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# Evaluation of the Spanish hot dip galvanising sector as a source of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans

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**Abstract**

A survey to estimate the polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) emissions of Spanish hot dip galvanising sector was carried out during 2002. This investigation is the first presenting Spanish experimental data related to this industrial sector. Three different matrices: flue gas, ash and filter dust were tested to quantify the PCDD/Fs generated during the galvanising process. The organic source of PCDD/F formation could be from the insufficient degreasing o from inhibitors or additives used in the pickling steps such as quinoline, isoquinoline, 8-methylquinoline or polyether phosphoric acid. Low levels PCDD/Fs were achieved in air emissions when air control devices are used. On the contrary, filter dusts are highly contaminated; indicating that the absence of air control devices would increase the risk of fugitive emissions. Homologue profiles and Principal Component Analysis demonstrate there are differences in the formation mechanisms in the bath zone (ashes) compared to the stack location (filter dusts and air emissions), related to the de novo synthesis and reaction time. The annual PCDD/F emission to the atmosphere for this sector during 2002 has been estimated in 0.023 g I-TEQ. The emission factor of plants with air control devices has been calculated at 0.030 μg I-TEQ/ton of galvanised steel.

*Keywords:* PCDD/Fs; Hot dip galvanising; Dioxin source; Emission factor; De novo synthesis

## 1. Introduction

In February 1993, the European Council of Ministers set the political goal to achieve a 90% reduction of dioxin emissions from known sources by the year 2005 as compared to the reference 1985 year. To achieve this ambitious aim, an inventory of all relevant emission sources and an estimate of the total emissions in the member states were required (The Fifth EC Environmental Action Programme, 1993). The community strategy for these compounds involves identification of dioxin sources and their quantification including the non-ferrous metal industry. According to this strategy, Spain is carrying out a national inventory of dioxin sources since 1998. Some of the more characteristic Spanish industrial sectors have already been evaluated as PCDD/Fs emitting sources. For instance, the incidence of municipal waste incineration sector in the PCDD/Fs releases was studied in the period of time from January 1997 to November 1999 (Fabrellas et al., 2001) and the first estimate of dioxin and furans emissions from cement manufacture sector was published in 2002 (Fabrellas et al., 2002). After these surveys, galvanising sector was considered an interesting activity to be researched as a dioxin

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source and some of their plants were studied during a 2002 Spanish monitoring programme.

### 1.1. Galvanising process description

The "hot dip galvanising" process consists of immersing clean, oxide-free iron or steel into molten zinc, in order to form a zinc coating which is metallurgically bonded to the iron or steel's surface. Thus, the zinc coating protects the iron and steel surfaces against corrosion (Langill, 2002). This process is adaptable to coating nearly all types of fabricated and non-fabricated products such as wire tanks, sheets, strip, pipes and tubes, fittings, hardware, wire cloth, hollowware and structural assemblies.

The zinc coating on galvanised steel will react with the atmosphere over time to form zinc compounds on its surface. These form a protective, chemically inert, layer that inhibits further reaction with the metal beneath. This layer can be comprised of zinc sulphate, zinc carbonate, zinc hydroxide and zinc oxide depending on the surrounding environment.

In general, galvanising consists of four steps: surface preparation, prefluxing, galvanising and finishing. The preparation steps consist of cleaning and pickling operations that free the surface of dirt, grease, rust and scale. The preflux step serves to dissolve any oxide that may have been formed on the iron or steel surface after pickling and prevents further rust from forming. Clean, oxide-free work is galvanised by immersion into molten zinc. Finishing operations include quenching, removing excess zinc and inspection. The description of each step is relevant to understand dioxin formation in the process (see Industrial Galvanisers Corporation <www.corp.indgalv.com.au>, European General Galvanizers Association <www.egga.com>).

