Characterization of PCDD/F and dl-PCB levels in air in Gipuzkoa (Basque Country, Spain)

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ABSTRACT

This research examines the levels and trends of pollutants, specifically 17 congeners of PCDD/Fs and 12 dl-PCBs, in the air measured in the province of Gipuzkoa (Basque Country, Spain). The study used PCDD/Fs, dl-PCB, and the sum of dioxin-like compounds as separate response variables. A total of 113 air samples were collected and analyzed using the method described in the European Standard (EN-1948:2006) from two industrial areas. The results were analyzed using non-parametric test to assess the variability of these pollutants based on different factors (year, season and day of the week) and General Linear Models to assess the weight of each factor. The study found that the toxic equivalents (TEQs) for PCDD/Fs were 12.29 fg TEQm^{-3} and for dl-PCBs were 1.63 fg TEQm^{-3}, which were in a similar range or lower than those observed in other national and international studies in industrial areas. The results showed temporal variations, with higher levels of PCDD/Fs in autumn-winter than in spring-summer and higher levels of PCDD/Fs and dl-PCBs during weekdays than on weekends. The industrial area where the energy recovery plant (ERP) will be located had higher levels of air pollutants due to the presence of two PCDD/Fs emitting industries nearby, as indicated by the Spanish Registry of Polluting Emission Sources. Both industrial areas showed similar profiles of PCDD/Fs and dl-PCBs, with the PCDD/F profiles dominated by OCDD, 1,2,3,4,6,7,8-HpCDD, and 1,2,3,4,6,7,8-HpCDF in terms of concentrations and 1,2,3,7,8-PeCDD, 2,3,4,7,8-PeCDF, and 2,3,7,8-TCDD in terms of TEQs. The dl-PCB profiles were dominated by PCB 118, PCB 105, and PCB 77 in terms of concentrations and PCB 126 in terms of TEQs. The findings of this study can serve as an indicator of the potential impact of ERP on the health of the resident population and the environment.

1. Introduction

Polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and dioxin-like polychlorinated biphenyls (dl-PCBs) are persistent organic pollutants (POPs) that were among the first twelve compounds listed in the Stockholm Convention (SC) on persistent organic pollutants (UNEP, 2001). Of the 210 PCDD/F congeners, 17 (seven dioxins and ten furans) have the highest toxicity, which is mediated through the aryl hydrocarbon receptor (AhR), a cytosolic protein receptor with a high affinity for 2,3,7,8-substituted PCDD/Fs and some non-ortho-substituted PCBs (Zhang et al., 2021). Similarly, 12 PCB congeners (four non-ortho substituted and eight mono-ortho substituted) have a similar biological activity as dioxins, and they are referred to as dioxin-like PCBs. Their individual toxicity is commonly assessed using the toxic equivalency factor (TEF) approach (Van den Berg et al., 2006).

PCDD/Fs are typically produced by incomplete combustion of organic materials, and the main sources are industries that use thermal or chemical processes, such as waste incineration, foundries, refineries, and chemical bleaching industries that use active chlorine (Antunes et al., 2012). However, there are other diffuse sources that emit these pollutants, such as vehicle emissions, domestic coal/wood combustion, and natural fires (Kaleka and Thind, 2020). Regarding PCBs, including dl-PCBs, the main sources are technical mixtures used as cooling/isolation fluid in transformers, hydraulic systems, gas turbines, and vacuum pumps, or as fire retardants in electric devices. They are also used as plasticizers in adhesives, textiles, surface coatings, and sealants (Trinh and Chang, 2018). In western countries, PCBs were banned in the 1980s, and therefore, nowadays, the most relevant sources result from volatilization and leaching from uncontrolled landfills. However, the incineration of materials that contain PCBs also releases these pollutants into the air. Moreover, several authors have concluded that the formation of PCBs during thermal processes has similar formation mechanisms as PCDD/Fs (Abad et al., 2006; Weber et al., 2001; Brubaker and Hites, 1998).

PCDD/Fs and dl-PCBs are a major public concern due to their toxicity to humans, leading to serious health issues such as cancer, immunological, teratogenic, reproductive and neuroendocrine alterations (Furue et al., 2021). These persistent organic pollutants accumulate in soils, sediments, and biota, and their slow degradation and biomagnification in the food chain make them a long-term environmental threat (Jeno et al., 2021). Air concentrations of these contaminants vary with emission sources, atmospheric conditions, and seasonal changes (Lonatti et al., 2007; Valenzuela et al., 2022; Muñoz-Arnanz et al., 2018), making monitoring of dioxins, furans, and PCBs in the air important for establishing baseline levels, detecting temporal changes, and understanding their regional and global transport.

