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ARTICLE

Environmental Levels of PCDD/Fs near Cement Plants in Catalonia, Spain. An Update of Human Health Risks

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ABSTRACT

Cement production is an important industrial activity that generates large amounts of pollutants, including, among others, polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs). These environmental contaminants are persistent and bioaccumulative, potentially causing serious adverse effects on human health, including cancer. The present paper was aimed at providing an update of the environmental concentrations of PCDD/Fs around various cement plants located in Catalonia, Spain. The non-carcinogenic and the carcinogenic risks associated to PCDD/Fs exposure were also assessed for the population living near the facilities. According to the present results, the environmental burdens of PCDD/Fs were highly dependent on the surroundings, rather than the technical specifics characteristics of each facility. Thus, higher concentrations were found near cement plants located in urban areas, where other emission sources (e.g., heavy traffic, domestic heating, etc.) may be present. The surveillance studies showed long-term stable concentrations in air, while PCDD/Fs levels in soil and vegetation were more variable. Although inhalation was the most relevant pathway of environmental exposure, the main uptake of PCDD/Fs occurs -in general- via dietary intake. Cancer risks were higher for people living near cement plants in urban areas than in rural environments, but at levels that are considered as acceptable by international regulations. In turn, the non-carcinogenic risks suggest a low concern, as the hazard quotient was <1. Long-term surveys conducted in Catalan cement plants indicate that these facilities, which are periodically (every two years) monitored, should not be of concern for human health, in terms of PCDD/F exposure.

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Keywords: PCDD/Fs; Cement industry; Environmental monitors; Long-term surveillance; Health risk assessment

1. Introduction

The global cement industry is responsible for approximately a 7% of worldwide greenhouse gases (GHG) emissions, becoming one of the largest contributors. In 2020, China accounted for over 60% of the cement production worldwide, with an overall production of 4.2 billion metric tons in 2021 [1]. Due to the fabrication process, cement production generates large amounts of air pollutants, which include various organic and inorganic pollutants. Among them, polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) have been identified as top-priority chemicals. Although the cement industry is constantly updating the production process, PCDD/Fs may be released in cement kilns [2, 3], as it occurs in any fossil fuel combustion. However, the implementation of new air emission control technologies, such as electrostatic precipitators or bag filters, has allowed to reduce the release of chemicals and dust by cement factories.

PCDD/Fs are characterized by their persistence, bioaccumulation potential and long-range transport capacity [4]. These chemicals can severely affect the human health by causing adverse reproductive and developmental effects, damaging the immune system, or even causing cancer [5]. In fact, the congener 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) was classified as carcinogenic to humans by the International Agency for Research on Cancer [6].

In 2000, our research group started several surveillance programs in all the cement plants located in Catalonia (Spain) in order to assess the impact of the emissions of PCDD/Fs in surrounding areas. Since then, a number of sampling campaigns have been carried out to evaluate the temporal trend on the levels of these compounds [7–13]. These surveillance programs were initiated just before the facilities started to partially substitute conventional fossil fuels by alternative fuels, such as sewage sludge or refuse derived fuel (RDF). This strategy is generally used to reduce great part of CO_2 emissions [14, 15], while collateral benefits include economic advantages like saving fossil fuels or cheaper production costs [8, 16, 17].

The present study was aimed at providing an update on the levels of PCDD/Fs in four cement plants located in Catalonia (Spain), from the most recent sampling campaigns conducted in the surroundings of these industries (period 2017–2023). Moreover, the levels of PCDD/Fs from the first monitoring studies—before fuel partial substitution–were considered as baseline to assess any long-term changes of PCDD/Fs environmental concentrations. Furthermore, the carcinogenic and non-carcinogenic risks linked to variations of the PCDD/Fs exposure were also assessed.

2. Methodology

2.1 Study area

Four cement plants located in different areas of Catalonia were included in the current study (**Figure 1**).

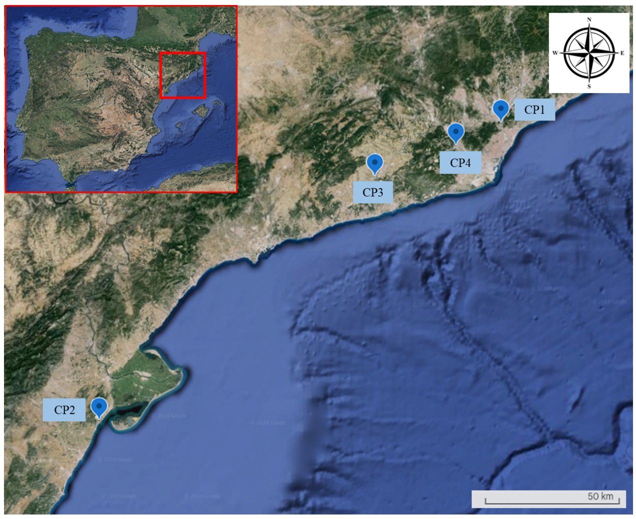

Figure 1. Sampling sites of the four cement plants (CP) located in Catalonia (Spain).

