PCDD/Fs, DL-PCBs, HCB AND PAHs EMISSIONS IN SECONDARY ALUMINUM CASTING PLANTS: EVALUATION IN THE FRAME OF SPANISH DIOXIN INVENTORY

Sanz P[1], Concejero MA[1], de la Torre A[1], Navarro I[1], Martínez MA[1], Martínez K[2], Rivera-Austrui J[2], Llerena JJ[2], Abad E[2], Rivera J[2]

[1]Environment Department, CIEMAT, Avda. Complutense 22, E-28040 Madrid, Spain; [2]Environmental Chemistry Department, IDAEA-CSIC, Jordi Girona, 18-26, E-08034, Barcelona, Spain.

Introduction

In 1998, MARM (Spanish Ministry of Environment), CIEMAT (Energetic, Environmental and Technological Research Center) and the CSIC (Spanish Council for Scientific Research) began developing the National Inventory of dioxin and furan sources. The aim of this project was to evaluate PCDD/F emissions into the atmosphere, soil and water, to characterize the residues from industrial activities (flue gases, fly ashes, slags, …) and to compare their relative contribution and the total release in the environment. In 2007, it was decided to increase the number of compounds considered, currently being PCDD/Fs, DL-PCBs, hexachlorobenzene (HCB) and polycyclic aromatic hydrocarbons (PAHs).

Aluminum production is considered an interesting activity to be researched as POP source, specially the thermal processing of scrap materials.. Basically all used aluminum can be recycled into aluminum, which has the same quality as primary aluminum. Secondary aluminum is obtained by remelting aluminum scraps, shavings, and other materials containing aluminum. Scrap material may be contaminated with oils, plastics, paints and other contaminants. Secondary aluminum production can be performed in a great variety of furnaces: rotary drum furnaces, hearth furnaces or induction furnaces. Releases of POP may occur from scrap melting where organic contaminantes and chlorine are present and also from refining and pretreatment such as thermal cleaning of scrap (1). Consequently, some Spanish Secondary Aluminum Production plants have been studied during the period 2007-2008. Data obtained in this survey, correspond with flue gas and fly ash matrices.

Materials and Methods

In the frame of the Spanish POP inventory, thirteen plants, at different locations spread in the national geography, were evaluated. In general terms, their production capacities ranged between 4500 and 53000 t/a. Four of them, those with higher production capacities, were sampling twice to check the repetibility of the industrial processes.

Although there is established an EU standard for the determination of PCDD/F and DL-PCB concentration in stack gas from waste incineration (European standard EN-1948:1, 2, 3, 2007, UNE-CEN/TS 1948-4:2009) (2), these standards are not actually valid for the determination of all the compounds considered. Therefore the method used in this work was developed for sampling all POP in a single run (3). The approach posed changing of some sampling parameters, particularly the amount of resin XAD2 to be used. Accredited firms engaged for sampling had to adapt their systems to the new specifications. The sampling train was performed by the filter /condenser method as described in EN-1948, 2007, Part 1. In this work large volumes of flue gas were collected (average volume of 10 Nm^3, equivalent to 6-8 hours of sampling) with an amount of XAD-2 no less than 60 g.

Extraction, clean-up and analysis fulfilled the minimum requirements described in the European Standard UNE-EN-1948-1,2,3:2007 for dioxins and furans; TS 1948 Part 4, 2007 for DL-PCBs and CARB 429 for PAHs (4). HCB analysis was performed using internal procedures. All analyses were based on the use of high resolution gas chromatography coupled to high resolution mass spectrometry and quantification was performed by isotope dilution.

Results and Discussion

Table 1 summarises results related to the two different matrices evaluated, fue gas and fly ash, coming from the gas cleaning systems of each aluminium secondary plant.

1. PCDD/Fs

Data show a wide range of PCDD/Fs concentrations in all matrices considered. Particularly, in the flue gas case, the results ranged between 0.03 and 49.94 ng I-TEQ/Nm^3, with a mean value of 3.78 ng I-TEQ/Nm^3 and a median of 0.38 ng I-TEQ/Nm^3 (n = 19). The highest datum belong to a plant that had no gas cleaning system (REF. 2), although a bag filter was installed by the end of this study. Next, a sampling episode was undertaken (REF. 2a). Reference 5b corresponds to facility 5 after implementating a dioxin abatement system. The results are comparable to those found in other European Countries as Italy (5), Germany and Luxembourg (6). It is remarkable that most plants present PCDD/F content below 0.5 ng I-TEQ/Nm^3, that is the value associated with the use of the Best Available Techniques in the Non Ferrous Metals Industries (7).

