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Dioxin Abatement Strategies and Mass Balance at a Municipal Waste Management Plant

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Since the thermal management of municipal solid waste (MSW) is considered to be one of the major sources of polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzo-furans (PCDFs), the purpose of this study was to show the results of a dioxin abatement program performed in the municipal waste incineration (MWI) plant of Tarragona (NE Spain). Previously, stack gas emission levels of PCDDs/PCDFs around 3.26 ng I-TEQ/Nm^3 were determined when the gas-cleaning system consisted only of an electrostatic precipitator (ESP). Decreased levels, below 0.1 ng I-TEQ/Nm^3, were observed when a new air pollution control system was installed. This new system was improved by the injection of activated carbon, which helped to lower the levels of PCDDs/PCDFs to around 0.01 ng I-TEQ/Nm^3. Considering the absence of a particular impact on herbages, soils, and ambient air around the plant, as reported in previous works, and the hypothesis that a modern installation could become a sink for dioxins instead of a source, a dioxin mass balance was evaluated. The study compared in a large-scale MWI plant the levels of PCDDs/PCDFs of all input and output contributors (MSW, ambient air, stack gas emission, fly ash, and slag) forming part of the inventory collected in various monitoring campaigns. The findings revealed a remarkable homogeneity in output values (between 1.19 and 2.62 ng I-TEQ/yr) in contrast to the large variability observed in input values. In the first sampling campaign, the dioxin content in MSW was around 64.15 ng I-TEQ/kg, and a negative balance of 7.68 g I-TEQ/yr was calculated. However, in the latest campaign, levels were about 2.36 ng I-TEQ/kg MSW, resulting in a positive balance of 2.28 g I-TEQ/yr.

Introduction

Municipal waste management covers certain procedures including re-utilization, recycling, landfill disposal, composting, and a variety of combustion processes. Combustion, commonly known as incineration, consists of a controlled oxidation process in which chemical reactions transform carbon species into CO_2. Hence the carbon content of waste cannot totally be converted into CO_2, and minor amounts of unwanted products of incomplete combustion are to be found.

Recently, waste incineration has been a subject of public concern since it leads to the emission of pollutants such as acid gases, particulate matter, nitrogen oxides, heavy metals, and highly toxic trace organic compounds to air, land, and water. As a result, stringent regulations mainly governing stack gas emissions have been enforced in recent years, with the aim of reducing the emissions of pollutants into the air. While organic pollutants such as polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs), or any other so-called dioxin-like compounds such as polychlorinated biphenyls (PCBs) or naphthalenes (PCNs) are produced by a wide range of processes, the incineration of municipal waste in old plants, equipped with an obsolete gas-cleaning system, has been recognized as one of the major known sources of dioxins and furans and is thus an important contributor to the presence of these contaminants in all environmental compartments (*1–3*). Understanding of the mechanism behind the formation of PCDDs/PCDFs is not yet fully understood because of the complexity of their formation reactions. Nevertheless, the novo synthesis appears to be the dominant mechanism of dioxin formation in the present combustion processes along with a wide variety of less important formation pathways (*4–7*).

The level of pollutants emitted depends both on the technology employed during the thermal process and on the composition of the waste treated. In modern plants, the first stage in dioxin abatement strategies consists of the application of primary combustion measures, which affect mainly the stability of the thermal processes (waste composition, turbulences, temperature variations in furnace, etc.). However, the raw gas produced during combustion processes requires exhaustive cleaning before being released into the air for the legislative standards to be achieved. Therefore, a second common step is the implementation of an appropriate gas-cleaning system, which drastically reduces the emission of these contaminants into the air. Given that the major content of PCDDs/PCDFs correlates with concentrations in particulate matter (*8*), an accurate dedusting process is essential. Owing to their simple design and low maintenance costs, electrostatic precipitators (ESP) were often used for this purpose in the oldest municipal waste incineration (MWI) plants. Although these systems permitted established dust emission standards to be met, they also seemed to be important precursors of dioxin formation (*9–11*). In this respect, bag filters provide an alternative for achieving better results, and a contributor to dioxin formation is thus avoided. Flue gas cleaning is generally complemented with another step, the purpose of which is to trap acid components by the injection of $Ca(OH)_2$. Even so, a substantial amount of PCDDs/PCDFs remain in the gases. Therefore, satisfactory dioxin abatement requires additional steps, such as the injection of charcoal or other additives (*8–13*).

