ENVIRONMENTAL MONITORING OF PCDD/Fs AFTER ALTERNATIVE FUEL IMPLEMENTATION IN A CATALAN (SPAIN) CEMENT PLANT. HEALTH RISK ASSESSMENT

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Introduction

In recent years, the European cement industry has been notably increasing the co-combustion rate of alternative fuels in cement kilns[1]. This practice is associated to a number of environmental and economic benefits, such as reduction of CO_2 emissions, reuse of by-products, solve waste management problem, and fossil fuel saving. However, information regarding any potential changes in the pollutant emissions is particularly scarce. Consequently, residents and local authorities from the vicinity of these facilities are generally concerned on the potential health and environmental effects, when alternative fuels are used in cement plants. Since polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) may be formed during the combustion processes of cement production[2,3], and subsequently released to the environment, these chemicals have received most of the social and political attention.

This study aimed at evaluating the potential changes in the PCDD/F emissions of a cement plant using sewage sludge as alternative fuel. PCDD/F levels were analyzed in samples of air, vegetation, and soil collected around a facility, before and after traditional (fossil) fuel was partially replaced by alternative fuels. Moreover, any potential changes in the human health risks associated to PCDD/F exposure were assessed for the population living around the cement plant.

Materials and methods

Between 2008 and 2009, three environmental monitoring studies were performed around a cement plant located in Montcada i Reixac (Catalonia, Spain) (Table 1). At that time, the facility was only using traditional fuel (petroleum coke and coal) to meet its energetic requirements[4]. In June 2010, a progressive implementation of alternative fuels (sewage sludge, refuse-derived fuel, and animal meal) was initiated, reaching up to a 35% replacement. In December 2011 and November 2014, two more studies were carried out to evaluate the impact of the cement plant on the surrounding environment. In each one of these surveys, 4 air, 7 vegetation, and 7 soil samples were collected at different distances and directions from the facility.

Table 1. Sampling information.

Survey	Matrices	Fuel used in the cement plant	References
November 2008	Air, vegetation, and soil	Traditional	Rovira et al.[4]
May 2009	Air, vegetation, and soil	Traditional	Rovira et al.[4]
November 2009	Air, vegetation, and soil	Traditional	Rovira et al.[4]
December 2010	Air, vegetation, and soil	Traditional + alternative (Biomass)	Present study
November 2014	Air, vegetation, and soil	Traditional + alternative (Biomass)	Present study

Soil samples, constituted of subsamples collected in an area of 25 m^2, were taken from the upper soil layer (5 cm) and stored in polyethylene bags. Once in the laboratory, samples were dried at room temperature and sieved through a 2 mm mesh screen. Around 150 g of vegetation (*Piptatherum* L.) were obtained by cutting the plants at 5 cm above ground, and dried at room temperature. Air samples were collected by means of TE-1000 PUF high-volume active samplers (Tisch Environmental, Cleves, OH, USA). PCDD/Fs in particle and gas phases were separately taken by using polyurethane foams (PUFs) and quartz fibber filters, respectively. Around 700 m^3 of air were collected during a sampling which lasted approximately 48 h. The determination of PCDD/Fs in soil and vegetation samples, which was based on the US EPA method 1613, was done via high-resolution gas chromatography coupled to high-resolution mass spectrometry (HRGC/HRMS), in combination with the isotope dilution technique. The concentrations of PCDD/Fs in air were also determined by HRGC/HRMS, following the

German VDI 3499 method. Appropriate labeled extraction standards ($^{13}C_{12}$-PCDD/Fs substituted congeners) were added to control the whole sample preparation process and to evaluate potential losses.