#### 1.1.1. Preparation step

A surface free from grease, dirt and scale prior to galvanising is essential. Contamination is removed by a variety of processes. A common practice is to degrease using an alkaline or acidic degreasing solution into which the component is dipped to remove organic contaminants. An alkaline degreasing solution consists of an aqueous solution of sodium hydroxide (>30%), sodium carbonate (20%) and sodium metasilicate (>10%). An acidic degreasing solution consists of phosphoric acid (50%) or hydrochloric acid (20%). In addition, surfactants such as ethanolamine, and soaps are used in the baths to emulsify oils and grease to remove them.

#### 1.1.2. Acid pickling

The article is then rinsed and dipped in an acid pickling solution based on hydrochloric acid at ambient temperature or hot (80 °C), sulphuric acid to remove corrosion products, metal oxides, scales and rust. Some additives and inhibitors such as quinoline, isoquinoline, 8-methylquinoline or polyether phosphoric acid, are used to avoid scale formation. After a water rinse, the components undergo a fluxing procedure.

#### 1.1.3. Fluxing

A flux is normally applied by dipping the articles into a flux solution, which is a 30% zinc ammonium chloride at 65–80 °C. This is done to prepare the surface and to prevent the formation of oxides and to create nucleus for the zinc coating.

#### 1.1.4. Galvanising

The clean iron or steel component is dipped into the molten zinc, which is commonly about 435–455 °C. A rapid metallurgical reaction is carried out to make zinc–iron alloys. Typical immersion time takes about four or five minutes. However, it can be up to 15 min for heavy articles having high thermal inertia or when the zinc is required to penetrate internal spaces. Galvanising is a diffusion process, where the reaction between the molten zinc and the steel or iron will proceed quickly at first, but will do slow as the alloy layer grows and becomes thicker. Aerosols and dust emissions formed by zinc oxides, iron oxides and organic compounds are emitted during the reaction. The organic compounds could come from previous articles dipped into the baths. While fumes and gaseous compounds arise as clouds or puffs from the kettle surface, ash remains on the surface of the kettle. The ash is mostly composed by zinc oxides (Sinclair Knight Merz, 2000).

Post-galvanising treatment can include quenching into a water bath or air cooling. Any zinc not forming a coating on the metal remains in the bath for further reuse. Galvanising residues, or dross, which is a mixture of zinc and iron and zinc ash, are recovered and zinc recycled for further reuse, often in the pickling step (Plachy, 1998).

Aqueous discharges consist mainly of spent acids used to prepare the steel and are removed by licensed waste management companies.

### 1.2. Galvanising activity as a source of dioxins

Factors favouring PCDD/Fs generation during galvanising are: (a) A 450 °C bath temperature, where exhaust aerosol and fume temperature drops relatively slowly to ambient temperature during travel to the air control devices and stack; (b) a chlorine presence; (c) a presence of particulate and aerosols; (d) organic matter traces from the remaining grease and additives used; (e) an existence of potential metallic catalysts from baths, such as zinc and iron chloride.

Owing to these process conditions the "Hot Dip Galvanising Sector" was considered a possible dioxin source in the European Inventory (Quass et al., 1997, 2001).

As a consequence of all previously mentioned, the evaluation of "The Hot Dip Galvanising Sector" was established in the Spanish Dioxin Inventory. The present study aims to characterize and quantify PCDD/Fs existing in different matrices of the hot dip galvanising sector during 2002.

### 1.3. Background of PCDD/Fs emissions from "the Hot Dip Galvanising Sector"

Reported data of PCDD/Fs in this sector, classified in CORINAIR as code no. 040307, proceed from the National Inventories of Germany and Switzerland (LUA, 1997), and from the Danish Environment Protection Agency (Hansen, 2000). In all cases, the principal pathway considered was atmosphere releases.