In Spain, municipal waste produced in 1997 was estimated at 15 620 000 Mg/yr. The typical Spanish waste stream was composed of approximately 46.5% organic matter, 20% paper, 11.8% plastic, 7.6% textiles, 3.8% wood, 3.3% metals, and 7% inert matter. The total waste thermally treated was around 1 163 000 Mg/yr, which represented approximately 7.45% of the total Spanish municipal waste (*14*). The MWI plant under study, called SIRUSA, began its activity in 1991 and was the fourth plant to operate in Spain. The annual capacity of the MWI was 145 000 Mg. This percentage represents approximately 12.5% of the total waste incinerated in Spain. The first layout of this plant presented two identical incineration units and a gas-cleaning system formed by an ESP connected to a stack. In 1997, the ESP was replaced by a modern air pollution control system (APCS). The plant is located 2 km from Tarragona. In the surroundings, two petroleum refineries and an important complex of petro-

			levels				
matrix	units	site	range	average	median	no. of samples	ref
ambient air	fg I-TEQ/Nm^3	Tarragona	10−500	50		12	18
		Constantí	50−620	260		8	18
soils	ng I-TEQ/kg dm	control site 1996	0.27−2.23	0.68		10	19
		surroundings 1996	0.22−5.80	1.08	0.80	24	19
		surroundings 1997	0.11−3.88	1.17	0.88	24	20
		surroundings 1999	0.15−4.89	1.20	1.00	24	21
herbages	ng I-TEQ/kg dm	surroundings 1996	0.15−62.09	4.11	0.33	24	22
		surroundings 1997	0.11−0.50	0.23	0.20	24	22
		surroundings 1999	0.04−0.28	0.08	0.11	24	23

[a] Levels of PCDDs/PCDFs in ambient air, soils, and herbage samples.

chemical industries are already operating, including a PVC manufacturing plant. The presence of a highway and two motorways with heavy traffic near the MWI plant is also noteworthy.

Some of the major known sources of atmospheric contamination by PCDDs/PCDFs are industrial activities in which a combustion process is involved. As a consequence, atmospheric deposition has been the main supplier of PCDDs/PCDFs onto the surface of soils. The presence of PCDDs/PCDFs on vegetation surfaces is due to the retention of PCDDs/Fs by direct deposition of airborne particles or absorption of vapor-phase contaminants, including those attributable to evaporation from soils (15). Although ambient air immediately reflects the impact of a major source, PCDD/PCDF levels in vegetation can provide information on the short-term exposure to these chemicals, and the concentrations in soils can be used to cautiously hypothesize on long-term exposure (16, 17).

Since it came into operation, the plant has been the subject of public concern. Great efforts and comprehensive studies have been made to evaluate the potential impact of the MWI plant. In 1996, we reported PCDD/PCDF levels in ambient air samples from different sites affected by several potential sources as part of the compliance monitoring survey undertaken by the Catalan authorities. The closest site to the plant (Constantí, a rural area affected by a major source) yielded 50 fg I-TEQ/Nm^3. Levels found in Tarragona (an urban air area) were around 260 fg I-TEQ/Nm^3 (18). Later, a comprehensive study on dioxin content in soil and grass samples collected from the surroundings of the plant was also conducted (19−23). The study was carried out over three different campaigns performed in 1996, 1997, and 1999. Values obtained for the 72 soil samples analyzed revealed a slight increase over time (Table 1). The authors argued that the increase probably reflected the cumulative deposition of contaminants. Nevertheless, they pointed out the presence of other major sources of PCDDs/PCDFs since this area is under the influence of other industrial activities that could also have contributed. However, in the majority of cases, levels remained below the optimal target of 5 ng I-TEQ/kg, and only a few cases were between 5 and 40 ng I-TEQ/kg (24). Regarding vegetable matrixes, these materials have been employed before in other monitoring programs. Nevertheless, the authors remarked that comparative data in the literature on the dioxin contents in vegetation affected by a primary source such as an MWI plant were scarce and therefore difficult to discuss. However, they found good correlations between soil and vegetable samples (19−23).

The first part of this work shows the results of the studies carried out to provide data on dioxin emission control and the survey program aimed at reducing the PCDD/PCDF emissions to comply with the limit of 0.1 ng I-TEQ/Nm^3 in the MWI plant located in Tarragona (Catalonia, NE Spain). This includes the optimization program performed after the replacement of an obsolete gas-cleaning system consisting only of an ESP by a complex system consisting of a semidry scrubber and a bag filter. In addition, the air pollution system was optimized by the injection of activated carbon.

However, the removal of pollutants from flue gas by sophisticated air pollution control systems necessarily produces solid materials derived from the combustion processes, formed mainly by bottom and fly ashes, which may also contain significant levels of dioxins and furans. To date, a number of strategies for their inertization (cement solidification, treatment by chemicals, melting and solidification, etc.) or possible re-utilization have already been developed so that any potential re-entering of these pollutants into the environment is avoided. The question of whether these materials can be discharged without having an impact on the environment has already arisen (8). In contrast, an often disregarded aspect concerns the control of materials to be incinerated. Most recent studies demonstrated the presence of significant quantities of dioxins and dioxin precursors in municipal waste around 50 ng I-TEQ/kg (8, 25−28) and other typical components in waste, such as textiles, wood, food, plastic, etc. (29−35). Bearing in mind the dioxin content in waste streams, the plant could hypothetically become a sink for PCDDs/PCDFs instead of a source. Therefore, the second objective of this study was to evaluate a dioxin mass balance in the MWI plant. To this end, the typical waste treated in the plant as well as slags, fly ashes, stack gas emission, and the air involved during combustion process were analyzed in various sampling campaigns.

