

# Emissions of PCDD/Fs, PBDD/Fs, dioxin like-PCBs and PAHs from a cement plant using a long-term monitoring system

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## ABSTRACT

The aim of the present work was to assess the emission of different persistent organic pollutants from a cement plant over a period of one year, under normal operational conditions. Thus, a long-term sampling device was installed in the clinker kiln stack of the cement plant. The factory uses petroleum coke as primary fuel, but also alternative fuels such as solid recovered fuel (SRF), automotive shredder residue (ASR), sewage sludge, waste tires, and meat and bone meal (MBM) wastes, with an energy substitution level of about 40 %. Both PCDD/Fs (together with dl-PCBs) and PBDD/Fs were continuously sampled, with a total of ten samples collected in 2-4 week periods. Also, PAHs were sampled during one-week periods, in order to evaluate their emissions in three different samples. The emission levels throughout the year were much lower than the set legal limits in all substances, being  $< 10$  pg I-TEQ /Nm<sup>3</sup> in the case of PCDD/Fs. The data obtained allowed calculation of updated emission factors for the cement sector, which were 8.5 ng I-TEQ/ton clinker for PCDD/Fs and 3.2 ng WHO-TEQ/ton clinker for PCBs. With respect to the congener distribution, 2,3,7,8-TCDF accounts for 60 to 68 % of the total toxicity for

PCDD/Fs, and in PBDD/F emissions, a clear predominance of octa-substituted species (both dioxin and furan) was found.

*Keywords: waste; co-combustion; stack sampling; brominated pollutants; dioxin like-PCBs.*

## 1. INTRODUCTION

Waste management comprises a set of operations, such as the collection, transport, recovery and disposal of waste, including the supervision of such operations and the after-care of disposal sites (European Commission, 2008). These operations are carried out in order to give the most appropriate destination to the waste produced in a particular area according to their characteristics and marketing opportunities, cost treatment and legal regulations (Conesa et al., 2011).

In the cement industry, there is a need for using solid wastes as supplementary fuel or as raw material substitute, as it is known to achieve a complete and safe destruction of wastes, with a simultaneous benefit of getting energy (Conesa et al., 2008). A great variety of wastes are currently used as supplementary fuels in cement kilns (Rahman et al., 2015; Rodrigues and Joekes, 2011). Basic research is still needed because the wastes are actually burned, but the thermal decomposition of such wastes has not always been studied from a scientific point of view (Conesa et al., 2011). Under adequate conditions, concrete can be used for encapsulation of waste materials such as tyres, plastics and glasses (Rodrigues and Joekes, 2011).

The reduction on the emission of POPs regulated by the Stockholm Convention concerns the control of 26 substances consisting of pesticides, industrial chemicals, and

unintentional by-products, such as hexachlorobenzene (HCB), pentachlorobenzene, polychlorinated naphthalenes and the highly toxic polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs) (UNEP, 2009). In the Convention, there is a mention to the sources “that have the potential for comparatively high formation and release of these chemicals to the environment”; the list includes waste incineration plants, cement kilns coprocessing hazardous wastes, pulp production, and some thermal processes in the metallurgical industry.

PCDD/Fs have been the target of several studies in the last decades and are well known as unintentionally generated POPs, which pose serious health and environmental risks on a global scale (Du et al., 2010; UNEP Chemicals, 2005). Their brominated homologues (PBDD/Fs) present the same structure but are halogenated with bromine atoms instead of chlorine atoms and therefore have similar properties and effects to PCDD/F (Birnbaum et al., 2003; Conesa and Ortuño, 2014; Olsman et al., 2007).

In comparison to PCDD/Fs, little is known about the occurrence and levels of emissions of the brominated species, maybe due to their analytical difficulties, (Du et al., 2010; Hagberg, 2009). PBDD/Fs have been found in matrices such as air, sediments, marine products, and human adipose samples (Choi et al., 2003; Li et al., 2008; Malmvärn et al., 2005; Wang and Chang-Chien, 2007). Since the use of brominated flame retardants (BFRs) became extensive, especially for polybrominated diphenyl ethers (PBDEs) and tetrabromobisphenol A (TBBPA), more brominated sources are available and there is an increased chance of PBDD/F formation in both natural environment and industrial processes (Du et al., 2010; Ortuño et al., 2014b). According

to the United Nations Environment Programme, the unintentional formation and emission of brominated POPs/by-products (such as PBDD/Fs) from cement kilns were not studied or reported in 2010 (UNEP, 2010), and this is still true today since there are no studies available on this topic in literature.

Different studies have investigated the environmental impact of alternative fuels in the cement industry. In 2004, cement plants in EU 27 countries mostly complied with the emission limit of 100 pg I-TEQ/Nm<sup>3</sup> set for incineration and co-incineration plants, independently of the thermal substitution rate (European Commission, 2000; Rivera-Austrui et al., 2014). In Spain, measurements from the period 2000-2003 at 41 kilns using different waste fuels showed that the emission values were similar for plants using only conventional fuel and other plants using alternative fuels (Fabrellas et al., 2004). In 2011, Conesa et al. found much lower values (5 pg I-TEQ/Nm<sup>3</sup>) than the limit set by the European regulations when monitoring a clinker kiln fired with solid recovered fuel (SRF) from municipal solid waste, and no correlation was found between SRF feeding rate and dioxin emissions (Conesa et al., 2011). Other studies on the effect of increasing the alternative fuel feeding rate reported no direct influence on dioxin and furan emissions when using tyres and sewage sludge (Conesa et al., 2008) or meat meal and tires (Abad et al., 2004). Meat and bone meal has been revealed to be the best alternative fuel option in places as Australia (Rahman et al., 2015). In addition, a comparative life cycle assessment has been carried out on the use of sewage sludge in clinker production (Valderrama et al., 2013), and a significant environmental improvement has been detected, compared to the non-substitution scenario. A global mass balance of dioxins in a cement plant indicated that there is a net destruction of such pollutants (Li et al., 2015). Wurst and Prey (2003) and Karstensen (2008) indicated

that the material used as fuel in industrial furnaces was not responsible for the dioxin emissions. The conditions of the furnace (very high temperature, good mixing and excess oxygen) make the cement kiln factory an ideal place to get a very good combustion.

PCDD/F emissions might vary significantly over time, showing considerably higher values under unstable conditions such as plant start-up or shut-down (Löthgren and Van Bavel, 2005; Tejima et al., 2007; Wang et al., 2007). However, the aforementioned studies were almost all based on PCDD/F analysis from short-term manual sampling measurements in the clinker kiln stack. Online determination of PCDD/Fs and dl-PCBs in the stack would be desirable, but is not feasible with current technology (Rivera-Austrui et al., 2014).