Hot dip galvanising installations are widespread over the area of Germany. According to information obtained from the European General Galvanisers Association, about 130 companies were counted in 1994. The European Dioxin Inventory (section on Germany) shows flue gas concentrations for hot dip galvanising plants in the range between 0.007 and 0.132 ng I-TEQ/m$^3$, whereas the content of dioxins in filter dust is in the range from 2150 to 9614 ng I-TEQ/kg (UBA/LAI, 1993). The emission factor resulting was 0.061 μg I-TEQ/ton galvanised product. The total consumption of zinc in Germany was 531.5 kt but no more information was obtained about the accurate amount used for galvanising purposes. According to European estimations, an average of 13 tons of steel are galvanised per ton of zinc. With the emission factor and the estimation of the annual production, the PCDD/F emission was calculated in 0.34 g I-TEQ/y for the German hot dip galvanising sector, (uncertainty range: 0.03–3.4 g I-TEQ/y).

If considering the Swiss inventory, the emission factor was acquired from mean results of measurements carried out in Germany (0.623 μg I-TEQ/t product). The galvanising emission factor was estimated in 3.85 μg I-TEQ/ton for 1985 and 0.7 μg I-TEQ/ton for 1990 and 1995. The annual PCDD/F emissions were estimated for this industrial sector in 0.418 g I-TEQ/y during 1985, and 0.071 g I-TEQ/y for 1990 and 1995 (Quass et al., 1997).

About 15 companies in Denmark carry out hot dip galvanising (Hansen, 2000). Based on information from Danish companies, the total production can be estimated at approx. 100 000 ton galvanised product per year, whereas the air emission comes up to approx. 33 000 N m$^3$/ton product. The quantity of filter dust generated may thus be assumed to be somewhat between 20 and 165 ton/y. Filter dust is directed to land-filling or temporarily stored. No measurements of dioxin formation have been carried out in Denmark. Based on the German figures, the turnover of dioxins by hot dip galvanising in Denmark may be estimated in 0.023–0.44 g I-TEQ/y for air emissions and less than 0.002 g I-TEQ/y for filter dust landfilled/stored.

It is not known whether the air emission factors quoted above include emission with dust when no cleaning of off-gases is employed. If not, the air emission may be higher than calculated.

## 2. Materials and methods

### 2.1. Description of the Spanish hop dip galvanising sector and survey design

Forty Spanish discontinuous hot dip galvanising plants were operating during 2002 with a total annual production of 502 000 ton of galvanised steel (Associación Técnica Española de Galvanización <www.ateg.es>). Twenty six of the plants (65%) used gas cleaning systems such as bag filters, and represented 72.7% of the annual production of steel. The other 35% of the plants were trying to fulfil the European Directive to install gas cleaning devices (IPPC96/61) and were the responsible for 27.3% of annual steel production.

Ten plants with bath enclosures and bag filter systems were chosen for this study. Four plants had an acid degrease (AD) process, four plants used a basic degrease (BD) process and two plants were without a degrease (WD) process.

### 2.2. Sampling strategy

Samples were taken of ash placed on the molten zinc bath surface, and filter dust during the same day of flue gas sampling. Although the ash is comprised mainly of zinc oxide, the present investigation tried to probe if the organic matter traces existing could contain dioxins and furans (Hansen, 2000). Emissions were monitored in eight plants at stack. The sampling and analytical methods for PCDD/Fs were carried out according to the European Standard (UNE-EN-1948 method, 1997). Because of discontinuous operation, where venting systems only work when immersion is carried out, the sampling times were restricted to the dipping in the bath. Sampling time was a function of the frequency of dipping and the suction flow of the ventilation system in the bath enclosure. Sampling time was slightly different in each plant but generally more than 6 h. Sampling temperature was about room temperature and the oxygen percentage was similar to atmospheric, owing to the flow induced by the ventilation system.

### 2.3. Analysis methodology

Solid samples, 10 g of ashes and dusts, were spiked with known amounts of 15 toxic congeners of PCDD and PCDF labeled with $^{13}$C and soxhlet extracted with toluene. After evaporation and solvent exchange the extracts were purified and cleaned-up by a Power Prep™ automated system (FMS Inc., MA) through a multilayer silica, basic alumina and PX-21 carbon adsorbent, respectively.