The PCDD/F concentrations in air and soil around the cement plant were used to evaluate the environmental exposure and to characterize the risks on the human health, before and after the partial fuel substitution. The numerical expressions to estimate the human exposure via air inhalation, soil ingestion and dermal absorption, were taken from the Technical Guide of the Spanish Royal Decree 9/2005, which in turn is based on the US EPA RAGS methodology[5]. Details on the equations have been recently reported[6]. In turn, inhalation risks were calculated using the most updated methodology of US EPA[7], which suggests that the amount of chemical reaching the target site through inhalation, is directly related to the exposure concentration (EC), being not a simple function of inhalation rate and body weight. Inhalation and oral reference doses (RfD_i and RfD_o), inhalation unit risks (IUR), and oral slope factors (SF_o) for each congener were obtained from the Risk Assessment Information System (RAIS)[8].

For data analysis, those PCDD/F congeners with levels below their respective limits of detection (LODs) were considered to have a concentration equal to one-half of that limit (ND=1/2 LOD). Statistical processing was carried out by means of the software package SPSS Statistics 20.0. The level of significance was considered in a probability lower than 0.05 ($p<0.05$). To evaluate significant differences between groups, the Levene test was applied to verify the equality of variances. Further, ANOVA or Kruskal Wallis test were applied depending on whether data followed a normal distribution or not. The Toxic Equivalents were calculated by using the most updated WHO-TEFs [9].

Results and discussion:

The mean levels of the 17 most toxic PCDD/F congeners, as well as the total concentrations (in WHO-TEQ), in the samples of air, vegetation, and soil collected in December 2010 and November 2014 around the cement plant, are summarized in Table 2.

Table 2. PCDD/F levels in air (pg/m^3), vegetation (ng/kg) and soil (ng/kg) around the cement plant in December 2010 and November 2014, after fuel substitution.

	Air *(n=4)*				**Vegetation** *(n=7)*				**Soil** *(n=7)*			
	December 2010		**November 2014**		**December 2010**		**November 2014**		**December 2010**		**November 2014**	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
2,3,7,8-TCDD	0.003	0.002	0.001	0.001	0.03	0.02	0.02	0.03	0.04	0.03	0.05	0.06
1,2,3,7,8-PeCDD	0.007	0.003	0.005	0.003	0.05	0.02	0.04	0.04	0.16	0.12	0.15	0.13
1,2,3,4,7,8-HxCDD	0.008	0.004	0.005	0.003	0.06	0.04	0.05	0.07	0.30	0.31	0.22	0.26
1,2,3,6,7,8-HxCDD	0.012	0.004	0.014	0.010	0.06	0.03	0.05	0.07	0.80	0.71	0.55	0.66
1,2,3,7,8,9-HxCDD	0.011	0.004	0.013	0.010	0.06	0.04	0.03	0.04	0.57	0.55	0.55	0.59
1,2,3,4,6,7,8-HpCDD	0.125	0.034	0.077	0.057	0.70	0.69	0.28	0.18	20.0	17.8	12.0	14.8
OCDD	0.247	0.044	0.142	0.102	2.79	3.13	1.66	1.87	114	95.5	87.7	128
2,3,7,8-TCDF	0.016	0.010	0.016	0.011	0.32	0.22	0.55	0.80	0.37	0.35	1.05	0.67
1,2,3,7,8-PeCDF	0.016	0.012	0.012	0.007	0.13	0.06	0.30	0.41	0.39	0.27	0.31	0.23
2,3,4,7,8-PeCDF	0.028	0.018	0.024	0.013	0.11	0.04	0.19	0.20	0.55	0.73	0.48	0.53
1,2,3,4,7,8-HxCDF	0.025	0.018	0.024	0.015	0.11	0.05	0.14	0.15	0.81	0.93	1.52	2.08
1,2,3,6,7,8-HxCDF	0.018	0.013	0.021	0.013	0.08	0.03	0.08	0.05	0.67	0.94	0.59	0.81
1,2,3,7,8,9-HxCDF	0.002	0.001	0.002	0.001	<0.03		0.02	0.02	0.08	0.07	0.06	0.06
2,3,4,6,7,8-HxCDF	0.022	0.016	0.027	0.018	0.11	0.05	0.06	0.02	1.12	1.89	1.02	1.82
1,2,3,4,6,7,8-HpCDF	0.061	0.042	0.074	0.048	0.64	0.49	0.22	0.15	16.8	11.5	5.35	7.55
1,2,3,4,7,8,9-HpCDF	0.007	0.007	0.012	0.008	0.04	0.03	0.04	0.02	0.89	1.21	0.55	0.98
OCDF	0.040	0.029	0.050	0.033	0.59	0.51	0.30	0.23	14.4	10.7	5.77	9.41
WHO-TEQ	**0.032**	**0.019**	**0.031**	**0.019**	**0.21**	**0.07**	**0.24**	**0.18**	**1.27**	**1.18**	**1.11**	**1.31**