A continuous monitoring system presents many advantages in comparison to short-term sampling. On the one hand the data is obtained in a continuous sampling of flue gas covering the total operation periods, being therefore more representative. On the other hand, larger sample volumes are involved in the analysis, allowing to lower LODs, enhancing the capacity to characterize profile information (Rivera-Austrui et al., 2014).

Other authors (Vicaretti et al., 2012) highlight the limitations of long-term sampling, as is the fact that emission levels detected in 15-30 days campaigns, when unsteady operating conditions can occur, as start-up and shut down, are not immediately comparable to the typical levels in a 6-8 h, when operating conditions are normally more stable. Moreover, there are often differences observed in the congener profiles between short- and long-term campaigns. Furthermore, as the main objective of the

present work is to assess the emission levels in normal plant operation, this limitation is of minor importance.

The present study presents a report on the emissions of long-term monitoring of PCDD/Fs, dl-PCBs, PBDD/Fs and PAHs (polycyclic aromatic hydrocarbons) in a clinker kiln stack. The sampling was extended over one year of normal operational use of the cement plant, considering this time period would be sufficiently long to get a representative view of the emission levels of the plant. As far as we know, there is no study that considers long-term sampling and analysis of brominated dioxins and furans from a cement plant. In this way, the present study will allow: to characterize the pollutant emissions from a cement plant, providing new information especially with regard to PBDD/F emissions; to obtain a more comprehensive and representative emission profile, compared to a short-term sampling, using a long-term monitoring device for one whole year; to calculate more realistic and updated average emission factors for the cement industry; and to evaluate whether the use of alternative fuels has an influence on the emissions of persistent organic pollutants.

## 2. MATERIALS AND METHODS

### **2.1. Case study**

The factory has a production capacity of 150 t/h of clinker and uses petroleum coke as primary fuel, but also alternative fuels like SRF (solid recovered fuel), ASR (automotive shredder residue), sewage sludge, waste tyres, and meat and bone meal

wastes, with an energy substitution level of about 40 %. The 71 m rotary kiln is equipped with an 8-stage cyclone pre-heater of 76 m high, and the flue gas treatment consists of a battery of baghouse filters working at a maximum temperature of 170 °C.

The work started with the installation of a long-term sampling device in the clinker kiln stack. The monitoring of PCDD/F, dl-PCB, PBDD/F and PAH emissions started in August 2013, and emission samples were regularly collected and sent to the laboratory for further analysis.

## **2.2.Sampling campaigns**

The study consisted of a total of 13 samples: ten samples (named DIOXIN1 to DIOXIN10) collected in 2-4 week periods, for the determination of PCDD/Fs, dl-PCBs and PBDD/Fs; and three samples (named PAH1 to PAH3) collected during one-week periods, for the determination of PAHs. Table 1 shows the most important data of the different samplings done, together with the percentages of the different fuels fed to the clinker furnace (percentages are energy-based).

The automatic long-term sampling device is a DioxinMonitoringSystem® (MonitoringSystems, Austria) and works according to the dilution method described in EN-1948:1 (CEN, 2006). Some of the advantages of this particular method are dry sampling (avoids humidity condensation inside the filter or adsorber), complete sampling of the dust fraction with high efficiency, use of low sampling temperatures (prevents further reactions, losses or formation, to occur) and measuring with two probes at two different positions (avoids traversing). The system has been described in detail previously (Rivera-Austrui et al., 2014; Steiner, 2003) and allows the continuous

isokinetic sampling for periods of up to several weeks, in contrast to 6-8 hour manual sampling methods. The sampling system was set up to automatically stop when the flue gas was below 70 °C for 4 min, and restart once this value had been above 70 °C for 15 min, in order to avoid sampling during plant outages.

At the end of each sampling period, the cartridge containing the adsorbent media (a corrugated particle filter and two dry polyurethane foams separated by a layer of 20 g of Amberlite XAD-2 resin) was sent to the laboratory for further analysis together with the sampling data (average filter temperature, relative flue gas humidity, oxygen content and sampling volumes, among others). The whole sampling process was controlled by the addition of a mixture of the standard solutions over the XAD-2 resin. During PCDD/F, PBDD/F and dl-PCB sampling EN-1948SS, P48-SS (Wellington Laboratories, Canada), and EF-5410 (Cambridge Isotope Laboratories, USA) standards were used containing: 4000 pg of both  $^{13}\text{C}$ -1,2,3,7,8-PeCDF and  $^{13}\text{C}$ -1,2,3,7,8,9-HxCDF, and 8000 pg of  $^{13}\text{C}$ -1,2,3,4,7,8,9-HpCDF for PCDD/Fs; 10000 pg of each of  $^{13}\text{C}$ -PCB-60,  $^{13}\text{C}$ -PCB-127 and  $^{13}\text{C}$ -PCB-159 for dl-PCBs; 4000 pg  $^{13}\text{C}$ -2,4,6,8-TBDF for PBDD/Fs. For PAH sampling, deuterated PAHs were used as sampling standards, specifically 150  $\mu\text{L}$  of standard solution L429-SS (Dr. Ehrenstorfer-Schäfers, Germany) containing 20  $\mu\text{g}$  of each fluorine- $\text{d}_{10}$  and p-terphenyl- $\text{d}_{10}$ .



- 1 *Table 1. Details on the different samplings done together with the rates of alternative fuels fed to the clinker furnace (percentages are energy-*  
 2 *based).*