Instrumental analysis of ashes and dusts were carried out by using a CP-3800 gas chromatograph equipped with a CP-8200 autosampler, coupled with a Saturn 2000 ion trap spectrometer (Varian, Walnut Creck, CA, USA) working in the MS/MS mode. More details are described elsewhere (Fabrellas et al., 2004).

Flue gas analytical methodology were in accordance with UNE-EN-1948:1997. Corresponding extracts were analysed using a Fisons CE 8000 Series gas chromatograph coupled to an Autospec Ultima mass spectrometer (Fisons Instruments), operating in the SIM mode at 10000 of resolving power, operating in the EI+ (32 eV) mode.

## 3. Results and discussion

### 3.1. PCDD/F emissions

Table 1 summarises results obtained from the three different matrices evaluated: ash, dust and flue gas. PCDD/Fs could originate by grease not being removed enough in the degrease steps (higher emission factors found in Without Degrease facilities (WD)), or from molecules used as inhibitors or additives in the pickling steps (polynuclear hydrocarbons such as quinoline). The final production was not reported in some plants and consequently, their air emission factors could not be calculated.

The dioxin results for ashes placed on the molten zinc bath surface are low, except for the plant number eight, that presents the highest content (AD treatment: 107.2 ng I-TEQ/kg). A high dioxin concentration appears in filter dust samples, where a WD plant presents the highest level, 8075 ng I-TEQ/kg. For air emissions, dioxin content is very low. This demonstrates the high efficiency of filter systems achieving 90–95% removal of particulates from air.

The range of emission factors is wide and depends on each installation (0.007–0.061 µg I-TEQ/ton of galvanised steel, see Table 1). WD installations have higher dioxin air emission factors than the rest of the plants. The mean value is 0.03 µg I-TEQ/ton of galvanised steel. However, considering that only plants with gas cleaning devices have been measured during the present study, this mean value is only representative for 72.7% of the total production. Due to the high content of PCDD/Fs in dust, it was presumed that the contribution of the rest of installations without cleaning devices (27.3% of total production) will increase this calculated emission factor, because the waste from the cleaning section contains the larger part of the PCDD/Fs formed. For this reason, involved parties in this survey (Spanish Ministry of Environment, ATEG, CIEMAT and CSIC) evaluated such contribution by assuming a penalty of 30% over the maximum emission factor obtained from the plants measured. In this way, the emission factor corresponding with installations without cleaning devices was estimated as 0.079 µg I-TEQ/ton of galvanised steel. These Spanish emission factors are much lower than those related to Germany and Switzerland, 0.623 and 0.7 µg I-TEQ/ton of galvanised steel, respectively (UBA/LAI, 1993). In view of the information obtained during the current investigation, we think the incorporation of bath enclosure capture and filter systems will be an adequate strategy for reducing dioxin emissions. Additionally, it is important to be aware of the possible recycling of filter dusts out of the galvanising process could involve the mobilisation, input, or maybe destruction, of PCDD/Fs to other industrial processes. The recycling of dusts in pickling and Zn baths could increase their presence in the galvanising process.

Table 1
PCDD/F in ash, dust, air emission and air emission factor calculated from 10 Spanish hot dip galvanising plants evaluated during 2002

| Sample reference | Ash pg I-TEQ/g | Filter dust pg I-TEQ/g | Flue gas pg I-TEQ/N $m^3$ | Air emission factor µg I-TEQ/$\mathrm{ton}_{\mathrm{galvanis.\ steel}}$ |
|---|---|---|---|---|
| WD1 | 10.9 | 8075 | 13.7 | 0.061 |
| WD2 | 0.7 | 487 | 4.8 | 0.041 |
| BD4 | 3.8 | 1708 | 5.4 | 0.024 |
| BD5 | 15.2 | 127 | – | [a] |
| BD6 | 2.3 | 755 | 3.85 | 0.007 |
| BD7 | 16.3 | 1766 | 7.86 | [a] |
| AD8 | 107.2 | 1093 | 5.8 | [a] |
| AD9 | 0.7 | 946 | 3.0 | 0.019 |
| AD10 | [a] | 821/695 | 4.0 | 0.027 |
| AD11 | 13.2 | 1804/1601 | –[a] | [a] |
| Range | 0.7–107.2 | 127–8075 | 3.0–13.7 | 0.061–0.007 |

[a] No data available.