Table 1. *PCDD/Fs, DL-PCBs, HCB and PAHs emissions from thirteen Spanish secondary aluminum production plants evaluated during 2007-2008.* No solid sample because the plant has not a gas cleaning system.*

	FLUE GAS				FLY ASH			
REFERENCE	**PCDD/Fs** (ng I-TEQ/Nm^3)	**DL-PCBs** (ng I-TEQ/Nm^3)	**HCB** (ng/Nm^3)	**PAHs** (ng/Nm^3)	**PCDD/Fs** (ng I-TEQ/g)	**DL-PCBs** (ng I-TEQ/g)	**HCB** (ng/g)	**PAHs** (ng/g)
1	0.07	0.01	37.76	510	2.68	0.04	6.72	107123
2	49.94	2.76	5.64	2738	*	*	*	*
2a	6.00	0.01	97.07	208	49.78	7.17	258.11	71831
3	0.63	0.18	NQ	1038	1.59	0.08	3.59	401482
4	3.78	0.18	65.51	12067	4.64	0.01	14.95	90785
5	0.73-0.03	0.15-0.01	98.90-1.45	22012-32080	0.67-1.03	0.02-0.1	5.82-27.23	20954-27396
5b	0.12	0.02	7.22	3755	1.48	0.08	29.34	248205
6	10.02	0.33	35.15	8538	102.09	0.51	52.85	146759
7	0.61	0.18	39.14	3488	9.16	0.29	2.32	951984
8	0.10	0.04	26.65	43	0.04	0.010	0.36	2349
9	0.06-0.18	0.005-0.01	27.36-38.13	1476-26163	0.08-2.14	0.001-0.15	0.41-97.04	51-1586
10	0.57	0.46	49.54	645	10.60	1.42	32.23	116882
11	0.10	0.03	30.39	573	7.81	0.31	39.07	104610
12	1.84-2.45	0.76-1.54	63.48-18.08	22-19095	4.53-5.34	0.39-0.79	27.22-94.23	20767-92508
13	0.38-0.06	0.07-0.04	59.58-43.30	4415-4516	1.82-0.25	0.10-0.02	5.64-0.7	656428-13012

PCDD/F concentrations associated to the fly ash varied between 0.04 and 102.09 ng I-TEQ/g, representing an average value of 11.43 ng I-TEQ/g and a median of 2.41 ng I-TEQ/g (n = 18). It is important to point out that the possible reutilization of such ashes would involve the mobilisation or incorporation of these pollutants to other industrial processes. This fact could increase and/or incorporate the POP contents in final products or other wastes.

It is not possible to find a particular pattern for congener distribution, to be repeated in most of the emissions, both flue gas and fly ash. Although it is observed that the greatest contribution to toxicity is due to the presence of furans.

Considering the results associated with the facilities in which the samplings have been repetead, it can be concluded that their behaviour is not reproducible. Figure 1 shows the behaviour of two of these four facilities. In facility (a) different types of raw material were used in the smelter, while facility (b) was fed without changing raw material. Thus, in case (a) the major congeners are different in the both samples while, in case (b), the congener profile is maintained. Since the process and type of oven are the same in both facilities, the variations are due mainly to the use of a different type of raw material to feed the furnaces. However it can not be ruled out any possible variation related to heterogeneity of the processes themselves or related technologies.

2. DL-PCBs

Presently there is no legislation to control the DL-PCB emission, but some countries are already including them in their POP inventories, such as Spain. In this way, the values measured in flue gas of the thirteen secondary aluminium casting plants ranged between 0.005 and 2.76 ng WHO-TEQ/Nm^3, average: 0.36 ng WHO-TEQ/Nm^3, median: 0.07 ng WHO-TEQ/Nm^3 (n = 19). Similarly, the results of DL-PCBs in fly ashes ranged between 0.001 and 7.17 ng WHO-TEQ/g, average: 0.64 ng WHO-TEQ/g, median: 0.10 ng WHO-TEQ/g (n =

18). The contribution of DL-PCB to gas emission and fly ash toxicity is lower to that related to PCDD/Fs in all cases. In general, there is a good correlation between PCDD/Fs and DL PCBs data.