In the 1980s and early 1990s, waste incinerators were identified as the primary source of dioxins (Burns et al., 2010). However, it is important to distinguish between older and modern facilities, as the latter are equipped with flue gas control technology and are more effective in controlling dioxin emissions (Giugliano et al., 2002; Düwel et al., 1991; Nzihou et al., 2012; Parera et al., 2013). Recent studies in Bizkaia-Basque Country and Girona (Spain) have shown no increase in levels of compounds with dioxin-like activity in populations living near modern incinerators (Zubero et al., 2017; Rovira et al., 2018).

The problem of urban waste management in Gipuzkoa (Basque Country, Spain) and the waste framework directive of the EU has led to the construction of an energy recovery plant (EPR). The construction of the plant marked the beginning of an air quality monitoring and control program aimed at assessing the levels of background contamination prior to the commissioning of the urban waste incinerator. In this way, from November 2017 to February 2020, a monitoring program was carried out with the objective of evaluating the influence of the EPR in the air quality.

The objective of this research was to characterize the concentrations of PCDD/Fs and dl-PCBs in the air at two selected zones in Gipuzkoa, including an area near the EPR under construction and another area with similar industrial characteristics located 29 km away. This study is significant because it will provide reference data for future controls of incineration activity and may be used to evaluate the risk of exposure to these substances in the population due to their presence in the environment. Notably, only one other study has monitored dioxin levels in environments where a EPR plant is going to be located (Caserini et al., 2004), making this study particularly relevant for understanding the potential impact of the EPR in the environment and public health.

2. Materials and methods

2.1. Study area

The study was conducted in two industrial environments in the

province of Gipuzkoa (Basque Country, Spain). In order to measure the background contamination level of exposure to the population, volume air samplers were placed in urban areas that were representative of immission levels and far from the industrial emission sources. The area where the ERP was under construction, named "Zone 1", had industries involved in the production and transformation of aluminum, steel, and cast iron. "Zone 2", the control zone, located 28 km away from the ERP (Fig. 1), was chosen due to its similar industrial characteristics and presence of industries emitting PCDD/Fs, with an important steel industry. Both areas had narrow valleys with little aerial dispersion and intense traffic (Lertxundi et al., 2010), and were similar in terms of population and presence of sources of industrial pollution, according to the Spanish Registry of Polluting Emitting Sources (PRTR-Spain).

2.2. Sampling procedures

Airborne PCDD/Fs and dl-PCBs were sampled using high volume air samplers (DIGITEL, Switzerland), with gas phase and particle sampling conducted using polyurethane foam cylinders (PUF, 10 cm diameter, 10 cm height, and 0.03 g cm-3 density; TechnoSpec, Spain) and circular glass fiber filters (GFF, 15 cm diameter; 0.26 mm thickness; GF/A grade; Whatman, UK), respectively. Two samplers were placed twice a month for 3–4 days on weekdays and for 2 days on weekends. In Zone 1, one from November 2017 to February 2020, and the other from November 2017 to February 2018. One sampler was placed in Zone 2 from June 2018 to February 2020. Sampling for baseline levels of PCDD/Fs and dl-PCBs ended in February 2020 due to the start of incinerator operations. Due to significant differences in pollutant values between the two samplers in Zone 1, the worst-case scenario sampler was selected as the sampling point from February 2018 onwards. A total of 113 samples were collected, with 63 from Zone 1 and 50 from Zone 2. Seasonal variability was recorded with 41 samples collected in spring-summer (April to September) and 72 in autumn-winter (October to March). In addition, 66 samples were collected on weekdays (Monday-Friday) and 47 on weekends (Saturday-Sunday) to observe the effect of industrial activity on PCDD/Fs concentration in the air.

