



Dioxin mass balance in a municipal waste incinerator

E. Abad, M.A. Adrados, J. Caixach, B. Fabrellas¹, J. Rivera^{*}

Mass Spectrometry Laboratory, Department of Ecotechnologies, CID-CSIC, Jordi Girona 18-26, 08034 Barcelona, Spain

Abstract

A dioxin mass balance in an Spanish municipal waste incinerator (MWI) is presented. Input and output inventories from two sampling collection episodes including the analysis of PCDD/PCDF in urban solid waste (USW), stack gas emissions, fly ash and slag are reported. In one collection the levels of USW were around 8 pg I-TEQ/g and non-thermal destruction was observed overall. In the other collection the levels of USW were higher (around 64 pg I-TEQ/g) and the dioxin balance revealed a thermal destruction. Analysis of the different waste materials (textile, organic, plastic, wood and paper) was performed separately and the textile samples presented the highest levels. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Dioxins; Furans; PCDDs/PCDFs; Combustion; Waste management; Mass balance

1. Introduction

Municipal waste management often combines different strategies such as recycling, composting, thermal treatment or landfill disposal. Recycling and composting are being successfully implemented in the early stages of waste management in several countries. However, additional operations such as combustion processes in urban solid waste management are always required to eliminate the residue generated by recycling or composting. In recent years, MWIs have been the subject of much controversy because of their emissions into the atmosphere, which constitute a potential risk to the environment. Accordingly, stringent regulations governing stack emissions are being enforced. In particular, European Union (EU) member countries have set limit values for PCDD/PCDF emissions for hazardous waste

incinerator plants of 0.1 ng I-TEQ/Nm³. In Spain urban solid waste management is 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. Therefore, the solid residues and recycling products should be carefully characterized before a final decision is taken (Krauß et al., 1994; Harrad et al., 1991).

On the other hand, it is common knowledge that the PCDD/PCDF and PCDD/PCDF-precursors are already present in waste. In fact, data about the levels of PCDD/PCDF in textile, wood, food, plastic, etc., the typical components of waste, are available (Klasmeier and McLachlan, 1998; Klasmeier et al., 1999; Horstmann and McLachlan, 1995; Wilken et al., 1991, 1992; Wagenaar et al., 1998). The most recent studies reveal a thermal destruction of PCDD/PCDF in a modern MWI (Vehlow, 1997). In this study, we analyzed the levels of PCDD/PCDF in different samples from a Spanish MWI in order to examine the dioxin mass balance.

^{*} Corresponding author. Fax: +00349-3-2045904.

E-mail address: jraeco@cid.csic.es (J. Rivera).

¹ Present Address: CIEMAT, Avda Complutense, 22. 28040 Madrid, Spain.

2. Materials and methods

2.1. 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 and urban solid waste (USW) samples at various sampling episodes. Moreover, refuse derived fuel (RDF) and compost samples obtained by processing USW in other plants were also analyzed.

Stack gas samples were collected using a filter/condenser method in accordance with EN-1948:1996. Fly ash and slag samples were simultaneously collected every 30 minutes during stack gas sampling. The MWI, which has been controlled over the past years (data previously reported in Vehlou (1997), MWI-2), has recently been retrofitted with a modern system cleaning gas in order to comply with the limit of the 0.1 ng I-TEQ/Nm³. Operating conditions of the MWI in 1998 are given in Table 1.

2000 kg of current RDF and USW were collected from different MWIs to prepare a 50 cm width base. After being sequentially mixed and divided into four identical portions, two opposite sides were rejected and the remainders were mixed again. The operation was repeated until a 25 kg sample was obtained. Next, the 25 kg sample was torn into 1 cm pieces and homogenized. From these, 2 kg were dried and weight losses of 44% w/w were observed. Subsequently, the 2 kg sample was triturated again prior to extraction, obtained particle sizes of 38–42 µm.

2.2. Extraction and clean-up

Prior to the extraction process, the samples were spiked with labeled PCDD/PCDF standards described in EPA 1613. Liquid-liquid extraction with dichloromethane was performed to remove dioxin compounds

from condensed water. Fly ash and slag were treated with HCl 3 M for 2 h prior to extraction. All the pollutants were removed from fly ash, slag, XAD-2 and the filter, USW and RDF by Soxhlet extraction using toluene for 48 h. The extracts of RDF and USW were transferred to *n*-hexane which produced a precipitate. The *n*-hexane solution was filtered and the solid was treated with tetrahydrofuran (THF) to dissolve PVC and other polymers, followed by *n*-hexane to extract the PCDD/PCDF. The PVC was re-precipitated with water. Next, both *n*-hexane extracts (from the THF solution and the filtered extract) were combined (Wagenaar et al., 1998) and then repeatedly treated with sulphuric acid to eliminate organic material. Owing to the organic nature, remarkable exothermic reactions during the sulphuric acid attack were observed in the USW samples. Finally, extracts were concentrated prior to the cleanup process.

Samples were cleaned up by two different methods. One method was based on the classic liquid-solid adsorption chromatography using silica (Merck, Germany), florisil (Merck, Germany), alumina (ICN, Germany) and Carboxpack C 80/100 (Supelco, PA) as adsorbents, in an open glass column at atmospheric pressure (Abad et al., 1997). The other method was based on use of the Power Prep™ system (FMS Inc., MA). The automated system cleanup employs multi-layer silica, basic alumina and PX-21 carbon adsorbents, prepackaged in columns made of Teflon and hermetically sealed (FMS Inc. Boston, USA) (Abad et al., 1999). All solvents, acetone, dichloromethane, toluene, *n*-hexane and ethyl acetate for organic trace analysis were purchased from Merck (Germany).