Materials and Methods

Sampling. *Stack Gas Emissions.* The first aim of this work was to evaluate the effect on PCDD/PCDF emission by replacement of the old gas-cleaning system (ESP). Consequently, a measurement program was carried out at several sampling positions in the installation. When the matrixes were in gaseous phase, sampling was made with a stack gas sampler of filter/condenser method. The filter was placed after the probe. The gas temperature in probe and filter was regulated at 120 °C. XAD-2 (Merck, Germany), previously cleaned, was used as an adsorbent trap. During the sampling process, the resin was cooled at 20 °C by recirculated water. The sampling process was controlled by spiking the filter with a standard sampling solution formed by a mixture of three labeled PCDFs (EN-1948-SS from Wellington, Guelph, ON, Canada) (36−38).

Dioxin Mass Balance Strategy. One of the biggest drawbacks in the assessment of a dioxin mass balance is the problem of collecting representative samples, particularly of municipal solid waste (MSW). To our knowledge, no data have been reported on a comprehensive study on a dioxin balance in a plant where the air pollution cleaning system had been previously replaced. Thus, the design of the dioxin

mass balance was performed in three different stages between 1998 and 2000: (i) a preliminary study, (ii) the dioxin mass balance, and (iii) the MSW reevaluation. The evaluation included analysis of the different components constituting the dioxin inputs and outputs, and subsequently, analyses of PCDDs/PCDFs were performed on stack gas, ambient air, fly ash, slag, and MSW samples.

The preliminary approach was attempted at the beginning of the assessment to define the sampling strategy for performing an accurate dioxin mass. Thus, fly ash, slag, and MSW samples were randomly collected, and a stack gas emission was performed as previously described.

In the second stage, eight sampling collections were made as a final proposal for the elaboration of the dioxin balance covering the two incineration units. Whereas the input components and stack gas samples were collected as previously described, the fly ashes and slag samples from the same incineration unit were simultaneously collected every 30 min during stack gas sampling. In parallel, as output components, 2000 kg of current MSW was collected to prepare a 50-cm-wide base. After the base was sequentially mixed and divided into four identical portions, two opposite sides were rejected, and the remaining two were mixed again. The operation was repeated until 25-kg samples were obtained and torn into 1-cm pieces so that homogeneity was achieved. From these, 2 kg was lyophilized and triturated again prior to extraction.

The heterogeneity of the MSW materials, the tedious tasks undertaken to perform an accurate analytical method, and the variability in dioxin content found in previous determinations gave rise to the elaboration of a new series of MSW. Thus, in a third stage, 8000 kg of MSW was collected over three serial weeks from the waste bunker and treated as previously described.

Finally, the air involved in the combustion reaction was assessed to evaluate its contribution to the balance. Consequently, ambient air samples were collected using a high-volume sampler (HVS) placed at the waste bunker where the air is sucked into the combustion chamber. A fiber glass filter was placed on the HVS head followed by a polyurethane foam plug (PUF) as an adsorbent medium. The process was controlled by spiking the PUF with a recovery standard formed by [^{37}Cl]-2,3,7,8-TCDD. The HVS was connected to a vacuum pump and approximately 1000 m^3 of air mass was sucked in for 24 h at a sampling speed of 45 m^3/h (18).

Extraction and Cleanup. Prior to the extraction process, the samples were spiked with labeled PCDD/PCDF standards described in EPA 1613 or EN-1948 methods (36, 37). Analytes were removed from fly ash, slag, soils, MSW, XAD-2, and the filter by Soxhlet extraction using toluene for 48 h. In addition, as a preliminary treatment, fly ash and slag were treated with 3 M HCl for 2 h before being extracted. The toluene extracts were then transferred to n-hexane and rotary-concentrated prior to the cleanup process.

However, the transfer of toluene MSW extracts to n-hexane produced a precipitate, and additional steps were always required before the cleanup process. First, the n-hexane solution was filtered, and a solid fraction formed mainly by PVC, plastics, and other polymers was separated from the liquid fraction. Next, the solid was treated with tetrahydrofuran (THF) to dissolve the whole matter, and a quantitate of n-hexane was subsequently added. THF and PVC were then removed by a precipitation with water while PCDDs/PCDFs remained in n-hexane fraction. The resulting n-hexane extracts were combined and repeatedly treated with sulfuric acid to eliminate organic material. Finally, extracts were concentrated prior to the cleanup process (29).