	DIOXIN1	DIOXIN2	DIOXIN3	DIOXIN4	DIOXIN5	DIOXIN6	DIOXIN7	DIOXIN8	DIOXIN9	DIOXIN10	PAH1	PAH2	PAH3
<b>Installation date</b>	06/08/2013	18/09/2013	30/10/2013	15/01/2014	03/02/2014	21/02/2014	18/03/2014	09/04/2014	30/04/2014	20/06/2014	15/11/2013	11/03/2014	13/06/2014
<b>Sampling time (days)</b>	43	42	16	19	18	18	22	21	16	34	6	7	7
<b>Filter temp (°C)</b>	49	51	49	48	48	48	48	50	50	53	48	49	54
<b>sampled flue gas (m3,nc,wet)</b>	549.6	876.1	375.8	584.7	508.8	546.0	638.3	524.7	503.0	578.8	130.0	208.9	178.6
<b>(m3,nc,dry, 10% O2)</b>	375.9	646.6	294.2	515.7	457.9	471.7	545.7	434.4	457.2	448.0	104.1	174.9	147.9
<b>Clinker production (Tn)</b>	70289	97003	46703	60702	50954	49123	60503	56577	44238	88924	16110	24114	18890
<b>Fuel mix (energy-based %)</b>													
<b>% Petroleum coke</b>	40.4	35.7	47.1	56.5	61.7	60.3	59.0	64.2	61.7	62.7	62.0	55.9	58.2
<b>% meat and bone meal</b>	6.0	5.1	2.1	3.0	1.8	1.4	2.0	1.3	2.8	1.0	3.9	0.9	5.4
<b>% tyre</b>	8.4	7.4	7.3	5.3	13.6	9.1	8.9	7.8	6.5	4.0	7.3	6.7	2.0
<b>% sewage sludge</b>	5.4	4.8	3.3	4.4	3.6	2.9	3.5	4.0	3.2	4.4	3.0	3.1	4.6
<b>% automotive shdreder waste</b>	1.4	0.7	0.2	0.0	0.0	0.5	2.6	3.0	3.5	0.5	0.6	4.4	0.0
<b>% solid recovered fuel</b>	38.4	46.4	40.0	30.8	19.3	25.9	24.1	19.6	22.2	27.4	23.3	28.9	29.8
<b>sum % alternative fuels</b>	59.6	64.3	52.9	43.5	38.3	39.7	41.0	35.8	38.3	37.3	38.0	44.1	41.8

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## **2.3. Analytical procedure**

### ***2.3.1. Dioxins and dioxin like compounds***

The analytical procedure used for the analysis of these pollutants has been adapted from a previous work (Rivera-Austrui et al., 2012). Sampling media (segmented polyurethane foams, Amberlite and filter) were spiked with labelled compounds, submitted to acid digestion with 3 M HCl and then Soxhlet extracted with toluene (Merck, Germany) for 24 h. Acid treatment with 3 M HCl for 2 h is necessary in order to break the matrix and remove PCDD/Fs and dl-PCBs from the particulate matter. Prior to extraction, sampling adsorbent media were spiked with different standard solutions containing: 4000 pg of tetra- to hexa-labeled compounds and 8000 pg of hepta- to octa-labeled compounds for PCDD/Fs (EN-1948ES standard solution, Wellington Laboratories, Canada) and 10000 pg of each labeled congener for dl-PCB (P48-W-ES standard solution, Wellington Laboratories, Canada). Also 40 µL of the standard mixture EDF-5408 (Cambridge Isotope Laboratories, USA) was used to verify the extraction of brominated dioxins and furans. An aliquot of 5 % of the extract is used for PCDD/F and PCB analysis (Rivera-Austrui et al., 2012), while an aliquot of 50 % was used for PBDD/F analysis, since lower levels of these contaminants were expected.

For chlorinated species analysis, clean-up and fractionation of the aliquot consisted of a prior manual step (acidic/basic silica column) followed by an automated clean-up step on a Power Prep™ system (FMS, Inc., USA). Prior to the injection, a mixture of the labelled recovery standard solutions EN-1948IS and P48-RS (Wellington Laboratories, Canada) was added to the samples, containing 400 pg of <sup>13</sup>C-1,2,3,4-TCDD and <sup>13</sup>C-

1,2,3,7,8,9-HxCDD, and 1000 pg of each labelled PCB-70, PCB-111, and PCB-170, respectively. Samples were analyzed in an Agilent gas chromatograph fitted with a DB-5MS or DB-XLB fused silica column (J&W Scientific, USA) for PCDD/Fs and dl-PCBs respectively, coupled to an Autospec Premier high resolution mass spectrometer (Waters, UK).

For brominated dioxin and furan analysis, the extracts were purified using a Power Prep system with silica gel, alumina, and active carbon pre-packed columns, with the addition of a previous acidic silica JUMBO column as an extra clean-up step. The extracts were concentrated in a rotary evaporator and with a gentle stream of nitrogen, and EDF-5409 (Cambridge Isotope Laboratories, USA) was added as recovery standard, containing 5000 pg of <sup>13</sup>C-1,2,3,7,8,9-HxBDD and 2000 pg of <sup>13</sup>C-1,2,3,7,8-PeBDF. Analysis was performed by gas chromatography coupled to high resolution mass spectrometry (HRGC-HRMS) using an Autospec Ultima NT mass spectrometer (Waters, UK) as explained in previous work (Ortuño et al., 2014a), using a DB-5MS capillary column (15m x 0,25mm x 0,10µm). PBDD/F recoveries were all within the limits stated by the US EPA method 1613 (see Table S1 in the Supplementary material).

Identification and quantification of the analytes were performed according to the isotope dilution method. For the analysis of the brominated species, samples were protected from light, using amber quartz or aluminium foil, in order to minimize photodegradation.

### 2.3.2. *Polycyclic aromatic hydrocarbons (PAHs)*

To determine the concentration of PAHs in the samples, an internal standard (5 µl of deuterated PAH Mix 26, Dr. Ehrenstorfer, Germany) was added to the resin before Soxhlet extraction for 24 h in a mixture of dichloromethane-hexane (1:1), following the U.S. EPA method 3540C (US EPA, 1996). The extract was purified by eluting the sample through a manual activated silica column.

The clean extract was concentrated in a rotary evaporator and with a moderate stream of nitrogen up to 1.5 ml. Lastly, 3 µl of a solution 2000 µg/ml anthracene-d<sub>10</sub> was spiked to the vials as a recovery standard. These compounds were analyzed by HRGC-MS in the SCAN mode in an Agilent system (6890N gas chromatograph coupled to a 5973N mass spectrometer), with an HP5-MS column (30 m x 0.25 mm i.d. x 0.25 mm) using the U.S. EPA method 8270D as reference (US EPA, 2007). The identification and quantification was carried out for the 16 priority PAHs established by the U.S. EPA (1998).

## 3. RESULTS AND DISCUSSION

Table 2 presents the results of the analysis of the chlorinated contaminants obtained in the campaigns shown before in Table 1. Table 3 presents the corresponding brominated dioxin and furan emissions. Emission values are expressed in the basis of normal cubic meters (Nm<sup>3</sup>); the total amounts are expressed in toxicity units (I-TEQ for dioxins and WHO-TEQ for PCBs) and are referred to the volume of stack gas (pg/Nm<sup>3</sup>) and to the amount of clinker produced (ng/ton clinker).

Table 2. PCDD/F and dl-PCB concentrations in 10 sampling periods, referred to the volume of stack gas (pg/Nm<sup>3</sup>) and to the amount of clinker produced (ng/ton clinker).