Cement plant 1 (CP1) is in Montcada i Reixac (Barcelona), an area with several industries and two highways with a heavy traffic. In this cement plant, the first sampling campaign was carried out in 2008, while two additional campaigns were conducted before the replacement of 20% of calorific value by sewage sludge (May 2009 and November 2009). Recently, four more sampling campaigns were carried out in March 2017, March 2019, February 2021 and February 2023.

Cement plant 2 (CP2) is in Alcanar (Tarragona), a rural area without important influence of traffic or industries. The first sampling was conducted in 2008, prior to the substitution of conventional fuel by RFD. In this case, the fuel substitution was 15%, reaching around 30% in 2017. Again, the most recent campaigns were done in the months of April of 2017, 2019, 2021 and 2023.

Cement plant 3 (CP3) is in Santa Margarida i Els Monjos (Barcelona), a rural area with almost no impact of heavy traffic or industrial activities. In May 2000 and 2001, two monitoring campaigns were conducted[12, 13]. In 2011, the plant started to use alternative fuels—a mixture of sewage sludge, RFD, animal meals, and agriculture by-products– until an energy replacement of 24%. Recent periodic monitoring campaigns were done in June 2017, May 2019, June 2021 and June 2023.

The last facility here examined, cement plant 4 (CP4) is located in Sant Vicenç dels Horts (Barcelona), an industrial area with two highways with heavy traffic. In 2011, two (January and July) monitoring studies were performed in that area. Afterwards, sewage sludge was introduced as an alternative fuel, with a potential substitution of 25% of the thermal energy requirement. The most recent environmental campaigns were those performed in June of the years 2017, 2019, 2021 and 2023.

2.2 Sampling

For all the studies the same sampling and analytical methodology was followed. To obtain complementary information, samples of different environmental matrices were collected around each cement plant (**Table 1**). Soil and vegetation samples were used as long- and short-term monitors, respectively[18], while air samples combining gas- and particulate phases were also collected. Specific details of the sampling procedure may be retrieved from previous publications[7–11].

Regarding vegetation, 500 g of *Piptatherum paradoxum* L. were obtained by cutting the plants at 10 cm above ground to avoid soil resuspension. Samples were kept in polyethylene bags and transported to the laboratory, where they were dried at room temperature. Afterwards, green leaves were crushed with a grinder and packed in aluminium double foils until analytical determination.

Soil samples of around 500 g consisted of four subsamples collected within an area of 25 m^2. Soils were taken from the upper 5 cm of ground, kept in polyethylene bags, and immediately transported to the laboratory. Subsequently, they were dried at room temperature and sieved through a 2 mm mesh screen to homogenize the particle size.

Air samples were collected for 48 h by using a high-volume active sampler TE-1000 (Tisch Environmental, Cleves, OH, USA), which was properly calibrated before each sampling campaign. Air volumes were within the range 530–650 m^3. Particulate and gas phases were separately collected with a quartz fibre filter (QFF) and a polyurethane foam (PUF), respectively. The foams were previously cleaned with dichloromethane (Merck KGaA, Darmstadt, Germany) in a Soxhlet for 24 h to eliminate any potential contamination. After sample collection, PUFs and QFFs were kept together at −20ºC in an amber glass to avoid any potential photodegradation of the compounds.

2.3 Analytical determination

The analysis of PCDD/Fs was done by high-resolution gas chromatography coupled to high-resolution mass spectrometry (HRGC/HRMS). First, appropriate labelled extraction standards ($13C_{12}$-PCDD/Fs substituted congeners) were added into the samples. Then, an Accelerated Solvent Extraction (DIONEX ASE 300) was carried out by using toluene (Merck KGaA, Darmstadt, Germany). Afterwards, a purification step was conducted in an open column by means of a solid-liquid chromatography with elution through gravity. Two types of columns were used: a) a neutral Merck 60 column, with a mixture of basic, neutral and acid activated silica gel, and b) an ICN Alumina B Super 1 column. Finally, samples were dried completely and reconstituted with an isotope-labelled standard.