For the cleanup, two different methods were applied. One was based on the classic liquid−solid adsorption chromatography using silica (Merck, Germany), Florisil (Merck, Germany), alumina (ICN, Germany), and Carbopack C 80/100 (Supelco, PA) as adsorbents in an open glass column at atmospheric pressure. The multilayer silica column was composed of sequential layers of 3 g of Na$_2$SO$_4$|12 g of SiO$_2$−H$_2$SO$_4$|1 g of SiO$_2$|6 g of SiO$_2$−NaOH|1 g of SiO$_2$|2 g of SiO$_2$−AgNO$_3$. Florisil (5 g) and basic alumina (6 g) adsorbents required conditioning at 600 and 300 °C overnight, respectively. The extracts were loaded through the columns, and PCDDs/PCDFs were eluted with different solvents as described in EPA 1613 (38). The second method was based on the use of the Power Prep system (FMS Inc., Boston, MA). The automated system cleanup employs multilayer silica, basic alumina, and PX-21 carbon adsorbents, prepackaged in columns made of Teflon and hermetically leaded (FMS Inc.). The extracts were loaded and pumped through individual sets of multilayer silica followed by a basic alumina column with 90 mL of n-hexane at 15 mL/min. Interferences were eliminated with 60 mL of n-hexane:dichloromethane (98:2) at 12 mL/min. Next, PCDDs/PCDFs were eluted from the alumina column and transferred to the PX-21 carbon column with 120 mL of n-hexane:dichloromethane (1:1) at 8 mL/min. The interferences were eluted with 12 mL of ethyl acetate:toluene (1:1) in the forward direction at 15 mL/min, and PCDDs/PCDFs were collected from the carbon column in the reverse direction with 65 mL of toluene at 8 mL/min. All solvents, acetone, dichloromethane, toluene, n-hexane, and ethyl acetate for organic trace analysis were purchased from Merck (Germany) (30, 39, 40).

Instrumental Analysis. Purified extracts were analyzed by HRGC−HRMS on a GC 8000 series gas chromatograph (Carlo Erba Instruments, Milan, Italy) equipped with a CTC A 200S autosampler and coupled to an Autospec Ultima mass spectrometer (Micromass, Manchester, U.K.), using a positive electron ionization (EI+) source and operating in the SIM mode at 10000 resolving power (10% valley definition). The two most abundant ions in the [M − Cl]$^+$ cluster were monitored at a 50-ms dwell time and a delay time of 20 ms. Chromatographic separation was achieved with a DB-5 (J&W Scientific, CA) fused-silica capillary column (60 m × 0.25 mm i.d., 0.25 μm film thickness). As a confirmation, a DB-DIOXIN (J&W Scientific, CA) fused-silica capillary column (60 m × 0.25 mm i.d., 0.25 μm film thickness) was employed when required. The temperature program was as follows: 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 the DB-5 column and 140 °C (1 min) to 200 °C (1 min) at 20 °C/min, then at 2 °C/min to 280 °C and maintained isothermally for 85 min at 280 °C for the DB-DIOXIN column (40).

Quality Assurance. Quality assurance criteria were based on applications of quality control (QC) measures such as the analysis of a blank sample covering the complete analytical procedure. Other performance checks taken into account were accurate isomer-specific GC separation, sensitivity check and 10000 resolution power of MS, sufficient recovery, fulfillment of the minimum requirements described in well-accepted methods EPA 1613 and EN-1948 (36, 37). Additional evaluation for ensuring good quality data was obtained by participating in interlaboratory studies, the results of which are given in refs 41 and 42 as participant codes 33 and 70, respectively.

Results and Discussion

Upgrading the Gas-Cleaning System. From 1993 onward, an extensive study of environmental PCDD/PCDF levels was undertaken in northeast Spain (Catalonia). The study was primarily initiated to obtain representative data on dioxin stack gas emissions from SIRUSA. At that time, the APCS consisted of an ESP. After analysis of 20 measurement
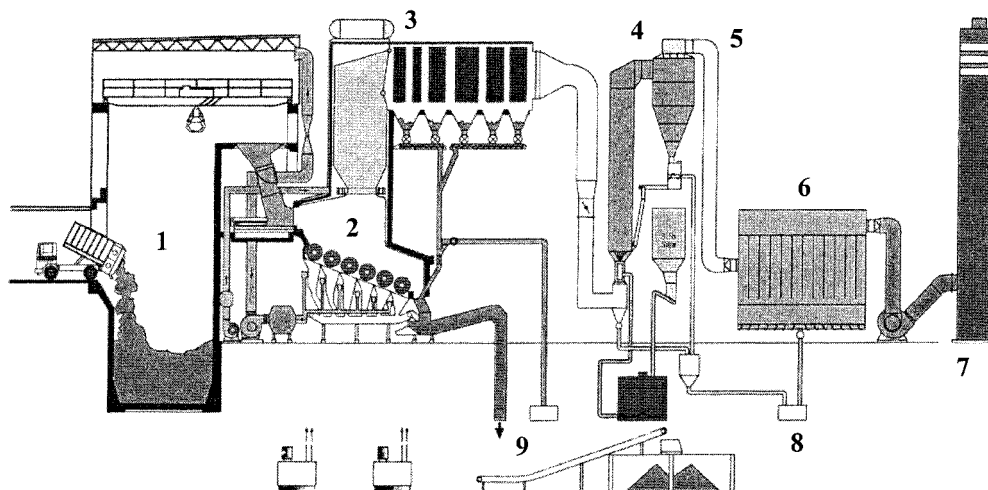
FIGURE 1. Final configuration of the MWI plant of Tarragona after APCS upgrading: (1) bunker waste, (2) furnace, (3) boiler, (4) spray absorber, (5) activated carbon, (6) bag filter, (7) stack, (8) fly ash treatment plant, and (9) slag treatment plant.