	DIOXIN1	DIOXIN2	DIOXIN3	DIOXIN4	DIOXIN5	DIOXIN6	DIOXIN7	DIOXIN8	DIOXIN9	DIOXIN10
PCDD/Fs (pg/Nm <sup>3</sup> )										
2,3,7,8-TCDF	64.6	47.7	14.0	28.3	11.2	17.1	20.8	11.9	6.09	40.0
1,2,3,7,8-PeCDF	3.80	3.25	0.75	1.93	0.75	2.07	1.48	0.67	0.39	2.98
2,3,4,7,8-PeCDF	4.08	2.84	0.74	2.46	0.90	0.87	1.18	0.63	0.40	3.05
1,2,3,4,7,8-HxCDF	0.51	0.29	0.08	0.39	0.10	0.38	0.19	0.11	0.11	0.55
1,2,3,6,7,8-HxCDF	0.43	0.30	0.09	0.32	0.08	0.22	0.15	0.09	0.10	0.50
2,3,4,6,7,8-HxCDF	0.40	0.20	0.06	0.32	0.09	0.12	0.14	0.10	0.10	0.59
1,2,3,7,8,9-HxCDF	0.08	0.11	0.07	0.10	0.08	0.10	0.08	0.12	0.12	0.09
1,2,3,4,6,7,8-HpCDF	0.46	0.18	0.07	0.29	0.26	0.25	0.22	0.28	0.26	0.39
1,2,3,4,7,8,9-HpCDF	0.32	0.03	0.07	0.23	0.26	0.25	0.22	0.28	0.26	0.27
OCDF	1.60	0.07	0.10	1.16	1.31	1.27	1.10	1.38	1.31	1.34
2,3,7,8-TCDD	0.79	0.70	0.16	0.26	0.16	0.12	0.31	0.15	0.07	0.32
1,2,3,7,8-PeCDD	0.18	0.12	0.07	0.11	0.06	0.09	0.06	0.06	0.06	0.31
1,2,3,4,7,8-HxCDD	0.08	0.04	0.06	0.10	0.06	0.08	0.06	0.07	0.05	0.19
1,2,3,6,7,8-HxCDD	0.19	0.08	0.06	0.14	0.06	0.08	0.07	0.07	0.04	0.28
1,2,3,7,8,9-HxCDD	0.11	0.02	0.07	0.10	0.07	0.08	0.07	0.07	0.04	0.18
1,2,3,4,6,7,8-HpCDD	0.88	0.46	0.10	0.61	0.27	0.58	0.48	0.34	0.26	0.71
OCDD	1.60	0.69	0.16	1.16	1.31	1.27	1.10	1.38	1.31	1.34
TOTAL PCDD/Fs I-TEQ (pg/Nm <sup>3</sup> )	9.77	7.23	2.05	4.63	1.85	2.53	3.17	1.80	0.99	6.41
TOTAL PCDD/Fs I-TEQ (ng/ton clinker)	20.46	15.14	4.30	9.70	3.88	5.30	6.64	3.77	2.08	13.42
dl-PCBs (pg /Nm <sup>3</sup> )										
PCB-81	53.7	45.2	34.8	65.9	45.5	18.3	41.8	25.2	18.8	109.8
PCB-77	476	398	300	714	182	192	356	428	199	1543
PCB-126	20.6	16.7	9.13	20.7	6.51	4.37	15.9	8.49	4.50	34.5
PCB-169	0.88	0.32	0.19	0.78	0.47	0.43	0.43	0.62	0.45	2.22
PCB-123	90.8	72.1	83.0	119	47.4	42.8	80.8	61.7	44.1	223

PCB-118	420	240	182	367	200	88.1	311	242	90.9	711
PCB-114	9.63	5.47	3.68	6.87	3.23	1.73	5.62	3.48	1.79	13.5
PCB-105	146	78.7	53.3	112	54.3	28.6	97.4	73.6	29.5	192
PCB-167	29.5	16.5	10.3	22.2	10.5	7.51	26.4	19.9	7.75	49.9
PCB-156	39.9	20.1	9.04	17.8	9.43	5.78	22.7	17.5	5.97	46.7
PCB-157	10.0	5.14	2.98	7.55	2.78	2.17	6.94	4.53	2.24	15.5
PCB-189	5.30	2.43	0.77	2.60	0.96	0.50	2.99	2.23	0.51	5.69
TOTAL PCBs WHO-TEQ (pg/Nm <sup>3</sup> )	2.22	1.78	0.99	2.23	0.72	0.48	1.70	0.95	0.50	3.79
TOTAL PCBs WHO-TEQ (ng/ton clinker)	4.65	3.72	2.07	4.68	1.50	1.01	3.56	1.99	1.04	7.93

Table 3. PBDD/F concentrations in 10 sampling periods, referred to the volume of stack gas (pg/Nm<sup>3</sup>) and to the amount of clinker produced (ng/ton clinker).

	DIOXIN1	DIOXIN2	DIOXIN3	DIOXIN4	DIOXIN5	DIOXIN6	DIOXIN7	DIOXIN8	DIOXIN9	DIOXIN10
PBDD/Fs (pg /Nm <sup>3</sup> )										
2,3,7,8-TBDF	0.33	0.22	0.08	0.16	0.02	0.03	0.33	0.18	0.10	0.28
2,4,6,8-TBDF	0.63	0.53	0.07	0.11	0.06	0.10	0.15	0.10	0.03	0.00
1,2,3,7,8-PeBDF	0.10	0.09	0.23	0.04	0.002	0.05	0.08	0.01	0.10	0.03
2,3,4,7,8-PeBDF	0.11	0.09	0.31	0.03	0.003	0.04	0.07	0.004	0.08	0.06
1,2,3,4,7,8-HxBDF	0.18	0.20	0.27	0.02	0.01	0.02	0.03	0.01	0.06	0.13
1,2,3,4,6,7,8-HpBDF	0.39	0.40	0.47	0.15	0.05	0.12	0.11	0.05	0.04	0.18
OBDF	2.80	1.48	2.39	2.02	2.15	1.81	0.59	0.75	1.19	1.76
2,3,7,8-TBDD	0.02	0.03	0.04	0.003	0.001	0.004	0.04	0.02	0.004	0.01
1,2,3,7,8-PeBDD	0.04	0.05	0.15	0.004	0.002	0.01	0.004	0.004	0.003	0.06
1,2,3,4,7,8+1,2,3,6,7,8- HxBDD	0.43	0.34	0.82	0.01	0.01	0.02	0.02	0.01	0.01	0.23
1,2,3,7,8,9-HxBDD	0.10	0.16	0.28	0.01	0.01	0.01	0.01	0.01	0.01	0.02
1,2,3,4,6,7,8-HpBDD	0.48	0.41	0.78	0.24	0.35	0.12	0.23	0.12	0.37	0.12
OBDD	0.31	0.25	0.56	0.48	0.31	0.16	0.17	0.24	0.24	0.68
TOTAL PBDD/Fs I-TEQ (pg/Nm <sup>3</sup> )	0.21	0.20	0.44	0.05	0.01	0.04	0.12	0.05	0.08	0.14

