DIOXIN MASS BALANCE IN A MUNICIPAL WASTE INCINERATOR

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INTRODUCTION

Modern concepts about municipal waste management often combine different strategies such as recycling, composting, thermal treatment or landfill disposal. Recycling and composting are being successfully applied in the early stages of waste managament in several countries. However, further operations such as combustion processes in municipal waste incinerators (MWI) are always required to eliminate the additional residue generated by recycling or composting. In recent years, MWI have been the subject of much controversy because of their emissions into the air, which constitutes a potential risk to the environment. As a result stringent regulations governing stack emissions are being enforced. In particular, European Union (EU) member countries have set limit values for PCDD/PCDF emissions of 0.1 ng I-TEQ/Nm^3. In Spain MWI are being retrofitted in order to comply with the EC directive. The question, now, is whether the removal of pollutants from the flue gas may increase the levels of the materials derived from the combustion processes and whether these materials can be discharged without impacting the environment. Furthermore, recycling products may also contain levels of PCDD/PCDF (1). It goes without saying, therefore, that the solid residues and recycling products should be carefully characterized before taking a final decision.

On the other hand, it is common knowledge that the PCDD/PCDF are already present in waste. In fact, data about the levels of PCDD/PCDF in textile, wood, food, plastic, etc. , all typical components of waste, are available (2,3). The most recent studies reveal a thermal destruction of PCDD/PCDF in a modern MWI (4,5). In this study, we analyze the levels of PCDD/PCDF in different samples from a MWI located in Spain in order to examine the dioxin mass balance.

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MATERIALS AND METHODS

Sampling

The assessment of a dioxin mass balance in a MWI plant includes the analysis of the different components which constitute the dioxin input and output. Analyses of PCDD/PCDF were carried out on stack gas, fly ash, slag, refuse derived fuel (RDF) and on urban solid waste (USW) samples from waste incinerator. Stack gas samples were collected using a filter/condenser method in accordance with EN-1948. The MWI, which has been controlled over the last years (data previously reported in ref. 7), has been recently retrofitted with a modern system cleaning gas in order to comply with the limit of the 0.1 ng I-TEQ/Nm^3. Table 1 shows the characteristics of the MWI studied.

Table 1. *Operation conditions of the MWI in 1997.*

	MWI
Annual capacity (Mg/y)	150.000
Percentage versus the total waste treated in Spanish MWI	11.0
Number of lines	2
Type of operation	24 h/day
Production of ashes (Mg/y)	1000
Production of slag (Mg/y)	34000
Flue gas per line (Nm^3/h)	80000
Recycling	-
Composting (Mg/y)	-
Fuel	USW

Extraction and clean-up

All the pollutants were removed from matrices by soxhlet extraction using toluene for 48 h. Liquid-liquid extraction with dichloromethane was performed to remove these compounds from condensed water. Fly ash and slag were treated with HCl 3 M for 2 h prior to soxhlet extraction. The RDF and USW were previously treated with tetrahydrofuran (THF) to dissolve the PVC. The PVC was precipitated with water. Next, the extract was transferred to hexane followed by acid treatment with sulphuric acid and finally the pollutants were totally removed from the matrix by soxhlet extraction using toluene for 48 h (6). Finally, extracts were concentrated prior to the cleanup process. The cleanup process was based on the classic liquid-solid adsorption chromatography using silica, florisil, alumina and carbopack C as adsorbents, in an open glass column at atmospheric pressure (7).

Instrumental analysis

Samples were carried out by high resolution gas chromatography coupled to high resolution mass spectrometry (HRGC/HRMS). For HRGC, a Fisons CE 8000 Series gas chromatograph equipped with a DB-5 fused silica capillary column (60 m, 0.25 mm ID, 0.25 µm film thickness) was used. The temperature programme was: 140 °C (1min) to 200°C (1min) at 20 °C/min, then at 3°C/min to 300°C and held isothermally for 20 min at 300 °C. For HRMS, an Autospec Ultima (Fisons Instruments) mass spectrometer with a positive electron impact (EI+) source was employed. The analyzer mode was selected ion monitoring (SIM) at 10000 of resolving power.

RESULTS AND DISCUSSION

Stack gas emissions, fly ash and slag samples were analyzed in order to examine the total dioxin output from the afore-mentioned MWI. Table 2 summarizes the results of the PCCD/PCDF levels determined in stack gas, fly ash and slag samples.

Table 2. *PCDD/PCDF levels in emissions, fly ash and slag samples from the MWI.*

	Stack Gas		**Fly Ash**		**Slag**	
	ng I-TEQ/Nm^3	*g I-TEQ/y*	*ng I-TEQ/g*	*g I-TEQ/y*	*ng I-TEQ/g*	*g I-TEQ/y*
MWI-2	0,04	0,05	0,65	0.65	0,06	2,04

These findings indicate that stack gas levels constitute a minor contribution to the total dioxin emitted by those MWI which comply with the limit of 0.1 ng I-TEQ/Nm^3. The highest concentration of PCDD/PCDF was found in fly ash. However, the highest production of slag is the responsible for an annual output of PCDD/PCDF comparable with the levels observed in fly ash. Table 3 shows the levels of the PCCD/PCDF determined in RDF, USW samples and Table 4 shows the dioxin mass balance for the MWI. In all the cases studied, the MWI constitute a source of dioxins and a non-thermal destruction is observed overall.

Table 3. *Levels of PCDD/PCDF in RDF, USW and compost samples.*

	Range *pg I-TEQ/g*	**Mean** *pg I-TEQ/g*
RDF	3,81-4,76	**4,34**
USW	4,40-13,27	**8,84**
Compost*	5,00-57,23	**31,20**

Table 4. *Dioxin mass balance.*

	INPUT *g I-TEQ/y*	**OUTPUT** *g I-TEQ/y*	**BALANCE** *g I-TEQ/y*
MWI-2	1,32	2,74	**1,42**

One of the biggest incovinient of the dioxin mass balance is the problem of collecting representative samples, mainly, on the input side because of the heterogeneity of these matrices and the difficulties

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* Compost being obtained by processing USW in other plants

us to resolve this problem and to evaluate whether or not the content of PCDD/PCDF in the RDF or UWS samples could be regarded as representative input values. Table 5 shows the percentage composition of RDF and USW and the levels of PCDD/PCDF found in the analysis of each component of RDF and USW. The metal and glass samples were not determined on the assumption that these matrices did not have significant levels of PCDD/PCDF.

Table 5. *Percentage composition and levels of PCDD/PCDF in RDF and USW.*

	PCDD/PCDF (pg I-TEQ/g)	RDF composition (%)	PCDD/PCDF in RDF (pg I-TEQ/g)	USW composition (%)	PCDD/PCDF in USW (pg I-TEQ/g)
Paper	6,02	46,8	2,82	20,0	1,20
Plastic	20,65	20,4	4,21	11,8	2,44
Textile	170,05	4,7	**7,65**	7,6	**12,92**
Wood	2,24	4,0	0,09	3,8	0,85
Organic	5,3	17,1	0,91	46,5	2,46
Metals	-	4,6	-	3,3	-
Inert	-	2,4	-	7,0	-
Total	-	-	**15,68**	-	**19,87**

To date, the sum of the results for each component is higher than that obtained for the RDF and USW samples. In our study, the textile samples are the biggest contributor to the PCDD/PCDF levels in the RDF and USW samples. Bearing these values in mind, the MWI present a thermal destruction of dioxins.

ACKNOWLEDGMENTS

The authors wish to thank G. Martrat, J. Sauló and M. A. Adrados for their collaboration in this study.

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