TABLE 2. Examination of Dioxin Levels from the Stack after Installation of the New Air Pollutant Control System

campaign	sample point	PCDDs/PCDFs (ng I-TEQ/Nm³)	sample point	PCDDs/ PCDFs (ng I-TEQ/Nm³)	remarks
1	after boiler (3)[a]	7.95	stack unit 1	0.0434	without carbon
2	after boiler (3)[a]	2.73	stack unit 1	0.0012	adding carbon
2	after boiler (3)[a]	0.51	stack unit 2	0.0032	adding carbon

[a] Raw combustion gases.

campaigns, findings revealed levels around 3.26 ng I-TEQ/ Nm³ (*18;* MWI-1). Analyses of solid residues were also performed, and the results yielded values of 1.58 ng I-TEQ/g for fly ash samples and 0.06 ng I-TEQ/g for slag samples (unpublished data). These results concurred with the data reported in the literature for plants whose gas-cleaning system was based solely on the use of the ESP (*8−11*).

In 1997, the APCS was upgraded. A new gas-cleaning system composed of a semi-dry scrubber and a fiber filter (FLS Miljo, Denmark) replaced the ESP system. Thus, the raw gas is first cleaned by a $Ca(OH)_2$ solution to trap the acid materials, followed by serial fiber filters to remove the particulate matter and other unwanted pollutants. In fact, initial specifications guaranteed stack gas emission values below 0.1 ng I-TEQ/Nm³ with no additional operation. Nevertheless, the system was also improved by injecting specific activated carbon for dioxin and mercury removal. The final configuration of the plant is given in Figure 1.

To examine whether the specifications of the new system could really be achieved, a number of flue gas emission samples were programmed in three different sampling episodes. The results are summarized in Table 2. During the first campaign, the whole new cleaning system operated without charcoal injection to check whether values below 0.1 ng I-TEQ/Nm³ could be achieved. Two gas emissions were simultaneously collected at two different points: one after the boiler to assess the dioxin content in raw gas and the other in the stack to evaluate the gas-cleaning system. The levels after the boiler were around 7.90 ng I-TEQ/Nm³ while the levels in the stack remained about 0.04 I-TEQ/ Nm³. Thus, the findings indicated that by replacing the ESP with a semi-dry scrubber and a bag filter, dioxin removal efficiency reached 99.4% even without the injection of activated carbon. This can be explained by the design of the spray absorber, which permits a drastic decrease in temperature and pressure of emissions so that "de novo synthesis" is partially inhibited.

In the next two sampling campaigns, an examination of the system was also made by adding activated carbon for dioxin removal (CARBOTECH) at a dosage between 40 and 50 mg/Nm³ for each combustion unit. To this end, two gas emissions were simultaneously collected for each combustion line at the same two points as described in the first campaign, i.e., after the boiler and in each stack unit. In both experiments, levels determined in the stack were 0.0012 and 0.0032 ng I-TEQ/ Nm³, respectively. This constituted an improvement in dioxin removal efficiency of approximately 93−97% with respect to that obtained without the injection of activated carbon; however, of more interest was the fact that overall dioxin removal was higher than 99.95%, bearing in mind the levels of dioxins determined after the boiler. In general, the findings verified the capability of the system cleaning device to successfully perform with the minimum requirements demanded, and levels far from the limit of 0.1 ng I-TEQ/Nm³ were soon reached. This tendency was subsequently corroborated during the dioxin mass balance.

Dioxin Mass Balance. The next objective of this study was to evaluate a dioxin mass balance.The balance attempts to assess the real situation after the thermal process, bearing in mind the effiency of the new APCS. In this respect, we would also like to mention that the evaluation of a dioxin mass balance is a very difficult task. Initially, we proposed to examine and cover point by point a major number of experiments to acquire valuable scientific data. However, the final study compared, in TEQ values, the total PCDD/ PCDF input via MSW with the sum of those measured in the output fraction in all three forms (emissions, fly ashes, and slags) in various sampling episodes on the assumption that the MWI plant behaves like a black box where dioxins present in the waste are destroyed during the thermal process but formed again during cooling of the combustion byproducts by so-called de novo synthesis. We considered TEQ values to evaluate and make more understandable the results of an analysis of a complex mixture of PCDDs/PCDFs. Unfortu-

TABLE 3. Operating Conditions of the MWI Plant

annual capacity (Mg/yr)	145 000
% vs total waste treated in Spanish MWI (%)	12.5
incineration units	2
combustion air (Nm³/h)	90 000
operation[a] (h/dy)	24
production of ashes (Mg/yr)	3120
production of slag (Mg/yr)	35 380
flue gas per unit (Nm³/h)	40 000
fuel	MSW

[a] 7800 h/yr.

nately, in the final proposal of the project, no intermediate study on the dioxins captured by the different elements forming the APCS were considered because of the difficulties in collecting representative samples. Table 3 gives the operating conditions and parameters considered for calculation of the dioxin mass balance such as annual amount of waste treated, annual production of solid combustion residues, number of combustion units, flow rates of gases released into the atmosphere, etc.

At the beginning of the study, a preliminary sampling approach allowed us to define the sampling strategy for the dioxin balance. The results revealed extremely low levels in gas emissions, under 0.01 ng I-TEQ/Nm³, which concurs with previous explanations. Fly ash samples presented levels around 0.65 ng I-TEQ/g, and slag samples remained at 0.06 ng I-TEQ/g. As an output component, levels found in a single sample of MSW were around 8.84 ng I-TEQ/kg. In these conditions, an annual dioxin formation of around 4.15 g I-TEQ/yr was calculated.