TOTAL PBDD/Fs I-TEQ (ng/ton clinker)	0.45	0.42	0.91	0.10	0.03	0.09	0.25	0.10	0.16	0.29
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The UNEP PCDD/Fs Toolkit (UNEP, 2005) assigns an emission factor of 50 ng I-TEQ per ton of cement to all dry kilns and wet kilns where dust collector temperature is held below 200 °C. In this study, considering an estimated average emission factor of 2094 Nm<sup>3</sup>/ton clinker (value given by the cement plant factory), the emission factors are 8.5 ng I-TEQ/ton clinker for PCDD/Fs and 3.2 ng WHO-TEQ/ton clinker for PCBs, both results are well below the value proposed by the United Nations. This is in accordance with that observed in previous studies in the Spanish cement industry, where real emission factors were found to be in the range 2.5 – 14.5 ng I-TEQ/ton clinker (Fabrellas et al., 2005; Rivera-Austrui et al., 2014). On the other hand, an average value for PBDD/Fs of 0.23 ng I-TEQ (equivalent)/ ton clinker can be given.

Figure 1 shows a comparison of the levels of PCDD/Fs, PBDD/Fs and PCBs, together with the percentage of alternative fuels fed to the furnace during each sampling period. The legal PCDD/F emission limit established in the Industrial Emissions Directive (European Commission, 2010) has also been depicted in the figure to help put the data into perspective.



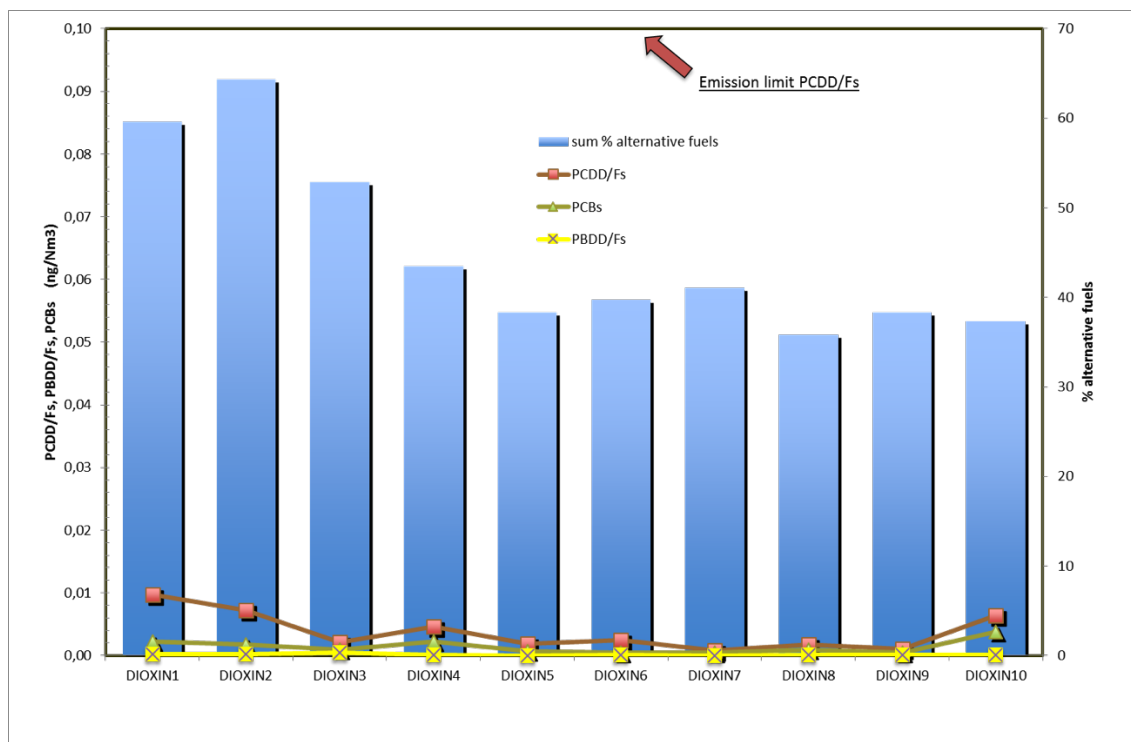


Figure 1. Comparison of the emissions ( $\text{ng}/\text{Nm}^3$ ) of PCDD/Fs, PBDD/Fs and PCBs during all sampling periods.

The results of the PCDD/F emissions can be compared to the emission limit of  $100 \text{ pg}/\text{Nm}^3$  set by the Industrial Emissions Directive (European Commission, 2010), and is clear that the emission is in all cases very low, independently of the conditions of the fuel mixtures fed to the clinker furnace. This behaviour has already been observed in other factories in Spain, and reported by several authors (Abad et al., 2004; Fabrellas et al., 2005; Rovira et al., 2010; Schuhmacher et al., 2004). The fact that the use of alternative feedstocks is not related with an increase in dioxin emissions has also been observed by others (Abad et al., 2004; Conesa et al., 2008; Conesa et al., 2011; Fabrellas et al., 2005; Karstensen, 2008).

Figure 2 presents the congener distribution of PCDD/Fs obtained in all sampling periods. A clear predominance of furans can be observed, specially of the 2,3,7,8-TCDF that accounts for 60-68 % for the total toxicity of the different samples.