SD: Standard deviation.

A higher contribution of the high-chlorinated (hepta- and octa-) PCDD/F congeners was observed. However, the total PCDD/F concentrations were similar in both sampling periods (2010 and 2014), in each one of the 3

environmental monitors. Airborne mean levels of PCDD/Fs were 0.03 pg WHO-TEQ/m^3 in December 2010 and November 2014. Similarly, very similar concentrations were registered for vegetation (0.21 vs. 0.24 ng WHO-TEQ/kg) and soil (1.27 vs. 1.11 ng WHO-TEQ/kg).

The temporal trends of the mean PCDD/F concentrations in samples of air, vegetation and soil collected around the cement plant, are depicted in Figure 1. A slight, non-significant ($p<0.05$) increase of the soil concentrations of PCDD/Fs was found between 2008 and 2014, following a similar trend to that observed in air. In contrast, PCDD/F levels in vegetation remained constant since the baseline (November 2008) study. Exceptionally, significantly lower concentrations of PCDD/Fs ($p<0.05$) were found in May 2009 in air and vegetation, while no changes were noted in the soil matrix. Therefore, a clear seasonal trend was detected between warm (May) and cold (November and December) studies in air and vegetation. Soil is a long-term monitor capable to register environmental levels for long periods of time, while air and vegetation are more desirable to detect seasonal/point variations.

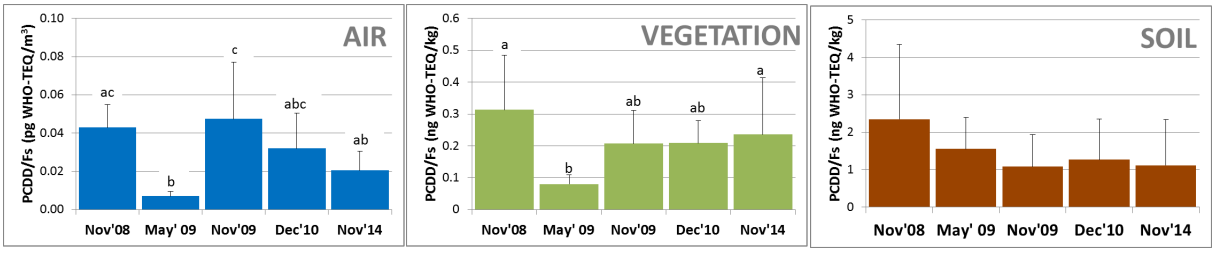

Figure 1. Temporal evolution of PCDD/Fs in samples of air, vegetation and soil around the cement plant.

When comparing the environmental burdens of PCDD/Fs before (November 2008, May 2009 and November 2009) and after (December 2010 and November 2014) the alternative fuel implementation, no significant differences were noted in any of the environmental monitors (air, vegetation, or soil). In fact, 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD were the only congeners which significantly decreased, while no differences in the levels of the 17 toxic PCDD/F congeners were observed in either soil or vegetation.