Second, the final proposal for the elaboration of the balance was designed over eight different campaigns covering the two incineration units. The overall results are summarized in Table 4. In the output balance, the three types of matrixes (stack gas emissions, fly ash, and slag samples) collected over the eight sample campaigns yielded a total of 24 values. Results determined from the stack ranged between 0.003 and 0.20 ng I-TEQ/Nm³, with a mean value of 0.008 ng I-TEQ/Nm³ and a median value of 0.007 ng I-TEQ/Nm³. Fly ash samples also presented a very narrow range of dioxin content, from 0.27 to 0.72 ng I-TEQ/g, with a mean and a median

TABLE 4. Dioxin Mass Balance: Overall Results of PCDDs/PCDFs in MSW, Stack Gas Emissions, Fly Ashes, and Slags over the Eight Campaigns (1998−1999)

campaign (data)	02/09/98	10/03/99	15/04/99	20/05/99	17/06/99	01/07/99	22/07/99	16/09/99
Output (Emissions, Fly Ashes, and Slags)								
combustion unit	1	1	2	2	1	1	2	2
emissions								
no. of samples	1	1	1	1	1	1	1	1
ng I-TEQ/Nm³	0.004	0.020	0.003	0.010	0.006	0.006	0.009	0.008
g I-TEQ/yr	0.002	0.012	0.002	0.006	0.004	0.004	0.006	0.005
contribution to output (%)	0.154	0.631	0.095	0.258	0.220	0.315	0.274	0.191
fly ashes								
no. of samples	1	1	1	1	1	1	1	1
ng I-TEQ/g	0.37	0.51	0.55	0.67	0.50	0.27	0.51	0.72
g I-TEQ/yr	1.15	1.58	1.72	2.09	1.56	0.83	1.58	2.26
contribution to output (%)	71.40	79.69	87.30	86.56	91.47	69.89	77.30	86.29
slags								
no. of samples	1	1	1	1	1	1	1	1
ng I-TEQ/g	0.013	0.011	0.007	0.009	0.004	0.010	0.013	0.010
g I-TEQ/yr	0.46	0.39	0.25	0.32	0.14	0.35	0.46	0.35
contribution to output (%)	28.45	19.68	12.60	13.18	8.31	29.79	22.43	13.52
total emitted (g I-TEQ/yr)	1.62	1.98	1.97	2.42	1.70	1.19	2.05	2.62
concn in RSU required for dioxin destruction (ng I-TEQ/kg)	11.15	13.64	13.56	16.66	11.74	8.19	14.14	18.05
Input (MSW)								
no. of samples	9	2	2	2	1	2	2	2
max (ng I-TEQ/kg)	87.48	3.67	3.98	4.33	2.29	7.58	2.26	2.41
min (ng I-TEQ/kg)	45.73	2.81	1.47	3.80	2.29	6.60	2.19	2.31
av (ng I-TEQ/Kg)	64.15	3.24	2.73	4.07	2.29	7.09	2.23	2.36
input (g I-TEQ/yr)	9.30	0.47	0.40	0.59	0.33	1.03	0.32	0.34
Dioxin Mass Balance								
annual (g I-TEQ/yr)	−7.68	1.51	1.57	1.83	1.37	0.16	1.73	2.28