2.3. Chemical analysis

The analytical methodology in this study followed the requirements described in the European Standard EN-1948:2006 method and is described in detail elsewhere (Muñoz-Arnanz et al., 2018). In brief, PUF and filters were spiked with known amounts of 13C-labelled standard solutions of dl-PCBs and PCDD/Fs (P48–W-ES and EN1948-ES solutions from Wellington Laboratories, Guelph, ON, Canada), prior to Soxhlet extraction, which was carried out with ~200 ml of n-hexane: dichloromethane (9:1) for 24 h. A subsequent cleaning was achieved by means of the DEXTech + automated sample preparation system (LCTech GmbH, Dorfen, Germany) that rendered to fractions: one with the bulk of mono-ortho PCBs and another one with the non-ortho PCBs and PCDD/Fs. Both fractions were evaporated with a TurboVap® system to around 1 mL, transferred to vials, and blown down to nearly dryness using a flow of nitrogen gas. A few microliters of ^{13}C-labelled PCDD/Fs and PCBs (solutions EN-1948-IS and P48-RS, respectively, from Wellington Laboratories, Guelph, ON, Canada) were added to the vials, intended as injection standards before undergoing instrumental analysis. 17 PCDD/Fs and 12 dl-PCB congeners were quantified. The 17 targeted PCDD and PCDF congeners were: 2,3,7,8-TCDD; 1,2,3,7, 8-PeCDD; 1,2,3,4,7,8-HxCDD; 1,2,3,6,7,8-HxCDD; 1,2,3,7,8,9-HxCDD; 1,2,3,4,6,7,8-HpCDD; OCDD; 2,3,7,8-TCDF; 1,2,3,7,8-PeCDF; 2,3,4,7, 8-PeCDF; 1,2,3,4,7,8-HxCDF; 1,2,3,6,7,8-HxCDF; 2,3,4,6,7,8-HxCDF; 1,2,3,7,8,9-HxCDF; 1,2,3,4,6,7,8-HpCDF; 1,2,3,4,7,8,9-HpCDF; OCDF. The 12 dl-PCBs were: 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, and 189. The congeners were quantified by GC-HRMS on a Trace GC Ultra gas chromatograph (Thermo Fisher Scientific, Milan, Italy) coupled to a high-resolution mass spectrometer (DFS, Thermo Fisher
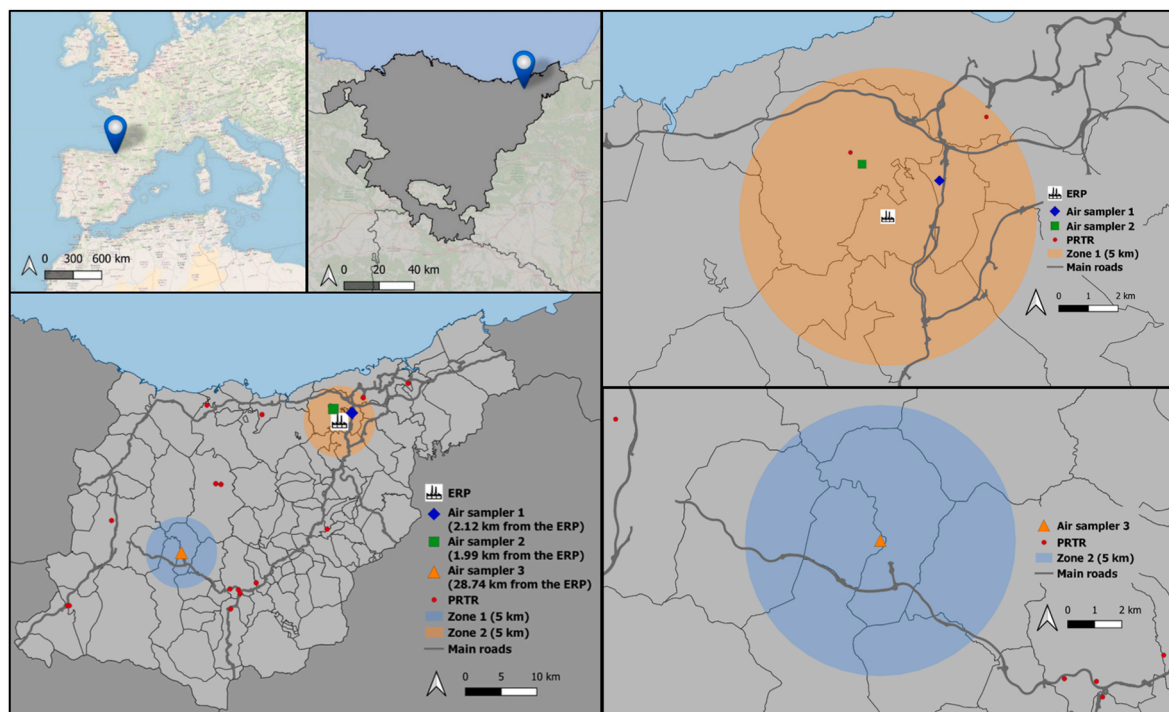
Fig. 1. Map of the studied area.

