50ml, and mixed. Samples were prepared in duplicate.

With the samples, Certified Reference Material BCR-143 (Trace elements in a sewage sludge amended soil), certified by the Commission of the European Communities, was also prepared, as was a blank sample, both having the same acid matrix as the samples. The reference material was spiked with a 1 mg/l standard containing all of the metals to be quantified, and the resulting recoveries were calculated:

$$\% \text{ Recovery} = (X1 - X2)/Y * 100$$

Where X1 = the mean value of the CRM
X2 = the mean value of the CRM and spike

Y is the spike concentration for X2

Following preparation the samples were analysed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), using a Varian Liberty-100 spectrometer. The following metals were quantified: manganese (Mn), chromium (Cr), zinc (Zn), copper (Cu), lead (Pb), nickel (Ni), cobalt (Co) and cadmium(Cd). Instrument calibration standards were matrix

matched to the samples (15% v/v hydrochloric acid, 5% v/v nitric acids), and the calibration itself was validated using an independently prepared quality control standard at 80% of the calibration range (10ug/l to 10mg/l). Samples exceeding this range were diluted, in duplicate, appropriately. All other instrument quality control procedures were adhered to.

Results

See appendix 1 for full sample descriptions and results.

Discussion

With the exception of Cd and Zn, the highest levels of heavy metals are found in the slag. The results compare well with much of the European data available for ashes and slags, with levels of Mn, Cu, Zn and Pb, greater than Ni and Cr which in turn are greater than Cd and Co (Sawhney and Frink, 1991; Mitchell, Wild and Jones, 1991; Fernandez, Martinez, Garcia and Espiell, 1992; Hwa, 1990; Belevi, Stampfli and Baccini, 1991).

Metals present in MSW derive from batteries (Pb, Ni, Cd), paints and ceramics (Pb, Cu and Cd), plumbing, metal foil, sheets and cans, fluorescent lamps etc. Leachibility studies have shown that even in a lined landfill site, metals from MSW incinerator ash have the capacity to leach into the surrounding environment in a relatively short period of time. A study by Williams (1990) concluded that leaching of heavy metals such as As, Cd, Cr, Pb and Zn from incinerator ash, in a simulated landfill site, took place after only 24 hours. It should be noted that in Europe, lined landfill sites, or sites equipped with leachate collection and treatment facilities are relatively unknown, thus the ability of such sites to contain these metals over long periods of time is much diminished.

At the present time, the residual ash from the Palma de Mallorca incinerator is not destined for landfill. Instead 5000 tonnes of ash sealed in concrete is being stored on site. This cannot continue indefinitely. Whilst cement will have the effect of stabilising the incinerator ash, with respect to metal mobility, and hence bioavailibilty, the efficiency of the mixing in this case is uncertain, and thus the reliability of the stabilisation effect must also be uncertain.

Both the ash and slag clearly contain considerably higher concentrations of many heavy metals than soils. Comparison with UK Department of the Environment figures on uncontaminated soils, indicate that the slag would be classified as being “heavily contaminated” with respect to Cu, Zn, Pb and Cd, and contaminated with respect to Mn and Ni. The ash would be classified as being heavily contaminated with respect to Zn and Cd, and slightly contaminated with respect to Pb (Department of the Environment, Interdepartmental Committee on the Redevelopment of Contaminated Land (ICRCL), Consultation Paper, 1980).

These data highlight the elements Zn, Pb and especially Cd as being of particular concern in MSW incinerator ash. In addition to the very high absolute concentrations present, if enrichment ratios are considered along with this data (Mitchell, Wild and Jones, 1992) one can conclude that these ashes will result in substantial contamination of the sub-soils above their natural background levels if applied to landfills. As there are numerous sources of Cd, Zn and Pb in municipal wastes (plastics containing stabilisers, pigments, batteries etc, U.S.E.P.A,1990) these levels are unlikely to diminish over time. Thirdly, with respect to Cd,

elevated levels must warrant concern as transfer into the human food chain can be considerable compared to other metals. Along with it's high toxicity, and it's long body retention time, the considerable mobility of Cd in the soil-plant system represents a potential hazard to human health when levels of Cd in soils are raised.