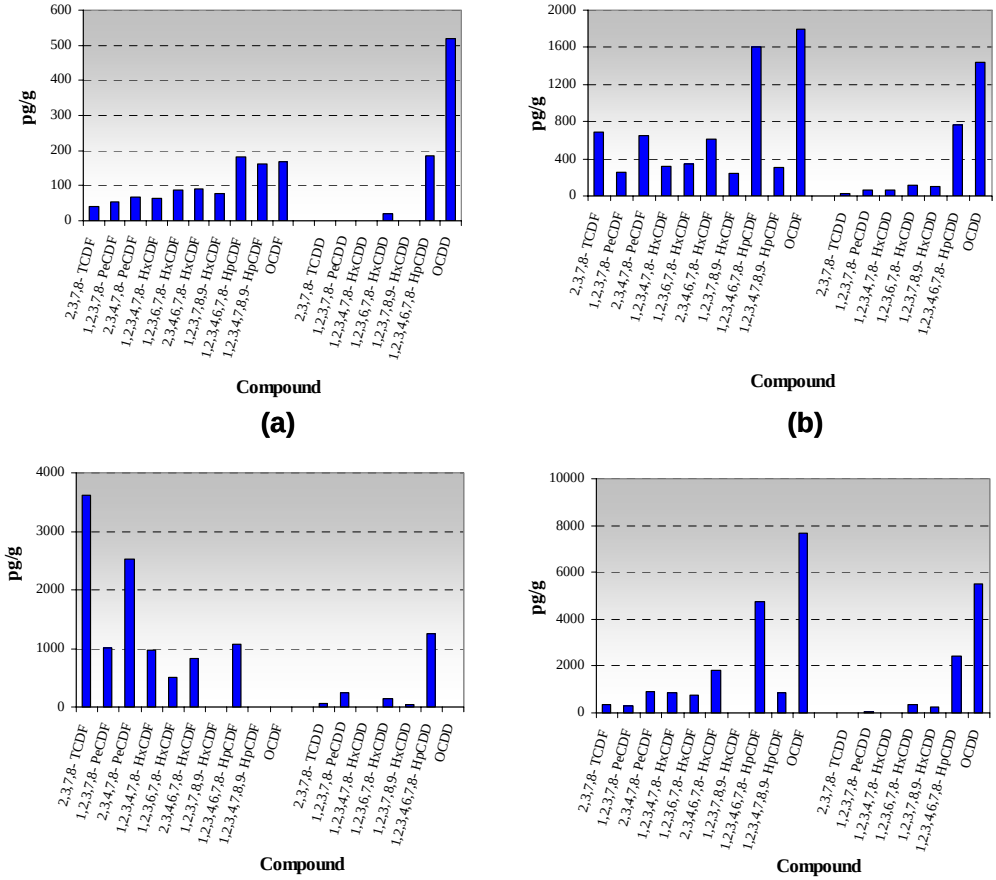

Figure 1. *Profiles of fly ashes coming from two aluminium secondary casting facilities: (a) using the same raw material (b) using different raw material.*

3. HCB

The values obtained for HCB ranged between 1.45 to 98.90 ng/Nm^3 in flue gas, average: 40.90 ng/Nm^3, median: 37.95 ng/Nm^3 (n = 18), and between 0.36 and 258.11 ng/g in fly ash, average: 38.77 ng/g, median: 21.09 ng/g (n = 18). It was not possible to quantify the HCB content in flue gas of facility 3 due to the high level present, which disturbed the chromatogram.

4. PAHs

The PAHs considered were the 6-Borneff ones, used by the World Health Organisation as indicators of the PAHs burden from a sample. The data ranged from 22 to 32080 ng/Nm^3 in flue gas, average: 7546 ng/Nm^3, median: 3488 ng/Nm^3 (n = 19), and from 0.051 to 952 µg/g in fly ash, average: 170.82 µg/g, median: 91.65 µg/g (n = 18). Regarding the distribution of the different congeners, the most abundant was fluoranthene in both matrices, which represents more than 50% of total PAHs in all flue gas samples and also in most of fly ashes. It is not clear any common profile for the rest of compounds.