The final determination of PCDD/Fs was carried out by a Fisons CE 8000 GC coupled to a VG Autospec Ultima system. Chromatographic separation was performed with a fused silica column (30 m × 0.25 mm internal diameter × 0.15 mm). The detection was done by an electronic impact (EI) mass spectrometer in positive mode (35–45 eV), with selected ion monitoring (SIM) and a resolution of 6000-10000 amu. The quantification was done by comparison with internal standards. Conventional procedures of quality assurance/quality control (QA/QC) were employed. Blank, replicate and reference samples were analysed for every batch of samples, which showed that the method displayed good repeatability[8].

Table 1. Characteristics of the samples collected around the cement plants.

Sampling sites	Sample	Matrix	Coordinates
CP 1	1	Air	X= 41.47212, Y= 2.18602
		Soil and Vegetation	X= 41.47087, Y= 2.18681
	2[a]	Air	X= 41.47654, Y= 2.18728
		Soil and Vegetation	X= 41.47700, Y= 2.19328
	3	Air	X= 41.48427, Y= 2.17717
		Soil and Vegetation	X= 41.48706, Y= 2.16307
	4	Air	X= 41.45564, Y= 2.20189
		Soil and Vegetation	X= 41.45826, Y= 2.19774
	5	Soil and Vegetation	X= 41.46763, Y= 2.18019
	6	Soil and Vegetation	X= 41.51998, Y= 2.13463
	7	Soil and Vegetation	X= 41.46892, Y= 2.09736
	8[b]	Soil and Vegetation	X= 41.47543, Y= 2.17104
CP 2	1[c]	Air	X= 40.59699, Y= 0.56913
		Soil and Vegetation	X= 40.59782, Y= 0.57029
	2	Air	X= 40.57254, Y= 0.54131
		Soil and Vegetation	X= 40.57206, Y= 0.54122
	3	Air	X= 40.55289, Y= 0.52999
		Soil	X= 40.55482, Y= 0.52684
		Vegetation	X= 40.55526, Y= 0.52706
	4	Air	X= 40.53906, Y= 0.47531
		Soil and Vegetation	X= 40.53850, Y= 0.47535
	5	Air	X= 40.62305, Y= 0.58713
		Soil and Vegetation	X= 40.61882, Y= 0.58230
CP 3	1	Air	X= 41.31896, Y= 1.66640
		Soil and Vegetation	X= 41.31896, Y= 1.66712
	2	Soil and Vegetation	X= 41.32922, Y= 1.66397
	3	Air	X= 41.29452, Y= 1.64228
		Soil and Vegetation	X= 41.29395, Y= 1.64344
	4[d]	Air	X= 41.30848, Y= 1.64729
		Soil and Vegetation	X= 41.30772, Y= 1.64753
	5[d]	Soil and Vegetation	X= 41.33402, Y= 1.68218
CP 4	1	Air	X= 41.39891, Y= 2.00179
		Soil and Vegetation	X= 41.39682, Y= 2.00005
	2	Air	X= 41.39058, Y= 2.00809
		Soil and Vegetation	X= 41.38920, Y= 2.00297
	3	Air	X= 41.42067, Y= 1.99635
		Soil and Vegetation	X= 41.41864, Y= 1.99577
	4	Air	X= 41.41175, Y= 2.01595
		Soil	X= 41.41270, Y= 2.01471
		Vegetation	X= 41.41278, Y= 2.01274
	5	Soil and Vegetation	X= 41.38574, Y= 2.01443
	6	Soil and Vegetation	X= 41.46909, Y= 1.97048
	7	Soil and Vegetation	X= 41.40282, Y= 1.96200

[a]new location for the last sampling campaign (2023), located in the same area as the previous one; [b]new sampling point added in 2023; [c]sampling point relocated 200 m away in 2023 due to the impossibility of setting the samplers up; [d]new sampling points added since 2019.