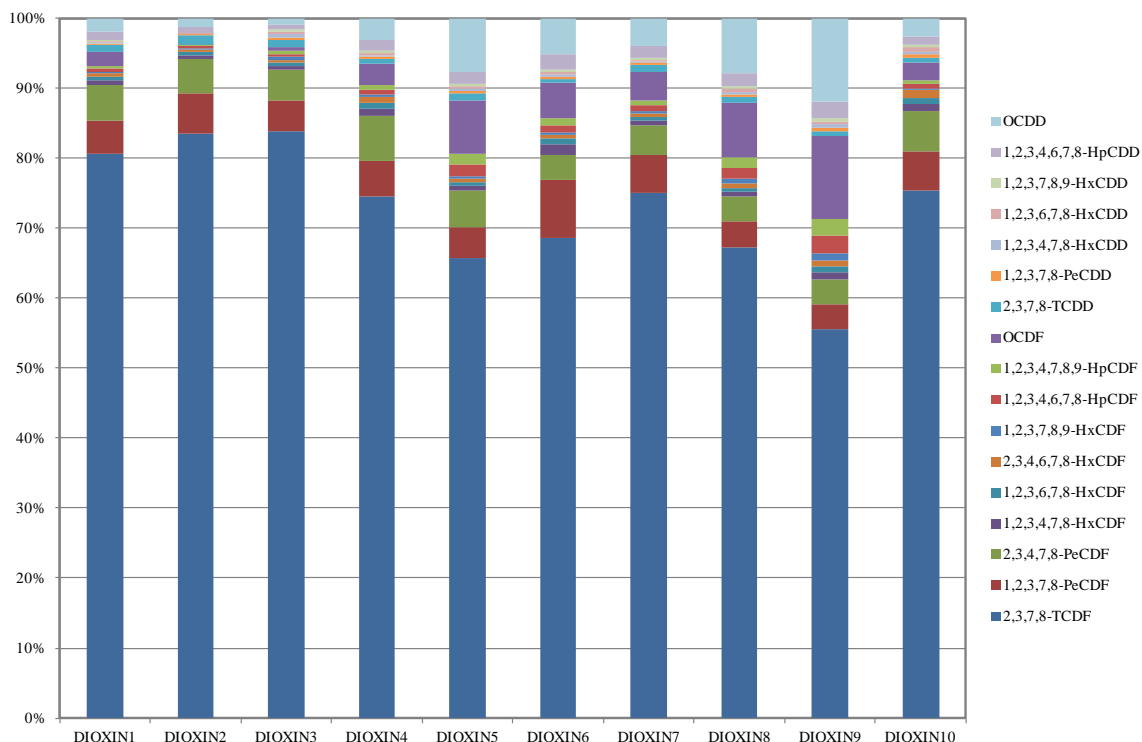


Figure 2. Congener distribution of PCDD/Fs obtained in all sampling periods.

The use of longer sampling periods and the large sample volume analyzed leads to a major capacity for robust profile determination; very few congener values are below the LOD. At first glance, there is a clear predominance of 2,3,7,8-TCDF and OCDD, as previously reported for other clinker kilns (Abad et al., 2004; Ames et al., 2012; Rivera-Austrui et al., 2014), independently of the use of alternative fuel. A recent study of the emission of these compounds in China, reported that tetra- and hexachlorinated furans were the two most abundant homologue groups, and that the homologue concentration decreased with rising chlorine number for dioxin (Chen et al., 2014).

Regarding dl-PCBs, Table 2 shows that the predominant congeners were PCB-118, PCB-105, PCB-123 and PCB-77, precisely the same congeners shown in previous studies of clinker kiln emissions (Rivera-Austrui et al., 2014).

On the other hand, PBDD/F emissions are not regulated by law in any country. Table 3 shows that for every sampling period, PBDD/F emission values were at least three orders of magnitude below the limit established by the European Directive 2010/75/EU for their chlorinated analogues. Total PBDD/F emission values ranged from 0.01 to 0.44 pg I-TEQ/Nm<sup>3</sup>, which are equivalent to 0.03 and 0.91 ng I-TEQ/ton clinker, respectively. Because in the cement plant there is not availability of bromine, this rather low value is expected; the only materials that might contain a slight amount of bromine are automotive shredder residue or perhaps sewage sludge, but in very low amounts.

Figure 3 presents the congener distribution in the emission of brominated dioxins and furans. In this case, a clear predominance of octa-substituted species (both dioxin and furan) is found, followed by the emission of 1,2,3,4,6,7,8-HpBDD. In all sampling periods a furan/dioxin ratio higher than one was measured, as it has been observed in different incineration processes (Conesa and Ortuño, 2014). Only one more research paper analyzing brominated dioxin emissions from cement kilns has been found (Yang et al., 2012), but PBDE contaminated soils were fed to the kiln, which makes the comparison difficult.

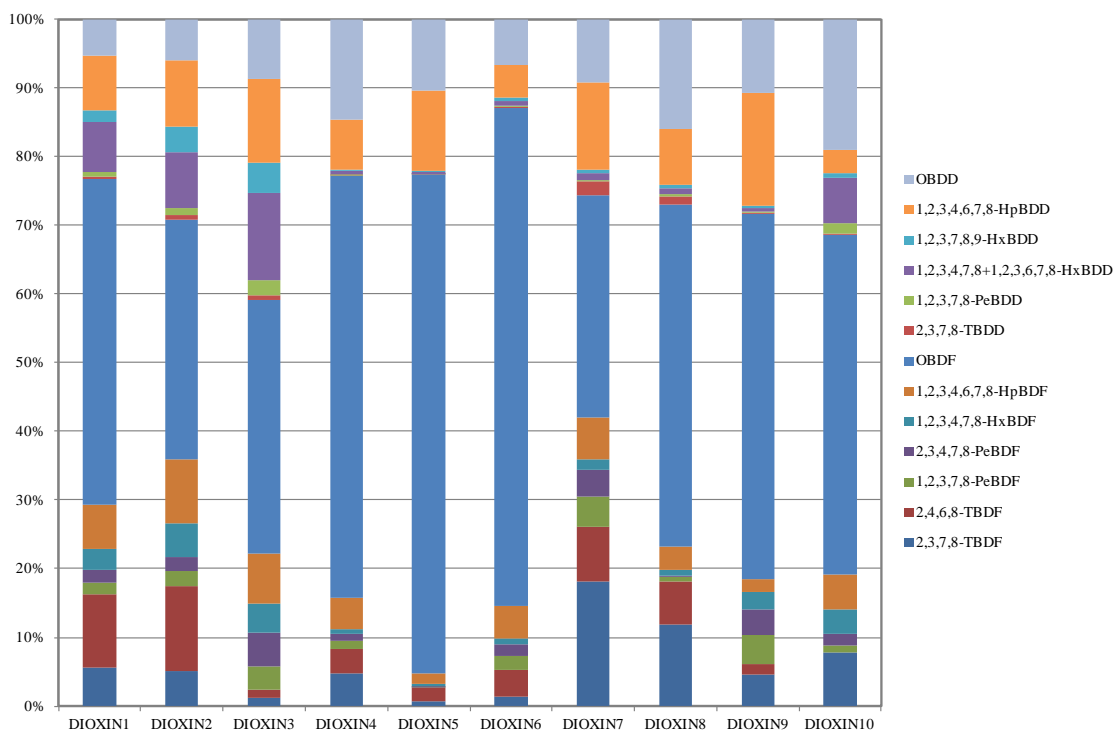


Figure 3. Congener distribution of PBDD/Fs obtained in all sampling periods.