| **Statistics**					
	no.	average	median	maximum	minimum
emissions					
ng I-TEQ/Nm³	8	**0.008**	**0.007**	*0.020*	*0.003*
g I-TEQ/yr		0.005	0.004	0.012	0.002
contribution to output (%)		0.267	0.239	0.631	0.095
fly ashes					
ng I-TEQ/g	8	**0.512**	**0.507**	*0.72*	*0.266*
g I-TEQ/yr		1.60	1.58	2.259	0.830
contribution to output (%)		81.24	82.99	91.47	69.89
slags					
ng I-TEQ/g	8	**0.010**	**0.010**	*0.013*	*0.004*
g I-TEQ/yr		0.34	0.35	0.460	0.142
contribution to output (%)		18.50	16.60	29.79	8.31
total emitted (g I-TEQ/yr)	8	**1.94**	**1.97**	*2.62*	*1.19*
concn in MSW required for dioxin destruction (ng I-TEQ/kg)	8	**13.39**	**13.60**	18.05	8.19
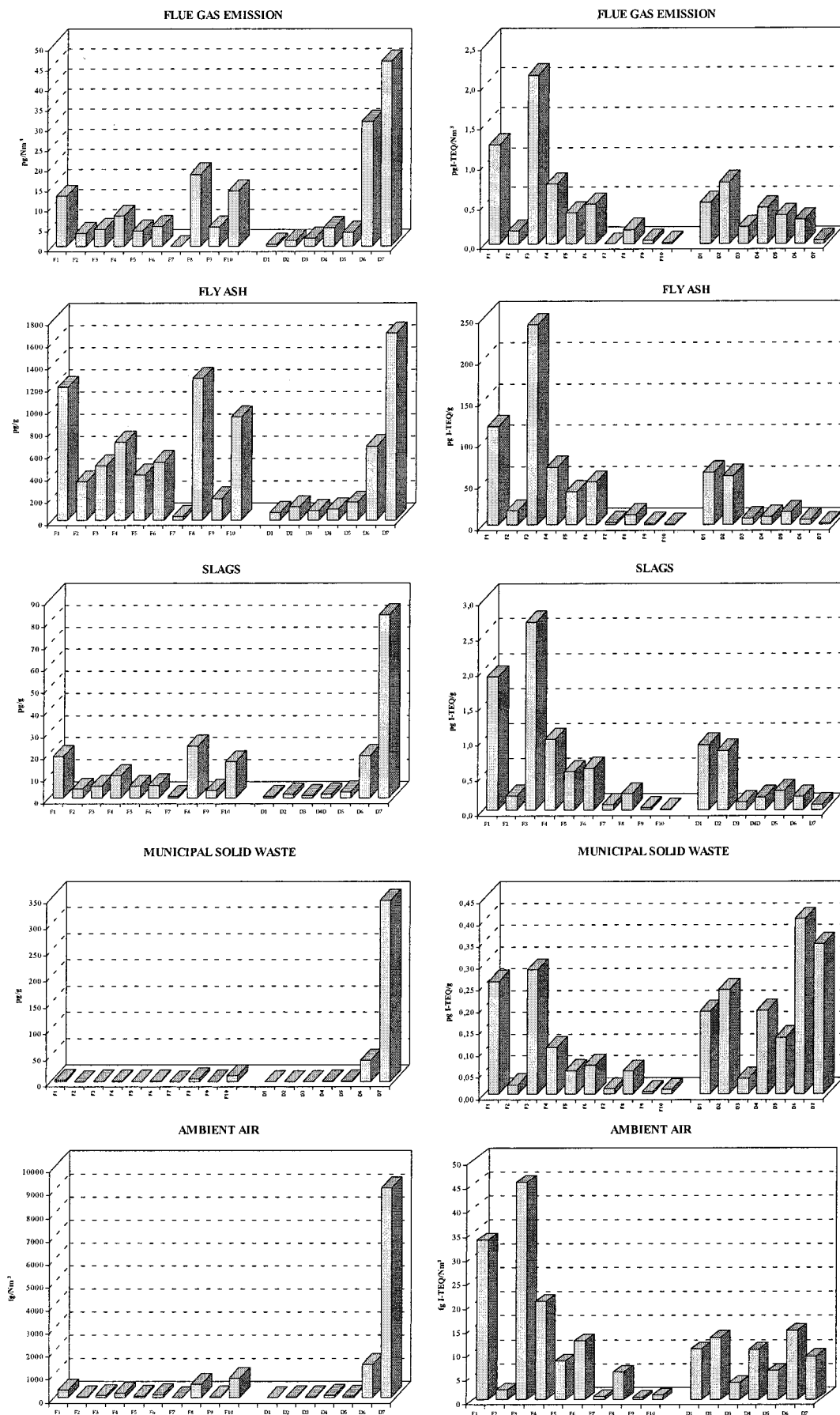
FIGURE 2. Isomer-specific profiles (expressed in concentration and TEQs). F1, 2,3,7,8-TCDF; F2, 1,2,3,7,8-PeCDF; F3, 2,3,4,7,8-PeCDF; F4, 1,2,3,4,7,8-HxCDF; F5, 1,2,3,5,7,8-HxCDF; F7, 1,2,3,7,8,9-HxCDF; F8, 1,2,3,4,6,7,8-HpCDF; F9, 1,2,3,4,7,8,9-HpCDF; F10, OCDF; D1, 2.3.7,8-TCDD; D2, 1.2.3.7,8-PCDD; D3, 1,2,3,4,7,8-HxCDD; D4, 1,2,3,6,7,8-HxCDD; D5, 1,2,3,7,8,9-HxCDD; D6, 1,2,3,4,7,8,9-HpCDD; D7, OCDD.

value of 0.51 ng I-TEQ/g, whereas slag samples presented the lowest levels, between 0.004 and 0.013 ng I-TEQ/g, with a median and mean value of 0.010 ng I-TEQ/g. Thus, in terms of annual production and considering the operating conditions given in Table 3, dioxin emission presented a slight variation between 1.19 and 2.62 g I-TEQ/yr with an average value of 1.84 g I-TEQ/yr and a median value of 1.97 g I-TEQ/yr. Expressed in percentage distribution, stack gas emissions constituted a minor fraction of the total dioxin output of around 0.26%, whereas the greatest contribution was attributed to fly ashes with 81.24% followed by slag with 18.50%. In consequence, theoretical levels of PCDDs/PCDFs in MSW for a null balance between input and output were determined between 8.19 and 18.05 ng I-TEQ/kg with a mean value of 13.39 ng I-TEQ/kg and a median value of 13.60 kg I-TEQ/kg MSW.