2.4 Health risk assessment

The evaluation of the health risks was performed as previously described[19]. Briefly, air and soil concentrations were used to evaluate the environmental exposure, which was calculated through three different pathways: soil ingestion (Exp$_{ing}$), dermal absorption (Exp$_{derm}$) and air inhalation (Exp$_{inh}$) by applying the following equations:

$$Exp_{ing} = \frac{C_{soil} \times 0.000001 \times EF \times IFP}{BW \times 365} \quad (1)$$

$$Exp_{clerm} = \frac{C_{soil} \times 0.000001 \times AF \times ABS \times EF \times SA}{BW \times 365} \quad (2)$$

$$Exp_{in} = \frac{C_{air} \times IR \times EF}{BW \times 365} \quad (3)$$

The meaning and value of all these parameters are summarized in **Table 2**. After exposure evaluation, the associated carcinogenic and non-carcinogenic risks were calculated by means of the following equations:

$$HQ_{ing/derm} = \frac{Exp_{ing/derm} \times ED}{RfD_o \times AT} \quad (4)$$

$$HQ_{inh} = \frac{EC_{inh}}{RfC} \quad (5)$$

$$CancerRisk_{ing/derm} = \frac{Exp_{ing/derm} \times ED \times SF_o}{AT} \quad (6)$$

$$CancerRisk_{inh} = EC_{inh} \times IUR \quad (7)$$

where EC_{inh} is inhalation exposure concentration (in ng/m^3):

$$EC_{inh} = \frac{C_{air} \times ET \times EF \times ED}{AT \times 365 \times 24} \quad (8)$$

Total carcinogenic risks were calculated by summing the cancer risks of the three exposure pathways (oral ingestion, dermal contact, and air inhalation). In Spain[20], the maximum acceptable value for cancer risks has been set at 10^{-5}, while international standards[3] establish a range between 10^{-6} and 10^{-4}. In turn, the hazard quotient (HQ) was used to assess the non-carcinogenic risks. HQ is defined as the relation between the estimated exposure and the respective reference dose (RfD). HQ values lower than one (HQ < 1) are considered as safe. Total non-carcinogenic risks were also calculated as the sum of the risks associated to the three exposure routes (oral ingestion, dermal contact, and air inhalation).

2.5 Statistical analysis

For the calculation of the concentrations of PCDD/Fs as toxic equivalents (TEQ), toxic equivalency factors (TEF) from the World Health Organization (WHO) were used[21]. PCDD/F congeners with undetected levels were assumed to have a concentration equal to one-half of the limit of detection (LOD). Data analysis was carried out with SPSS v.28. The Levene test was used to compare the homogeneity of the variances. Subsequently, significant differences of the data were computed by an ANOVA (parametric data) or Kruskal-Wallis (non-parametric data) test. The level of significance was set at $p < 0.05$. Outliers were detected by representing boxplots, but only extreme outliers were excluded for data treatment.

3. Results and discussion

3.1 Air

Mean levels of total PCDD/Fs in air samples from the selected cement plants, before fuel substitution and in the last four sampling campaigns (2017–2023), are depicted in **Figure 2**. CP1, located in an urban area, showed generally the highest levels after the partial substitution of fuel, with mean levels ranging from 0.025 to 0.053 pg WHO-TEQ/m3. In contrast, when using 100% of fossil fuel for cement production, the highest levels of PCDD/Fs were found in CP4 (0.071 pg WHO-TEQ/m3), which is also located in an urban area. In turn, CP2 and CP3, both facilities located in rural areas, showed the lowest levels in all the sampling campaigns.

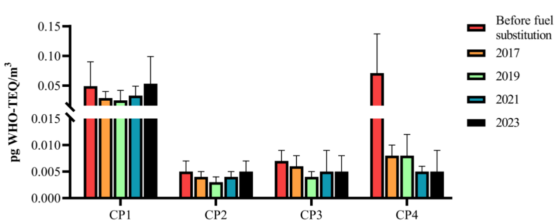

Figure 2. Mean levels (pg WHO-TEQ/m3) of PCDD/Fs in air samples from four cement plants before fuel substitution and the last sampling campaigns (2017–2023).

An individual analysis of the results, before and after the partial replacement of fossil fuel by alternative fuels, indicates the lack of a significant increase of PCDD/F levels in air ($p>0.05$). In CP1, a slight (8%)—non-significant ($p>0.05$)—increase of the mean PCDD/F concentration was observed in the last campaign (2023) compared with the mean of the baseline survey (2008). In addition, a notable (59%), but not significant ($p>0.05$) increase, was found when comparing the two most recent campaigns (0.033 and 0.053 pg WHO-TEQ/m^3 in 2021 and 2023, respectively).

CP2 data indicate that levels before and after the partial substitution of fuel remained constant with time, showing only a very slight decrease (-3%) between the first (2008) and last (2023) surveys. In turn, an increase of 29% was found when comparing the changes in the period 2021-2023. Nonetheless, none of the differences was statistically significant ($p>0.05$).