Sixteen PAHs were analyzed, which are designated as priority pollutants by the U.S. EPA, including seven that are considered carcinogenic: (benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, chrysene, dibenzo(ah)anthracene, and indeno(1,2,3-cd)pyrene (US EPA, 1998). Of these compounds, four have also been listed as substances subjected to emission reduction in Europe: benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, and indeno(1,2,3-cd)pyrene (European Council, 2004). The results are shown in Table 4 (see Table 1 for details on the conditions of the sampling). The limit of detection of all PAHs (0.01 µg) was set as the lowest detectable amount of compound, and was calculated by analysing different standards with decreasing PAH concentrations.

Table 4. PAH concentrations ( $\mu\text{g}/\text{Nm}^3$ ) in 3 sampling periods.

	PAH1	PAH2	PAH3
PAHs ( $\mu\text{g}/\text{Nm}^3$ )			
naphthalene	9.77	6.88	6.10
acenaphthylene	0.794	0.924	0.368
acenaphthene	0.014	0.034	0.014
fluorene	0.052	0.125	0.082
phenanthrene	4.23	4.86	2.33
anthracene	0.057	0.042	0.008
fluoranthene	0.287	0.182	0.054
pyrene	0.102	0.085	0.009
benzo(a)anthracene	0.0004	nd	nd
chrysene	0.005	0.004	0.003
benzo(b)fluoranthene	nd	nd	nd
benzo(k)fluoranthene	nd	nd	nd
benzo(a)pyrene	nd	nd	nd
indeno(1,2,3-cd)pyrene	nd	nd	nd
dibenz(a,h)anthracene	nd	nd	nd
benzo(g,h,i)perylene	nd	nd	nd

nd: not detected

Regarding the 16 U.S. EPA priority PAHs analyzed (from two to six aromatic rings), in all cases naphthalene was the most abundant ( $6.10 - 9.77 \mu\text{g}/\text{Nm}^3$ ), followed by phenanthrene ( $2.33 - 4.86 \mu\text{g}/\text{Nm}^3$ ) and acenaphthylene ( $0.368 - 0.924 \mu\text{g}/\text{Nm}^3$ ). No PAHs of 5 or 6 aromatic rings were detected. With respect to the 7 PAHs considered as carcinogenic compounds, the only ones detected were chrysene ( $3 - 5 \text{ ng}/\text{Nm}^3$ ), and  $0.4 \text{ ng}/\text{Nm}^3$  of benzo(a)anthracene in one sample. The levels found in the present study are similar to those reported by Yang et al. for different industrial sources, such as blast furnace, basic oxygen furnace, coke oven, electric arc furnace, heavy oil plant, power plant and cement plant (Yang et al., 1998). The authors also pointed out that the formation of heavier PAHs (4 to 7 rings) was promoted by the use of heavy oil as fuel. In the present work, such heavy hydrocarbons were not found, as they also were not detected in previous studies at the same plant (Conesa et al., 2008; Conesa et al., 2011).

The different samples collected in the present study yielded similar PAH amounts. The legal limit set by the Waste Incineration Directive for total organic carbon (TOC) is 10 mg/Nm<sup>3</sup>, which includes the PAHs analyzed here (European Commission, 2000). With total values ranging 0.009 – 0.015 mg/Nm<sup>3</sup>, it can be concluded that their contribution to the emission of TOC is very slight.

In addition, no correlation was observed between the emission of any of the pollutants measured and the degree of substitution with alternative fuels.

#### 4. PRINCIPAL COMPONENT ANALYSIS

Two different Principal Component Analysis (PCA) were performed in the present work, in an attempt to find correlations between the studied parameters, by using the commercial software SPSS 15.0. On the one hand, the different concentrations of PCDD/Fs obtained in each sampling series, together with the corresponding percentage of petroleum coke, tires, meat and bone meal, sewage sludge, automotive shredder waste and solid recovered fuel were subjected to a principal component analysis. This procedure was used in a previous work in order to analyze the correlation between the emissions and the alternative fuels (Conesa et al., 2008). This kind of method gives us an overview of the dominant patterns and can be used for the classification of groups. Note that during PCA the data table is pre-processed before the analysis, in such a way that, when the variables are measured with different units (as is the case in the present PCA), each element is divided by its variance, in order to standardize the observations. Figure 4 shows the scores plot of the PCA for this data. The PCA is able to explain more than 74 % of the data with only two components. In Figure 4 it can be observed

that a great majority of PCDD/F congeners does not correlate with the percentage of any residue fed to the cement kiln. It can also be observed that total I-TEQ is very much influenced by 2,3,7,8-TCDF, as stated previously. Also, % Sludge and SRF are somewhat related with the emission of 2,3,7,8-TCDD but % MBM, Pet Coke, ASR and tyres seems to be independent from any PCDD/F emission.