Figure 2 represent the comparison between the levels of PCDD/Fs, DL-PCBs, PAHs and HCB in (a) flue gas and (b) fly ash, for all plants evaluated. While PCDD/Fs and DL-PCBs are expressed as toxic content, pg I-TEQ/Nm^3 or ng I-TEQ/g, HCB and PAHs are expressed in concentration (ng/Nm^3 or ng/g). The ranges of variation of POPs analyzed are very wide and it has been observed a significant lack of reproducibility in their

levels. The great variability of the data is mainly due to the differences between production processes (type of furnace, raw material used ...). It seems that the use of a single raw material, free of grease and / or paints, enamels, etc ... can lead to samples with lower levels of POPs.

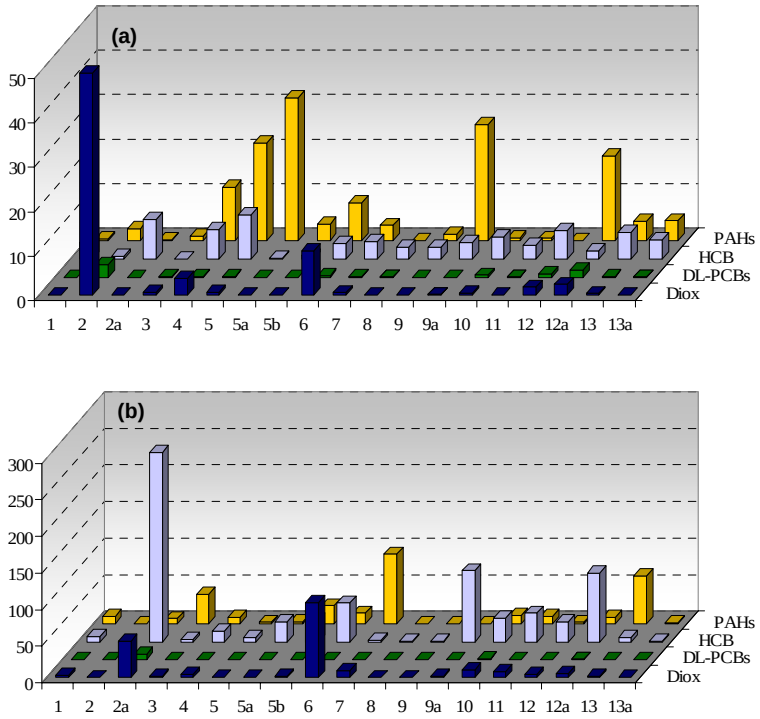

Figure 2. *Levels of PCDD/Fs, DL-PCBs, PAHs and HCB for (a) flue gas and (b) fly ash. Flue gas scale: PCDD/Fs and DL-PCBs in ng I-TEQ/Nm^3; PAHs in1000 x ng/Nm^3 and HCB in 10 x ng/Nm^3. Fly ash scale: PCDD/Fs in ng I-TEQ/g; DL-PCBs in ng WHO-TEQ/g; HCB in ng/g and PAHs in 10000 x ng/g. Samples 5a, 9a, 12a and 13a correspond to the repeated sampling in plants 5, 9, 12 and 13 respectively.*

From this study, the Working Group has concluded that it is not suitable to calculate an average emission factor representing the Spanish secondary aluminum casting sector. POP content average (arithmetic mean) is above the median, and therefore it is influenced by very high values of some of the plants evaluated. Thus, each of them should calculate its emission factor and finally, from these data and considering the annual production related to each facility, the annual emission for flue gas and fly ash, would be estimated.

Acknowledgements
Authors are grateful for the support of the facilities participating in this study. They also thank ASERAL and especially Mr. J.L Vicente for his valuable help.

References

1. Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases, UNEP 2005.
2. UNE-CEN/TS 1948-4:2009. Stationary source emissions. Determination of the mass concentration of PCDD/Fs and dioxin-like PCBs. Part 4: Sampling and analysis of dioxin-like PCBs.
3. Grochowalski A, Lassen C, Holtzer M, Sadowski M, Hudyma T. *Env Sci Pollut Res* 14 (5) 326-332 (2007)
4. California Environment Protection Agency. Air Resources Board. Method 429, 1997.
5. ENEA/AIB/MATT 2003. "Valutazione delle emissioni di inquinanti organici persistenti da parte dellíndustria metallurgica secondaria". Rapporto finale.
6. LUA 1997. Identification of relevant industrial sources of dioxins and furans in Europe. Materialien No. 59. Landesumweltamt Nordrhein-Westfalen, Essen, Germany 1997.
7. Integrated Pollution Prevention and Control (IPPC). Reference Document on Best Available Techniques in the Non Ferrous Metals Industries December 2001.