Regarding CP3, there is not a full set of results on PCDD/Fs because no air sampling was performed in the two first monitoring campaigns (2000 and 2001). Therefore, air PCDD/Fs concentrations from the survey conducted in 2011 were used as reference values. A non-significant reduction of 30% on the levels of PCDD/Fs was observed between 2011 and 2023 ($p>0.05$), while a slight increase (4%) was noted between 2021 and 2023.

Table 2. Parameters used for human exposure and health risk assessment.

Parameter	Description	Value	Units
EF	Exposure Frequency	350	days·year^{-1}
IFP	Soil ingestion rate	114	mg·day^{-1}
BW	Body weight	70	kg
AF	Adherence Factor soil to skin	1	mg·cm^{-2}
ABS	Dermal Absorption from soil	Chemical Specific	unitless
SA	Surface Area	4050	cm^{2}·day^{-1}
ET	Exposure Time	24	hours·day^{-1}
AT	Averaging Time	70*/25**	years
ED	Exposure Duration	30	years
IR	Inhalation rate	20	m^{3}·day^{-1}
RfDo	Reference Dose	Chemical Specific	mg·kg^{-1}·day^{-1}
RfC	Reference Concentration	Chemical Specific	mg·m^{-3}
SFo	Oral Slope Factor	Chemical Specific	mg^{-1}·kg·day
IUR	Inhalation Unit Risk	Chemical Specific	µg^{-1}·m^{3}
	Unit conversion factor	365	days·year^{-1}
	Unit conversion factor	24	hours·day^{-1}
	Unit conversion factor	0.000001	kg·mg^{-1}
Csoil	Mean concentration in soil	Site-specific	mg·kg^{-1}
Cair	Mean concentration in air	Site-specific	mg·m^{-3}

Finally, there was a substantial reduction (−93%) on the concentrations of PCDD/Fs around CP4, when the first and last monitoring studies were compared (2011 vs. 2023). In contrast, values remained very similar in the most recent surveys. In all cases, the differences among campaigns did not reach the level of statistical significance (p>0.05).

In general, the concentrations of PCDD/Fs remained stable in the long-term surveillance of the four cement plants, with the only exception of CP4, where a notable decrease was registered after the partial replacement of fossil fuel by alternative fuels. The analysis of the four surveys indicates that the operational change of fuel did not derive in changes in the emission of PCDD/Fs.

3.2 Soil

The average levels of PCDD/Fs in soil samples collected around the cement plants are depicted in **Figure 3**. Comparing the environmental data among the facilities, CP4 showed the highest levels of PCDD/Fs, specifically in the samplings conducted in 2019 and 2021 (3.23 and 2.62 ng WHO-TEQ/kg, respectively). As for air, the two cement plants located in an urban area (CP1 and CP4) presented relatively higher mean levels of PCDD/Fs than those operating within rural environments, mainly due to the impact of the traffic and other nearby industries.

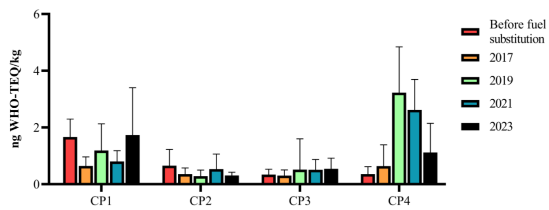

Figure 3. Mean levels (ng WHO-TEQ/kg) of PCDD/Fs in soil samples from four cement plants before fuel substitution and the last sampling campaigns (2017–2023).

PCDD/Fs soil concentrations around CP1 varied through time, with higher levels in 2008 (1.66 ng WHO-TEQ/kg) and 2023 (1.73 ng WHO-TEQ/kg), and lower levels in 2017 (0.64 ng WHO-TEQ/kg) and 2021 (0.8 ng WHO-TEQ/kg). According to the results from the last monitoring campaign, there was an increase of PCDD/Fs levels when comparing the values of 2023 with those registered in precedent studies, with percentages of 4% and 116% compared to surveys performed in 2008 and 2021, respectively. However, none of these rises were statistically significant (p>0.05).

Regarding CP2, the mean PCDD/Fs levels in soils found through time remained more or less constant, especially after the partial replacement of fuel. The highest values were actually found in the baseline study (0.653 ng WHO-TEQ/kg), while those observed in the last study (2023) were reduced in 53%. A similar profile was found near CP3, which is also located in a rural area. However, in this case, a 61% non-significant increase of soil PCDD/Fs levels were found between the first and last samplings ($p>0.05$), probably because of the addition of two new sampling points in 2019, which resulted in an increase of the variability.