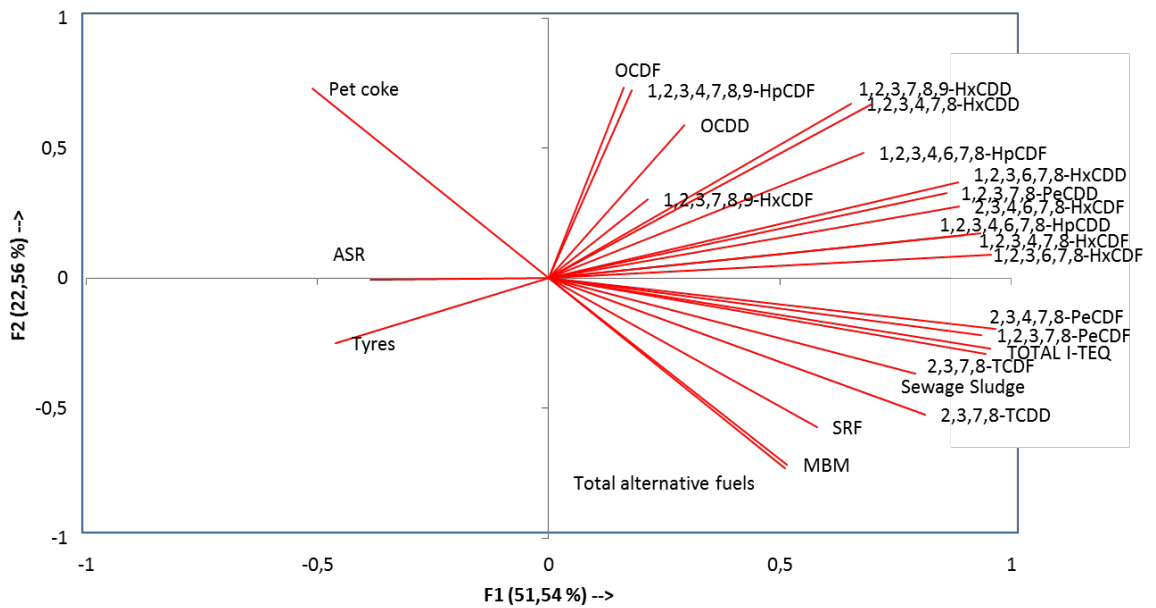


Figure 4. Principal component analysis scores plot of the correlation between the emissions of PCDD/Fs and the fuel mixture consumed during the sampling period.

On the other hand, PCDD/F and PBDD/F emissions were also used for a PCA, in search of correlations in the emissions between the two groups of pollutants. Figure 5 shows the results of this statistical analysis, which explains 72 % of the data with two components. The scores plot in Figure 5 represents the results for principal components or factor 1 (F1) and 2 (F2). Note that:

- F1 correlated positively with all congeners of both PCDD/Fs and PBDD/Fs. This behaviour implies that if one of the compounds increases, so do all the others too, in

such a way that there are runs with almost all the congeners above or under their respective averages.

- F2 is, in general, correlated positively with PBDD/Fs and negatively with PCDD/Fs. In this way, emission data can be divided into two different groups; one group incorporating most of the PCDD/Fs and the other containing PBDD/Fs.

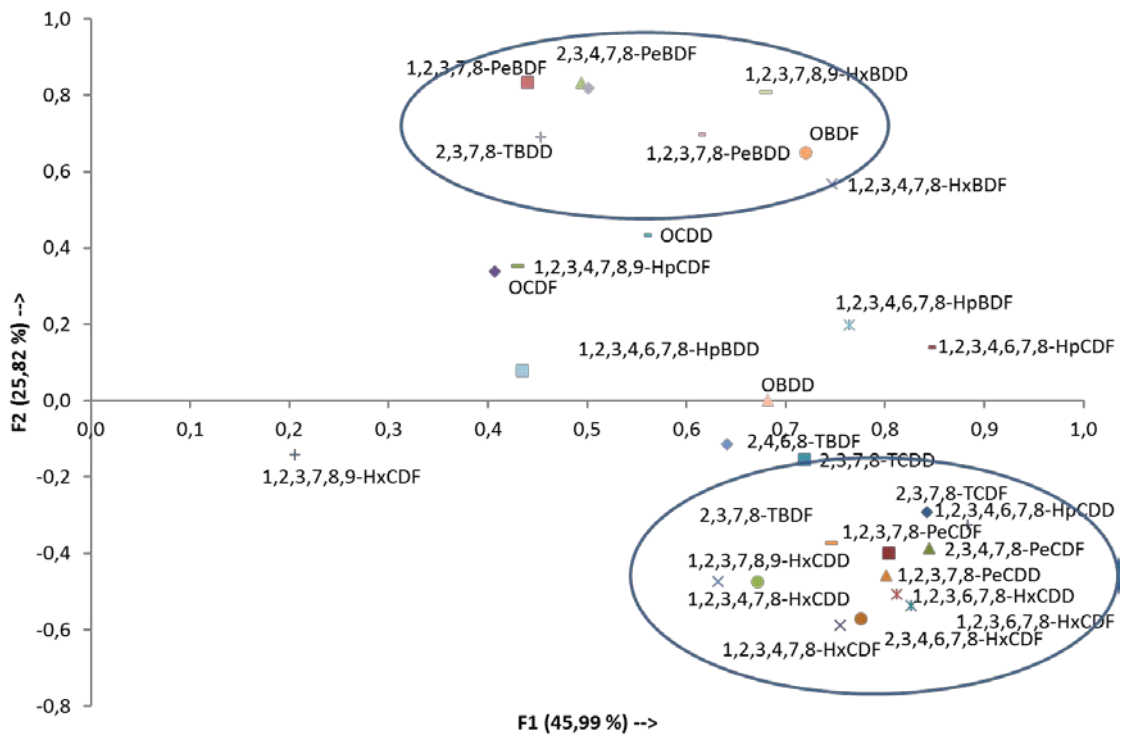


Figure 5. Principal component analysis scores plot for the correlation between the emissions of PCDD/Fs and PBDD/Fs.

The positive correlation with F1 in this PCA denotes that the emission of these two groups of pollutants have a similar behaviour, increasing or decreasing at the same time, i.e., the samples (periods of time) presenting high levels of PCDD/Fs also present a high levels of PBDD/Fs. This is true for all congeners but not in the same extent (depending on the specific value of the coefficients).



Nevertheless, F2 statistically distinguishes two different groups (chlorinated and brominated); this indicates that the production or destruction for each group is due to different reasons (for example in different locations of the cement kiln) system in such a way that there is a statistical difference between them. It is worth mentioning that there is a clear segregation in the plot of the congeners with low-substitution degree, and only the more substituted species are mixed in the scores plot.

## 5. CONCLUSIONS

After taking samples over a year of operation of a cement factory using a long-term sampling device, we can conclude that the emission levels throughout the year are much lower than the legal limits set for all substances, being  $< 10 \text{ pg I-TEQ /Nm}^3$  in the case of PCDD/Fs.

The data obtained allowed calculation of updated emission factors for the cement sector, which resulted to be  $8.5 \text{ ng I-TEQ/ton clinker}$  for PCDD/Fs and  $3.2 \text{ ng WHO-TEQ/ton clinker}$  for PCBs. Average emission of PBDD/Fs is  $0.23 \text{ ng I-TEQ (equivalent)/ ton clinker}$ .

With respect to the congener distribution, 2,3,7,8-TCDF accounts for 60-68 % for the total toxicity for PCDD/Fs, and in PBDD/F emissions, a clear predominance of octa-substituted species (both dioxin and furan) is found.

No correlation was observed between the emission of any of the pollutants measured and the degree of substitution with alternative fuels. Brominated and chlorinated dioxins and furans have a similar behaviour, increasing or decreasing at the same time.

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