Scientific, Bremen, Germany). Positive electron ionization (EI+) was used by operating in the selected ion monitoring (SIM) mode at a resolving power of 10,000 at 10% valley. Quantification was performed using the isotopic dilution technique. The QA/QC protocols applied were in accordance to the European Standard EN-1948:2006 method, including the analysis of a laboratory blank within each batch of five samples covering all steps of the analytical treatment. Throughout the analytical procedure, exposure to UV light was minimized.

2.4. Data treatment and statistical analysis

The TEQ values (fg m^{-3}) of the 17 PCDD/F and 12 dl-PCB congeners were calculated based on their toxic equivalency factors (TEFs) derived from the 2005 World Health Organization (WHO) system (Van den Berg et al., 2006). The arithmetic means (CI 95%), geometric means (GM) (CI 95%), and medians with the 25th and 75th percentiles of the PCDD/F and dl-PCB TEQ values, as well as their individual congeners and sums, were determined and presented in Supplementary Material Table S1. For concentrations below the limit of determination (LOD), upper bound values were used. An atypical value or outlier was detected in Zone 1 during the weekend of June 23–24, 2018, which coincided with the night of San Juan, a festive celebration in Spain involving bonfires. The PCDD/F concentration in this sample was 304 fg TEQm^{-3}, which was 3514.4% higher than the average for Zone 1. This outlier was excluded from statistical analyses. Mann-Whitney U test (p < 0.005) were used to compare concentrations between zones, seasons, and weekdays since the data did not have a normal distribution. Composition profiles were created based on the relative contribution (%) of each PCDD/F and dl-PCB congener to the sum of PCDD/Fs ($\sum$PCDD/Fs) and dl-PCBs ($\sum$dl-PCB) in terms of concentrations and TEQ$_{WHO2005}$ values for different years, seasons, weekdays, and zones. General linear models (GLMs) were used to evaluate the influence of sampling year, season, weekday, and zone, with PCDD/Fs, dl-PCBs, and the sum of dioxin-like compounds as separate response variables.

3. Results

3.1. Concentrations of PCDD/Fs and dl-PCBs in air

More than 50% of the samples analyzed contained detectable concentrations of all PCDD/F and dl-PCB congeners except for congeners 2,3,7,8-TCDD and 1,2,3,7,8,9-HxCDF, which were found in a low percentage of samples. Among the 113 air samples analyzed, the range of $\sum$PCDD/Fs in the Gipuzkoa area was 1.33–43.12 fg TEQm^{-3}, with an average of 12.29 fg TEQm^{-3}. The range of $\sum$dl-PCBs was lower, from 0.04 to 9.68 fg TEQm^{-3}, with an average of 1.63 fg TEQm^{-3}. The most abundant PCDD/F congener was 1,2,3,7,8-PeCDD, and the most abundant dl-PCB congener was PCB 126 (Table 1). The sum of all dioxin-like compounds ranged from 1.61 to 45.62 fg TEQm^{-3}, with an average of 13.92 fg TEQm^{-3} and a geometric mean of 10.07 fg TEQm^{-3}. Minimum concentrations of all pollutants were found in zone 2, while maximum values except for PCDFs and PCDD/Fs + dl-PCBs were found in zone 1. However, the mean concentrations of all pollutants were significantly higher in zone 1 ($\sum$PCDDs: 8.3 fg TEQm-3, $\sum$PCDFs: 8.46 fg TEQm-3, $\sum$PCDD/Fs: 16.76 fg TEQm-3, $\sum$dl-PCB: 2.29 fg TEQm-3, and the sum of dioxin-like compounds: 19.05 fg TEQm-3) compared to zone 2 ($\sum$PCDDs: 2.94 fg TEQm-3, $\sum$PCDFs: 3.73 fg TEQm-3, $\sum$PCDD/Fs: 6.66 fg TEQm-3, $\sum$dl-PCB 0.8 fg TEQm-3, the sum of dioxin-like compounds: 7.46 fg TEQm-3) (Table 1).

Regarding temporal variability, there were differences in the minimum and maximum values of all pollutants between the periods 2019–2020, with minimum values being lower and maximum values being higher. However, no temporal changes in the geometric means were observed, except for the case of the furans (in the years 2017–2018: 8.41 fg TEQm^{-3} and in the years 2019–2020: 4.91 fg TEQm^{-3}) (Table 2). Those differences were noted in almost all furan congeners, with 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF and 2,3,4,6,7,8-HxCDF being the most relevant ones.