2.3. Instrumental analysis

Analysis was carried out by high resolution gas chromatography coupled to high resolution mass spectrometer (HRGC/HRMS). For HRGC, a Fisons CE 8000 Series gas chromatograph (Fisons Instruments, Milan, Italy) equipped with a DB-5 (J&W Scientific, CA, USA) fused silica capillary column (60 m, 0.25 mm ID, 0.25 µm film thickness) was used. The temperature programme was: 140°C (1 min) to 200°C (1 min) 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, Manchester, UK) mass spectrometer with a positive electron impact (EI+) source was employed. The analyzer mode was selected ion monitoring (SIM) at 10 000 of resolving power. Details are given in Abad et al. (1997, 1999).

3. Results and discussion

Stack gas emissions, fly ash and slag samples were analyzed in order to examine the total dioxin output

Table 1
Operating conditions of the MWI in 1998

Annual capacity (Mg/yr)	150 000
Percentage versus the total waste treated in Spanish MWI	11.0
Numbers of lines	2
Combustion air (Nm ³ /h)	90 000
Operation	24 h/day ^a
Production of ashes (Mg/yr)	4000
Production of slag (Mg/yr)	3400
Flue gas per line (Nm ³ /h)	80 000
Recycling	–
Composting (Mg/yr)	–
Fuel	USW

^a 7500 h/yr.

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/yr	ng I-TEQ/g	g I-TEQ/yr	ng I-TEQ/g	g I-TEQ/yr
1st sample collection	0.004	0.0048	0.65	2.60	0.06	2.04
2nd sample collection	0.004	0.0048	0.37	1.48	0.013	0.44

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		
1st sample collection	4.40–13.27	8.84
2nd sample collection	45.73–87.48	64.15
Compost	5.00–57.23	31.20

Table 4
Dioxin mass balance

	Input (g I-TEQ/yr)	Output (g I-TEQ/yr)	Balance (g I-TEQ/yr)
1st sample collection	1.33	4.64	3.31
2nd sample collection	9.62	1.92	–7.70

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

	PCDD/PCDF (pg I-TEQ/g)	No. of samples analyzed	RDF composition (%)	PCDD/PCDF in RDF (pg I-TEQ/g)
Paper	6.26	2	46.8	2.93
Plastic	21.77	2	20.4	4.44
Textile	157.35	2	4.7	7.40
Wood	2.71	2	4.0	0.11
Organic	2.71	2	17.1	0.94
Metals	–	–	4.6	–
Inert	–	–	2.4	–
Total	–	–	–	15.82

from the aforementioned MWI in two different sample collection episodes. Table 2 summarizes the results of the PCDD/PCDF levels determined in stack gas, fly ash and slag samples.

These findings indicate that stack gas levels constitute a minor contribution to the total dioxin emitted by the MWI which complies with the limit of 0.1 ng I-TEQ/Nm³. The highest concentration of PCDD/PCDF was found in fly ash. However, the high production of slag is responsible for an annual output of PCDD/PCDF comparable with the levels observed in fly ash. Another question concerns the dioxin levels present in combustion

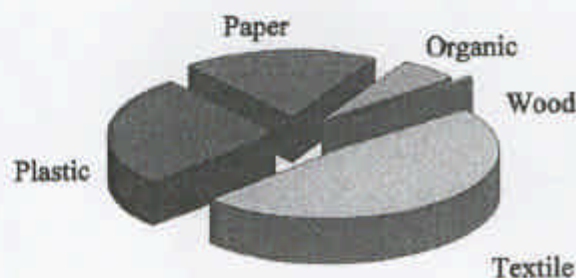


Fig. 1. PCDD/PCDF distribution in RDF.

- benzo-p-dioxin and octachlorodibenzofuran. *Chemosphere* 36, 1627–1635.
- Klasmeier, J., Mühlebach, A., McLachlan, M.S., 1999. PCDD/Fs in textiles – Part II. Transfer from clothing to human skin. *Chemosphere* 38, 97–108.
- Krauß, Th., Krauß, P., Hagenmaier, H., 1994. Formation of PCDD/PCDF during composting. *Chemosphere* 28, 155–158.
- Vehlow, J., 1997. Modern strategies in waste incineration. *Technol. Environ.* 1, 60–74.
- Wagenaar, H., Langeland, K., Hardman, R., Sergeant, Y., Brenner, K., Sandra, P., Rappe, C., Tiernan, T., 1998. Analysis of PCDDs and PCDFs in virgin suspension PVC resin. *Chemosphere* 36, 1–12.
- Wilken, M., Cornelsen, B., Zeschmar-Lahl, B., Jäger, J., 1991. PCDD/PCDF balance of different municipal waste management methods. *Chemosphere* 23, 1481–1489.
- Wilken, M., Cornelsen, B., Zeschmar-Lahl, B., Jäger, J., 1992. Distribution of PCDD/PCDF and other organochlorine compounds in different municipal solid waste fractions. *Chemosphere* 25, 1517–1523.