In order to quantify source strength, an emission rate must be determined as an annual mass flow rate of PCDD/PCDF expressed in grams TEQ of PCDD and PCDF released per year (UNEP, 2005). The annual releases for all vectors of a source or a source category are calculated as follows:

$$\text{Source Strength(Dioxin Emissions per year)} = \text{Emission Factor} \times \text{“Activity Rate”} \qquad (1)$$

According to Eq. (1), annual PCDD/PCDFs emission to the atmosphere, corresponding with 100% of Spanish hot dip galvanising sector during 2002, has been determined by multiplying the release of PCDD/PCDF, in µg I-TEQ/ton of galvanised steel, by the amount of galvanised steel per year. The annual emission has been calculated for the installations with filter bags, 0.012 g I-TEQ/y, and for installations without gas cleaning devices, 0.011 g I-TEQ/y. Consequently, 0.023 g I-TEQ/y is the PCDD/PCDFs emission related to all the Spanish hot dip galvanising sector during 2002. This result is lower than those obtained in Germany, Switzerland and Denmark.

### 3.2. PCDD/F homologue distribution and patterns

Due to the high variability of data, box charts have been used for evaluating PCDD/F homologue distribution and patterns. By default, the box is determined by the 25th and 75th percentiles. Mean, median, maximum and minimum values are also plotted with the interquartile range. Thus, Fig. 1 represents the distribution of 2,3,7,8 congeners toxic contribution for the three matrices, indicating that such distribution is very similar in all plants evaluated. In all cases, the congener with the highest toxic contribution is 2,3,4,7,8-PeCDF. It is followed by 1,2,3,7,8-PeCDD in