Finally, CP4 showed a high variation of PCDD/Fs concentrations in soil among the sampling campaigns. Significant increases of PCDD/Fs levels were registered in the periods 2011-2021 and 2017–2021 (631% and 310%, respectively; $p<0.05$), while a significant decrease (−57%; $p<0.05$) was found between 2021 and 2023. Since the PCDD/Fs concentrations decreased in the last campaign, it is plausible to conclude that the high levels registered in 2021 could be the result of an episode of point pollution in the area.

In general, soils are a good monitor to assess the long-term contamination; therefore, temporal variations usually reflect the heterogeneity of environmental conditions around the different cement factories. It includes the presence of other potential emission sources, including traffic and other industries.

The number of scientific studies aimed at assessing the soil burdens of PCDD/Fs near cement factories is very limited. Notwithstanding, our data can be compared with those published Han et al.[22], who observed a mean PCDD/Fs concentration of 0.177 ng WHO-TEQ (range: 0.073–0.418 ng WHO-TEQ) in soils around the first cement kiln co-processing municipal wastes in northwest China.

3.3 Vegetation

Mean levels of PCDD/Fs in vegetation samples collected around the four cement plants are depicted in **Figure 4**. The highest PCDD/F levels were again found in the areas surrounding the facilities located in urban areas, both CP4 (0.646, 0.547 and 0.506 ng WHO-TEQ/kg in 2011, 2017 and 2021, respectively) and CP1 (0.530 ng WHO-TEQ/kg in 2019).

With respect to CP1, a 35% reduction of PCDD/Fs levels in vegetation was noted between the sampling conducted before fuel substitution (2008–2009) and the last sampling (2023). In fact, the concentrations in 2023 were the lowest of the temporal series, with the highest reduction being noted when compared to the 2019 campaign (75%). Regarding CP2, most of the sampling campaigns presented similar levels of PCDD/Fs in vegetation through time, with a range of 0.067-0.093 ng WHO-TEQ/kg. Notwithstanding, there was an increase in these levels in 2021 (0.279 ng WHO-TEQ/kg), being the highest of the series. In 2023, a non-significant reduction (66%; $p>0.05$) in the levels of PCDD/Fs, in comparison to those of the baseline survey, was noted.

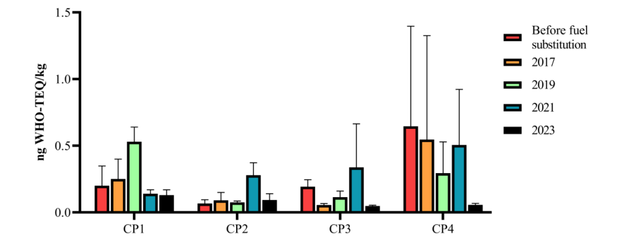

Figure 4. Mean levels (ng WHO-TEQ/kg) of PCDD/Fs in vegetation samples from four cement plants before fuel substitution and the last sampling campaigns (2017–2023).

For CP3, a high variability throughout the campaigns was observed, with the lowest value detected in 2023 (0.048 ng WHO-TEQ/kg), and the highest in 2021 (0.338 ng WHO-TEQ/kg). The difference between these two campaigns was notable (−86%) but not statistically significant ($p>0.05$). Moreover, there was also a 75% reduction in the levels of PCDD/Fs when comparing the monitoring studies according to the fuel use. For CP4, there was a substantial reduction (−91%) of PCDD/Fs concentrations before (0.646 ng WHO-TEQ/kg) and after (0.056 ng WHO-TEQ/kg) the partial replacement of fossil fuel by alternative fuels. Nevertheless, because of the low number of samples, the difference did not reach the level of statistical significance ($p>0.05$).

As for air and soil, the concentrations of PCDD/Fs in vegetation were generally higher in the cement plants located in urban areas (CP1 and CP4) than in rural environments (CP2 and CP3). It highlights the importance of other co-emission sources of PCDD/Fs nearby, including traffic, domestic heating, as well as other industries that could be also emitting PCDD/Fs.

In 2021, our group conducted a review of the monitoring campaigns carried out around several cement plants until 2017[3]. In agreement with the results of the present review, no significant differences were found between sampling studies ($p>0.05$), concluding that emissions of PCDD/Fs by cement plants in Catalonia should not mean significant negative effects, either on the environment or the human health. However, some differences on the environmental burdens of PCDD/Fs were observed when the different cement facilities are compared. Basically, higher levels of PCDD/Fs were observed near factories located in urban areas (CP1 and CP4), contrasting with those operating within rural environments (CP2 and CP3). This is a clear indication that traffic is a key factor when assessing the impact by PCDD/Fs emissions. Moreover, although all the plants work by following the best available techniques (BAT) according to the Industrial Emissions Directive (IED), the different operational conditions in each factory may be an additional factor to be considered.