Cd is a confirmed carcinogen (Sittig,1994), and some others are also either confirmed or suspected carcinogens, eg. Cr, Ni. These metals, along with Pb and Zn are also known to cause neurological and pulmonary system damage in humans at low doses. Many of these same common metals are reproductive toxicants. All are both acutely and chronically toxic to aquatic and terrestrial wildlife.

It should be mentioned that most heavy metals will have much greater mobility and , therefore, bioavailibily in incinerator ash compared to soil and indeed sewage sludge, because of the total amount of organic matter. This is much lower in the ash, and thus the capacity to bind the metals is much reduced and the potential for metal dispersal through leaching or on airborne dust particles is considerably greater than would be the case for sewage sludge. These factors must be taken into account when assessing the hazards of ash storage and dumping.

Finally, the environmental impact of incinerator plants is not limited to the production and consequent disposal of ash and slag; there is also the contamination due to stack emissions, and the outflow of wastewater to consider, both of which will contain elevated levels of heavy metals, as well as many toxic organic compounds including dioxins and furans. Metals are only redistributed in the waste, they can not be destroyed or detoxified by incineration. Therefore further studies on metal mobility in incinerator waste residues, including cement and lime blocks, are urgently needed before the environmental impact of storage and disposal of incinerator waste, indeed before incineration itself, can be comprehensibly assessed.

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References

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INORGANIC ANALYTICAL RESULTS

Palma de Mallorca 1996

Sample type: Solid waste
Sampling date: 23.08.96
Lab. code: MI6113a

Other information: Municipal solid waste incinerator slag.

Analysis method: ICP-AES

METAL	CONCENTRATION (mg/kg)
Manganese	695.6
Chromium	89.5
Zinc	1494.7
Copper	1898.3
Lead	1332.5
Nickel	50.9
Cobalt	10.5
Cadmium	12.3

INORGANIC ANALYTICAL RESULTS

Palma de Mallorca 1996

Sample type: Solid waste
Sampling date: 23.08.96
Lab. code: MI6113b

Other information: Municipal solid waste incinerator slag.

Analysis method: ICP-AES

METAL	CONCENTRATION (mg/kg)
Manganese	620.4
Chromium	90.7
Zinc	1249.7
Copper	1516.7
Lead	1189.8
Nickel	31.5
Cobalt	8.3
Cadmium	14.8

INORGANIC ANALYTICAL RESULTS

Palma de Mallorca 1996

Sample type: Solid waste
Sampling date: 23.08.96
Lab. code: MI6114a

Other information: Municipal solid waste incinerator ash.

Analysis method: ICP-AES

METAL	CONCENTRATION (mg/kg)
Manganese	176.9
Chromium	43.3
Zinc	2462.5
Copper	188.5
Lead	928.9
Nickel	20.2
Cobalt	3.9
Cadmium	46.2

INORGANIC ANALYTICAL RESULTS

Palma de Mallorca 1996

Sample type: Solid waste
Sampling date: 23.08.96
Lab. code: MI6114b

Other information: Municipal solid waste incinerator ash.

Analysis method: ICP-AES

METAL	CONCENTRATION (mg/kg)
Manganese	248.0
Chromium	41.8
Zinc	2391.8
Copper	184.7
Lead	896.9
Nickel	22.5
Cobalt	2.0
Cadmium	44.9

INORGANIC ANALYTICAL RESULTS

Palma de Mallorca 1996

Sample type: Reference Soil for MI6113 and MI6114
Preparation date: 09.10.96
Lab. Code: BCR-143

Other information: Trace metals in a sewage sludge amended soil.

Analysis method: ICP-AES

METAL	% RECOVERY
Manganese	102.5
Chromium	91.7
Zinc	87.2
Copper	84.0
Lead	85.6
Nickel	86.0
Cobalt	86.4
Cadmium	88.9

INORGANIC ANALYTICAL RESULTS

Palma de Mallorca 1996

Sample type: Quality Control Standard for MI6113 and MI6114
Preparation date: 09.10.96
Concentration: 8.0 mg/l

Other information: Lower limit of 7.2 mg/l, upper limit of 8.8 mg/l acceptable.

Analysis method: ICP-AES

METAL	CONCENTRATION (mg/l)
Manganese	8.69
Chromium	8.50
Zinc	8.17
Copper	7.77
Lead	8.12
Nickel	8.00
Cobalt	8.10
Cadmium	8.06