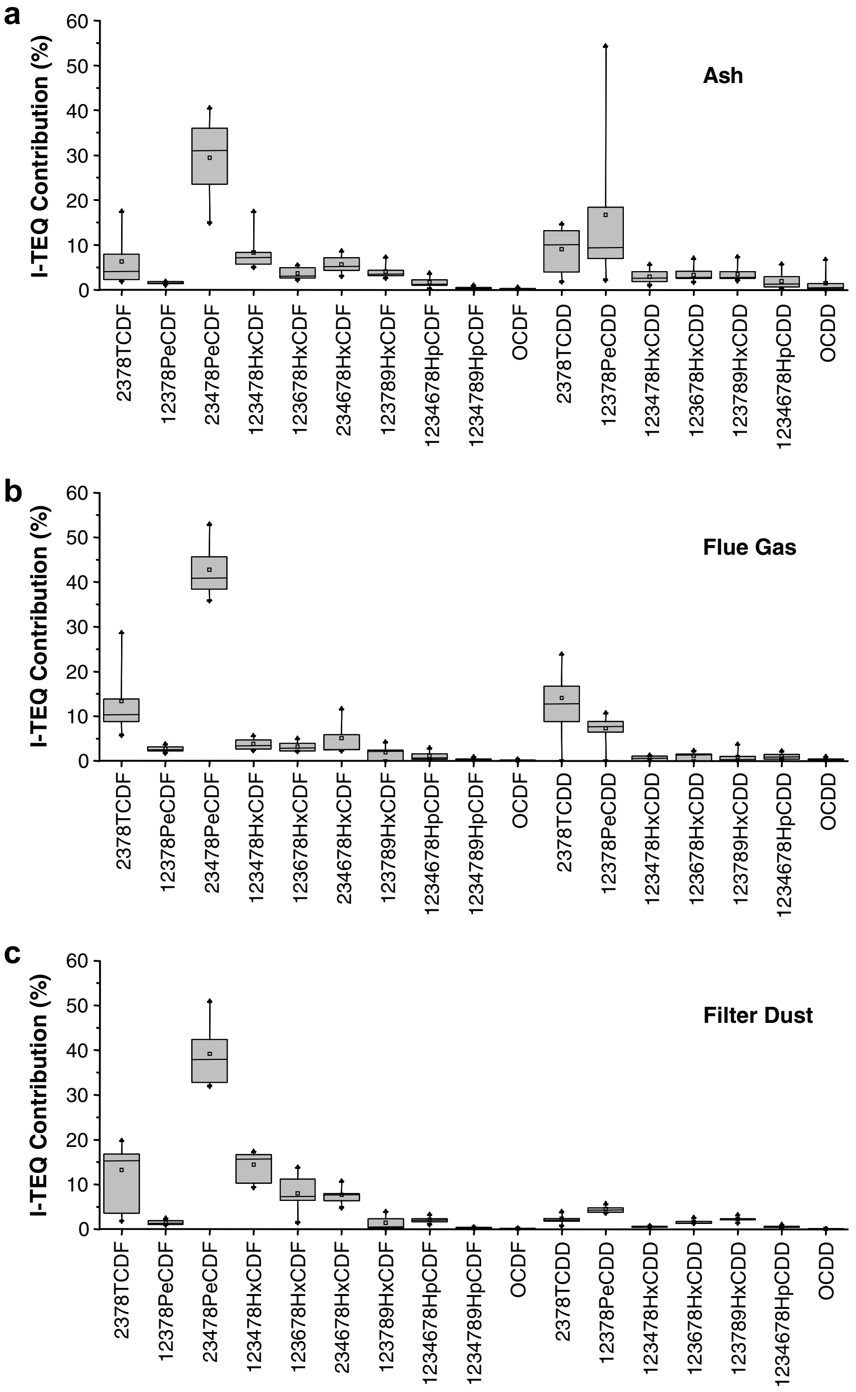

Fig. 1. Patterns of I-TEQ contributions for each matrix: ash (a), flue gas (b) and filter dust (c). ▲ Maximum. ▼ Minimum. □ Mean. – Median. ▯ Interquartile range.

ash, by 2,3,7,8-TCDD in flue gas; and by 1,2,3,4,7,8-HxCDF in filter dust.

The homologous group contribution to mass concentration and TEQ, for all matrices, have been plotted in Fig. 2. Additionally, Table 2 shows the ratio of toxicity and mass contribution of furan to dioxin groups. Furan group toxicity is more than twice that for dioxins in emissions, and much higher in dust. Also, furan content is appreciably higher compared to dioxin in mass concentration in dust and emissions, 73.5% and 72.7%, respectively, but it appears in the same proportion in ash (50.8%). The higher mass contribution of heavy HxCDF group in dust is important to total toxic content in comparison with the more volatile tetra- and penta-isomers enrichment found in emissions. OCDD is the main congener found in ash. In all cases the PeCDF group contributes the most to TEQ.

The PCDD/Fs homologue distribution in the stack emissions from ferrous and non ferrous metals production