3.4 Health risk assessment

Figure 5 shows the environmental exposure to PCDD/Fs through different routes, namely oral ingestion, dermal contact and inhalation, for each of the four evaluated cement plants. For CP1, inhalation was the most important contributor for the exposure, with values ranging from 64% to 79%. For CP2, the inhalation was also the most important exposure pathway, but with lower percentages (36%–56%). In this case, dermal contact was the second major contributor, with a contribution percentage of 22%–32%. Similarly, inhalation was also the major contributor to the exposure in CP3, with a contribution between 38% and 64%. Surprisingly, for CP4 the inhalation pathway contributed up to 94% of the exposure in the campaign conducted before fuel substitution. Afterwards, dermal contact was the major contributor to human exposure in most campaigns performed in the period 2019–2023, with values between 36% and 44%.

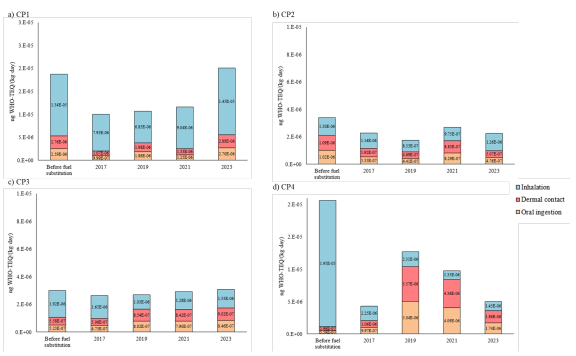

Figure 5. Environmental exposure to PCDD/Fs (ng WHO-TEQ/kg/day) through oral ingestion, dermal contact and inhalation for the adult population living near four cement plants in Catalonia (Spain).

It is well known that diet is the main exposure pathway to PCDD/Fs, with values above 95% of total exposure[23, 24]. According to González et al.[25], the dietary intake of PCDD/Fs in Catalonia is estimated 1.22·10-4 ng WHO-TEQ/kg/day. Considering this value, the environmental exposure of the population living in the surroundings of a cement plant in Catalonia would be between 1.4% and 14.5% of the total exposure (**Table 3**). For CP1, the environmental exposure contributed 13.3% of the total exposure in the monitoring study performed before fuel substitution, while in the campaigns between 2017 and 2021, it was reduced to 7.58-8.70%. In the last monitoring study (2023), the contribution of the environmental exposure increased up to 14.2%. For CP2 and CP3, both facilities located in rural environments, the contribution of the environmental exposure to the total exposure to PCDD/Fs was low, with values ranging between 1.40 and 2.70%. Finally, for CP4, the environmental exposure contributed up to 14.5% of the total exposure to PCDD/Fs. However, in the last campaign it was reduced to 3.97%, suggesting a decrease in the environmental contamination in that area.

Non-carcinogenic risks, evaluated as HQs, and carcinogenic risks in each of the cement plants in every sampling campaign are summarized in **Table 4**. The highest HQ corresponded to the population living near the CP4 in 2019 (0.015), followed by 2021 (0.012). All the HQ values were lower than one, suggesting little concern for the non-carcinogenic risks. In turn, higher carcinogenic risks were found in the campaign conducted before the fuel substitution in CP1 and CP4 (1.06·10-6 and 1.18·10-6, respectively). However, all the values were lower than 10-6, being therefore acceptable according to international regulations. Furthermore, risk values were similar to those estimated for populations living in other areas in Catalonia, away from the impact of cement factories[26].

Importantly, it cannot be generalized that cement plants do not pose any health risks for the population living nearby, as conclusions are different on a case-by-case scenarios. While some studies conclude that there are no potential health risks for the population living near these facilities due to PCDD/Fs exposure[22], or the health risks are within the legal standards[8–11], other investigations point out a different outcome. For instance, in another recent study carried out in Valencia region (Spain) a slightly higher cancer risk

Table 3. Percentage of the contribution to total exposure of the environmental and the dietary pathways for the population living in the vicinity of four cement plants in Catalonia (Spain).