The study of input samples over the eight sampling periods led to a total of 22 values. In the first sampling campaign, nine replicates ranged from 45.73 to 87.48 ng I-TEQ/kg with a mean value of 64.15 pg I-TEQ/kg. In terms of annual dioxin input management, this represents a total entry of 9.30 g I-TEQ. For this particular case, the dioxin output emitted was established at around 1.62 g I-TEQ/g. This signifies a negative dioxin balance of about 7.68 g I-TEQ/yr. However, the seven successive campaigns gave rise to a total of 13 determinations. The findings, expressed in average values, varied from 2.23 ng I-TEQ/kg (sixth campaign) to 7.09 ng I-TEQ/kg (fifth campaign). In terms of annual dioxin input management, this means a total entry between 0.32 and 1.03 g I-TEQ, and as a consequence, a positive dioxin balance was observed.

On the other hand, conventional analysis of isomer and congener distribution, commonly called chemical fingerprint analysis, is widely employed as an important tool to link the presence of these contaminants to a specific source. Representative isomer-specific profile of the 2,3,7,8-chlorosubstituted PCDDs/PCDFs is shown in Figure 2 in both concentration (left column) and TEQ (right column) units. In general, combustion byproducts presented large similiarities in both concentration and TEQ profiles. In concentration units, combustion byproducts presented a typical profile characterized by a notable presence of PCDFs, HpCDD, and OCDD. In contrast, remarkable differences could be found in comparison to those representing input contributors, whereas the MSW profiles were clearly dominated by a high content of OCDD followed by HpCDD. These profiles were previously reported for textile samples (29). Although the authors postulated the existence of potential dioxin contamination from PCP byproducts, this fact could not be clearly demonstrated. An analogous situation could be found when TEQ profiles were compared. Combustion byproducts presented great similiarities as expected, with a typical combustion profile characterized by a major content 2,3,7,8-PCDFs versus 2,3,7,8-PCDDs, with a ΣPCDF/ΣPCDD relationship of about 3:1. In contrast, large differences could be noted in comparison with the MSW profile. In this case, PCDD levels were slightly higher than those of PCDFs, which corroborates the absence of potential contamination by a thermal process. This could be explained by a variety of unknown sources affecting these materials.

At this point, the results permit us to affirm that the plant behaved very stably throughout the study, with comparable data between emission values and great similiarities in PCDD/PCDF profiles. This situation, however, was not observed in MSW samples, which presented great variability among values. In view of this, the results did not permit a firm position to be taken on the dioxin balance in the MWI plant. All dioxins present in waste were thermally destroyed but also formed during the cooling of gases, as corroborated by isomer-specific assessment. However, the plant became a

TABLE 5. Dioxin Mass Balance: Reevaluation of Dioxin Content in MSW (Campaign March 2000)

sample collection	no. of samples	range (ng I-TEQ/kg)	mean (ng I-TEQ/kg)	median (ng I-TEQ/kg)
1	6	1.55−6.30	3.47	3.17
2	6	3.57−8.57	4.94	4.26
3	6	5.74−45.16	15.31	11.43

TABLE 6. Dioxin Mass Balance: Levels of PCDDs/PCDFs in Ambient Air Collected from the Municipal Waste Bunker Site

ambient air samples	levels of PCDDs/PCDFs (fg I-TEQ/Nm^3)
sample 1	4603.11
sample 2	1906.99
sample 3	196.50
sample 4	159.26
sample 5	85.97

sink or a source of dioxins depending on the levels present in MSW since the levels of dioxins produced during combustion were established early between 1 and 2 g TEQ/yr. Therefore, a reevaluation of MSW seemed appropriate. To this end, a new series of dioxin analyses of MSW was performed in a third stage in March 2000; 8000 kg of MSW was taken from the waste bunker over three serial weeks and treated as previously described. The results are summarized in Table 5. Analysis of six replicates from each sample gave a total of 18 values. Again, the findings reflected the same tendency as that found in the second stage of the study, and remarkable variability in the dioxin content of MSW was observed. The lowest level of PCDDs/PCDFs of 1.55 ng I-TEQ/kg MSW contrasted with the highest level of 45.16 ng I-TEQ/kg MSW, which is critical for the whole dioxin balance, since the theoretical value for null balance is 13.39 ng I-TEQ/kg.

Another point considered in the study is related to levels present in ambient air and their possible influence on the dioxin balance since the consumption of air during thermal processes is around 90 000 Nm^3/h. Thus, samples of air used for the combustion reactions were collected from the waste bunker in different campaigns. The results are listed in Table 6. Five different campaigns resulted in five values ranging from 86.97 to 4603.11 fg I-TEQ/Nm^3. Since PCDD/PCDF levels found in ambient air samples presented in some cases a high dioxin content as compared with those found in the surroundings (Table 1), these findings did not represent, from a quantitative point of view, an important impact on the overall balance (between 0.06 and 3.23 mg I-TEQ/yr). Nevertheless, an interesting qualitative aspect is the large variability in these values, which concurs with the same situation found in waste samples. A further interesting aspect was the profile determined for these matrixes (Figure 2). Ambient air samples presented a miscellaneous distribution between MSW and combustion profile. This fact could be expected since these kinds of samples are potentially affected by both MSW and emission gases.

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