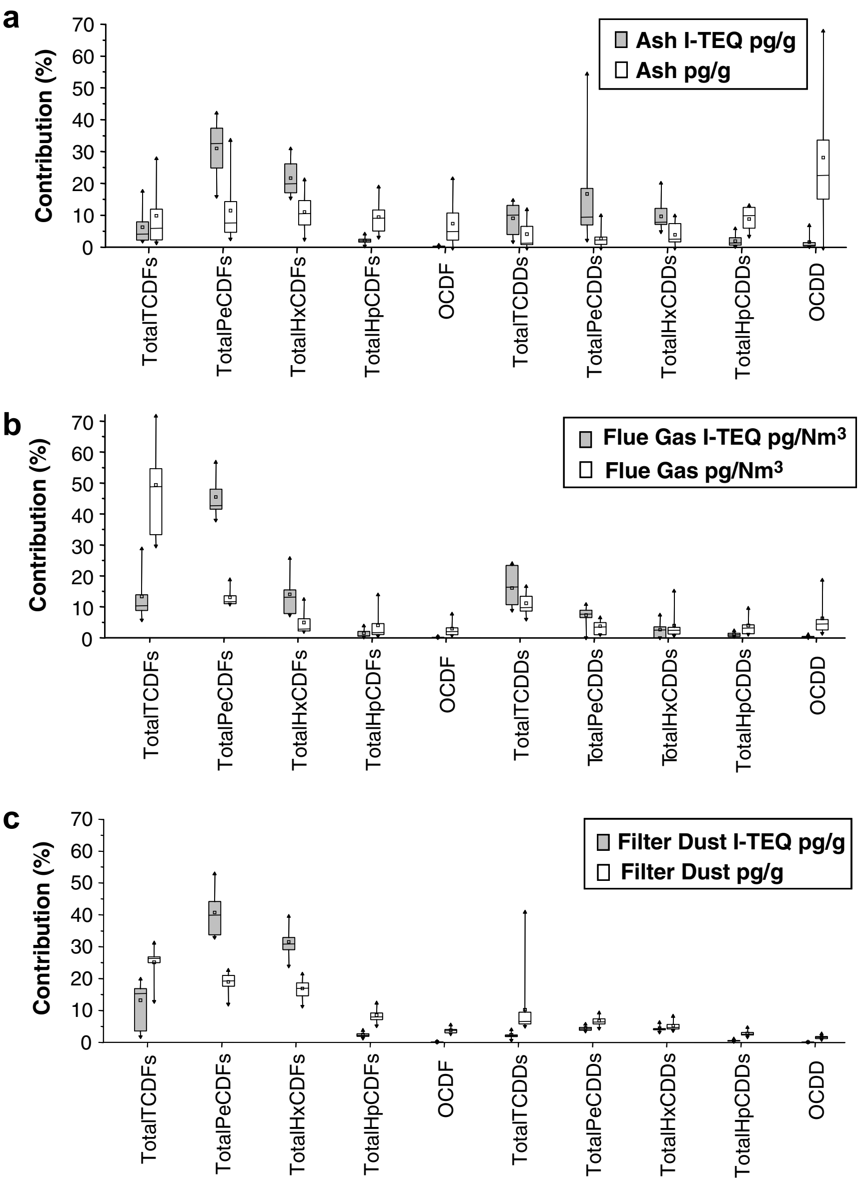

Fig. 2. Homologous group contribution to mass concentration and I-TEQ for ash (a) flue gas (b) and filter dust (c). ▲ Maximum. ▼ Minimum. □ Mean. – Median. ▯ Interquartile range.

Table 2
Furan and dioxin ratio in toxicity and mass contribution in each matrix

| | Flue gas | Dust | Ash |
|---|---|---|---|
| % Dioxin toxicity contribution | 27.51 | 11.93 | 38.90 |
| % Furan toxicity contribution | 72.49 | 88.07 | 61.10 |
| Ratio furan/dioxin toxicity | 2.71 | 7.38 | 1.58 |
| % Dioxin mass concentration | 27.30 | 26.50 | 49.20 |
| % Furan mass concentration | 72.7 | 73.50 | 50.80 |
| Ratio furan/dioxin mass concentration | 2.66 | 2.76 | 1.03 |

have already been reported by other authors (Buekens et al., 2000) and dioxin emissions with a predominance of furans have also pointed out for sinter plants and electric arc furnaces (Hofstadler et al., 2000). Additionally, from the study of filter dust obtained during aluminium recycling processes, tetra- and penta-chlorinated dibenzofurans were detected, as possible result of the de novo synthesis (Laue et al., 1994) and the importance of HxCDF was also found by Harnly et al. (1995). Our results confirm the high contribution of furans in these metallurgical sources.