Cement Plant	Exposure pathway	Before fuel substitution	2017	2019	2021	2023
1	Environmental	13.3	7.58	8.10	8.70	14.2
	Dietary	86.7	92.4	91.9	91.3	85.8
2	Environmental	2.70	1.80	1.40	2.20	1.80
	Dietary	97.3	98.2	98.6	97.8	98.2
3	Environmental	2.40	2.11	2.16	2.33	2.46
	Dietary	97.6	97.9	97.8	97.7	97.5
4	Environmental	14.5	3.41	9.44	7.44	3.97
	Dietary	85.5	96.6	90.6	92.6	96.0

Table 4. Non-carcinogenic and carcinogenic risks associated to the oral ingestion, dermal contact and inhalation for the population around cement plants in Catalonia (Spain).

Cement Plant	Before fuel substitution	2017	2019	2021	2023
		Cancer risk			
1	1.06E-06	5.68E-07	6.04E-07	6.59E-07	1.14E-06
2	1.92E-07	1.29E-07	9.82E-08	1.51E-07	1.27E-07
3	1.70E-07	1.49E-07	1.51E-07	1.64E-07	1.73E-07
4	1.18E-06	2.43E-07	7.11E-07	5.48E-07	2.83E-07
		Hazard Quotient			
1	0.009	0.004	0.006	0.004	0.009
2	0.003	0.002	0.001	0.003	0.002
3	0.002	0.002	0.002	0.002	0.003
4	0.003	0.003	0.015	0.012	0.005

(>10-6) was detected for some sampling sites near a cement plant [27]. Furthermore, the exposure to other co-pollutants, like fine particulate matter, maybe associated to health risks to adults and children, despite the calculated risks are still acceptable [28].

In recent years, the cement industry has decreased its carbon footprint, derived from their reduction of GHG emissions. This has been achieved through the implementation of sustainable practices and novel technologies, including the use of alternative fuels and the carbon capture, utilization, and storage (CCUS). However, operators and regulators should assure that the application of these new technologies does not imply the release of other chemicals. The present review confirms that the partial use of alternative fuels instead of fossil fuels does not means an increase of PCDD/Fs emissions. Future studies must be targeted to evaluate the effect on other co-pollutants.

4. Conclusions

An update of the levels of PCDD/Fs in the vicinity of various cement plants located in Catalonia (Spain) is here presented. In general, higher environmental concentrations of PCDD/Fs were found near CP1 and CP4, both located in urban areas with a high traffic density of traffic and the presence of other industries. Regarding air samples, PCDD/Fs remained stable at long-term surveillances, except for the non-significant substantial decrease of PCDD/Fs levels in CP4 between the last campaign (2023) and the sampling carried out before the fuel substitution ($p>0.05$).

For soils, a higher variability among sampling periods was noted, especially in the cement plants located in urban environments. It must be considered that soils are good long-term monitors and, therefore, these temporal variations reflect the heterogeneity of geographic and demographic characteristics of the cement plants. Regarding vegetation, a certain variation in PCDD/Fs levels among campaigns was observed, but the last campaign (2023) showed the lowest levels around the four cement plants here examined.

With respect to human health risks, air inhalation was the main contributor to the total environmental exposure, with the only exception of CP4, for which dermal contact was the most important exposure route (36-44%). However, when considering the dietary intake, environmental exposure to PCDD/Fs would contribute a 14.5% of the total exposure in the worst-case scenario. The assessment of the non-carcinogenic and the carcinogenic risks was conducted for all the cement plants and all the sampling periods. In all cases, the HQs were below one, while carcinogenic values were lower than the range considered as acceptable by international regulations (10-6 and 10-4).

Summing up, the partial use of alternative fuels to replace fossil fuel was not associated to an incremental environmental impact by PCDD/Fs near the evaluated cement plants. It confirms that this sustainable practice is not only beneficial in terms of saving CO_2 emissions but also it does not mean health risks for the population living nearby. However, although no significant variations of PCDD/Fs levels were found with time in the three environmental matrices here monitored, it is basic to keep conducting periodical samplings around cement plants to ensure that the PCDD/Fs concentrations remain at low levels, with no significant effects on human health. Moreover, future investigations must focus on other co-pollutants and the effect of these chemical mixtures.

Author Contributions

Neus González: Formal analysis; Investigation; Data curation; Writing—Original draft. Joaquim Rovira: Investigation; Data curation; Writing—Review & Editing. Martí Nadal: Conceptualization; Data curation; Supervision; Writing—Review & Editing. José L. Domingo: Funding acquisition; Writing—Review & Editing.

Conflict of Interest

There are no conflicts of interest.

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