On the basis of the concentrations in soil and air, the exposure to PCDD/Fs for the local population was calculated. Three different direct exposure pathways were considered: soil and dust ingestion, soil dermal absorption, and air inhalation. The total exposure before the alternative fuel implementation was $1.93 \cdot 10^{-5}$, $6.63 \cdot 10^{-6}$ and $1.65 \cdot 10^{-5}$ ng WHO-TEQ/kg·day in November 2008, May, and 2009, respectively. In turn, a slight reduction of the PCDD/F exposure was noted when alternative fuel was used, with total values of $1.29 \cdot 10^{-5}$ and $9.21 \cdot 10^{-6}$ ng WHO-TEQ/kg·day in December 2010 and November 2014, respectively. The inhalation was the main exposure route, with a contribution of 61%-79%. Because of the low air levels, inhalation only contributed 28% in the study performed in May 2009. In any case, the environmental exposure to PCDD/Fs was clearly lower than the dietary intake of PCDD/Fs estimated for the Catalan population[10] ($6 \cdot 10^{-4}$ ng WHO-TEQ/kg·day) in any of the scenarios, being less than 3% of the total (environmental+dietary) exposure.

The non-carcinogenic risks (hazard quotient –HQ-) were estimated to be 0.012, 0.007, 0.006, 0.007, and 0.005 in November 2008, May 2009, November 2009, December 2010, and November 2014, respectively, being far below the threshold limit, set at the unity. Similarly, carcinogenic risks (Figure 2) were also below the Spanish threshold (10^{-5}) and within the range considered as acceptable by international agencies (10^{-6}-10^{-4}). Similarly to PCDD/F levels, no significant differences were observed in the human health risk after the partial replacement of fossil fuel by alternative fuel.

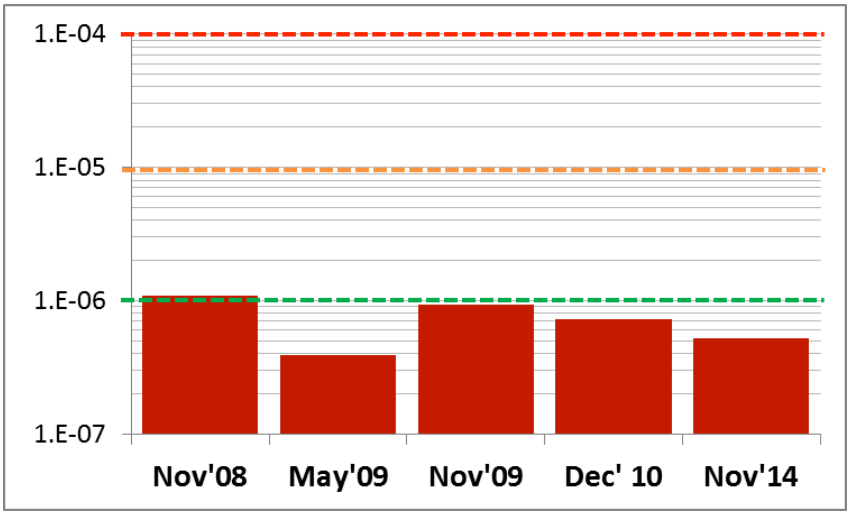

Figure 2. Carcinogenic risk associated to the exposure to PCDD/Fs for the population living near the plant.

In summary, no significant differences were noted in the PCDD/F concentrations in samples of air, vegetation and soil collected near the cement plant, before and after the implementation of alternative fuel. A slight, non-significant decrease was actually found in air and soil, while no increases were observed in vegetation. Furthermore, carcinogenic and non-carcinogenic risks due to the exposure of PCDD/Fs were below the national and international safety limits. Long-term environmental studies have proven to be a more reliable source of knowledge to evaluate the impact of operational changes in the industry, rather than point investigations. However, since this investigation was only focused on PCDD/Fs, potential changes of other combustion-related pollutants, such as PAHs or metals, should be controlled to ensure that the use of alternative fuel does not cause changes of health risks associated to other chemical substances.

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