Regarding the possible formation mechanism we could point out that the time dependence of PCDD/Fs formation could play an important role in the different behaviour found between ash, stack emissions and filter dust. In fact, the PCDD/Fs ratio is dependent on the reaction time (Hell et al., 1997). In addition, PCDFs production proceeds via formation of main pre-dibenzofuran structures (Hell, 1999) that takes place at much slower rates (Grabic et al., 2002). This time dependence could be the key point to understand the differences found in the PCDD/Fs content of ash from molten zinc and that for stack emissions

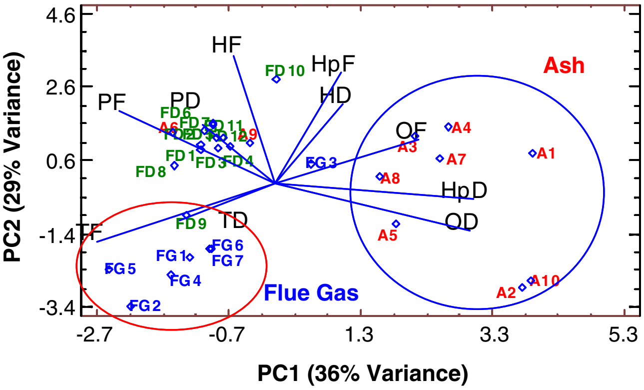

Fig. 3. Results of multivariate statistical analysis of sampling from galvanising plants.

and filter dusts. The reaction time could explain why the PCDFs formation is less significant in the zinc bath (ash matrix) than in the stack (flue gas and filter dust matrices). Since in the stack the reaction times should be longer, we think the pre-dioxin structures disappear mainly in the molten bath. In parallel, "de novo synthesis" of furans on the particulates and metallic impurities working as catalysts, could increase the PCDFs formation.

### 3.3. Principal component analysis

Statistical calculations such as the principal component analysis, PCA, are an important tool for evaluating similarities in isomeric patterns (Laue et al., 1994; Wehrmeier et al., 1998; Blumenstock et al., 2000; Masunaga et al., 2001). In the present investigation, this multivariate statistical analysis, performed with Statgraphics Plus Version 5.0, has been utilised to establish the different PCDD/Fs generated in the zinc molten bath and in the stack. PCA has provided the first two components, PC1 (36% variance) and PC2 (29% variance), which account for 65% variability of the 29 data considered (ash, flue gas and filter dust samples), being the variables the 10 homologue families. The variable values have been standardised by subtracting their means and dividing by their standard deviations. The PC1 and PC2 behaviour for the ten variables, represented by the loading of these variables, and the score of such components as a function of the 29 samples are shown in Fig. 3. PC1 is associated with chlorination degree of the different homologue groups. Thus, it can be observed that positive values are mainly related to homologue groups with high chlorination degree (OCDD, HpCDD and OCDF) as well as ash samples. On the contrary, PC1 negative values are related to homologue groups with low chlorination degree (TCDF, PeCDF, TCDD and PeCDD) and, also to flue gases and filter dusts. Simultaneously, these both matrices are divided as a function of positive and negative values of PC2. This different performance confirms that the PCDD/PCDFs formation mechanism varies in the two zones studied, as already mentioned previously.

## 4. Conclusions

Experimental data obtained in this study are, up to our knowledge, the first related to the Spanish hot dip galvanising sector and corroborate the PCDD/F formation in this non-ferrous metal production sector. Although very low levels are found in flue gas when gas filter devices are used, PCDD/Fs are highly present in dust taken from filter bags. Consequently, the absence of air control devices could increase the PCDD/Fs content in the stack emission. Ash contains low PCDD/F levels except for one plant working with an acid degrease treatment.

Air emission factors depend on the presence or absence of air control devices being 0.030 and 0.079 μg I-TEQ/ton of galvanised steel respectively. Annual PCDD/Fs emission has been estimated in 0.023 g I-TEQ.

Furans are predominant both in flue gas and dust but PCDD/Fs ratio is similar in ash. The 2,3,4,7,8-PeCDF is the most relevant isomer in all matrices.

PCA study corroborates possible different PCDD/Fs formation mechanisms between ash, flue gas and dust. Time dependence could be the key point to understand the differences found in the PCDD/Fs content of ash from molten zinc and that for stack emissions and filter dusts.

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