Concerning seasonal variability, maximum pollutant concentrations were mostly observed in autumn-winter, while minimum concentrations were found in spring-summer. The exception was $\sum$dl-PCBs, where both the minimum and maximum values were found in spring-summer.

Table 1

Minimum (Min) and maximum (Max) values, arithmetic means (CI 95%), geometric means (GM) (CI 95%) and medians with the 25th and 75th percentiles of the sum of PCDD, PCDFs, PCDD/Fs, dl-PCB and PCDD/Fs + dlPCBs TEQ equivalencies (fg TEQm^{-3}) in air samples of Gipuzkoa and for the zone 1 and zone 2. Values in bold indicate statistical differences between areas. Mann-Whitney test results (p-values) comparing the zones were also reported, significant p-values being indicated in bold.

	$\sum$PCDDs	$\sum$PCDFs	$\sum$PCDD/Fs	Σdl-PCBs	ΣPCDD/Fs + dlPCBs
TOTAL SAMPLES					
Gipuzkoa N = 113					
Min	0.92	0.3	1.33	0.04	1.61
Max	29.41	33.15	43.12	9.68	45.62
Mean [CI 95%]	5.93 [4.95, 6.9]	6.36 [5.24, 7.49]	12.29 [10.41, 14.17]	1.63 [1.37, 1.89]	13.92 [11.89, 15.95]
GM [CI 95%]	4.21 [3.61, 4.91]	4.09 [3.39, 4.94]	8.65 [7.35, 10.18]	1.21 [1.05, 1.41]	10.07 [8.61, 11.77]
Median [P25–P75]	3.96 [2.21, 8.49]	4.46 [2.27, 8.38]	9.01 [4.46, 18.54]	1.23 [0.72, 2.16]	9.98 [5.61, 20.43]
BY ZONE					
Zone 1 N = 63					
Min	1.66	1.78	3.78	0.51	4.82
Max	29.41	20.84	41.41	9.68	44.54
Mean [CI 95%]	8.3 [6.92, 9.68]	8.46 [7.1, 9.81]	16.76 [14.35, 19.16]	2.29 [1.91, 2.67]	19.05 [16.48, 21.62]
GM [CI 95%]	6.79 [5.78, 7.98]	6.91 [5.88, 8.12]	14.1 [12.12, 16.42]	1.95 [1.69, 2.23]	16.34 [14.17, 18.86]
Median [P25–P75]	6.93 [4.43, 10.54]	6.36 [4.13, 11.77]	13.74 [9.52, 21.98]	1.83 [1.35, 2.81]	16.76 [11.13, 25.79]
Zone 2 N = 50					
Min	0.92	0.3	1.33	0.04	1.61
Max	17.22	33.15	43.12	2.82	45.62
Mean [CI 95%]	2.94 [2.12, 3.76]	3.73 [2.08, 5.37]	6.66 [4.49, 8.83]	0.8 [0.66, 0.95]	7.46 [5.21, 9.71]
GM [CI 95%]	2.3 [1.94, 2.74]	2.11 [1.59, 2.8]	4.67 [3.77, 5.8]	0.67 [0.56, 0.81]	5.46 [4.46, 6.7]
Median [P25–P75]	2.19 [1.5, 2.9]	2.44 [1.04, 3.94]	4.35 [2.58, 7.85]	0.7 [0.5, 1]	5.65 [3.2, 8.6]
p-value	<0.001	<0.001	<0.001	<0.001	<0.001

Additionally, the arithmetic means, geometric means, and medians of $\sum$PCDDs, $\sum$PCDFs, $\sum$PCDD/Fs, $\sum$dl-PCBs, and the sum of dioxin-like compounds were higher in autumn-winter than in summer, except for the arithmetic mean of $\sum$dl-PCBs. These differences were statistically significant, with median values of $\sum$PCDD/Fs being 10.42 fg TEQm^{-3} in autumn-winter and 6.11 fg TEQm^{-3} in spring-summer. The sum of dioxin-like compounds was 11.97 fg TEQm^{-3} in autumn-winter and 7.42 fg TEQm^{-3} in spring-summer. The seasonal differences observed in $\sum$dl-PCBs were not statistically significant.

During the study period, PCDD/F concentrations were found to be significantly higher on weekdays (Monday to Friday) with a median value of 11.33 fg TEQm^{-3}, compared to weekends where the median value was 5.93 fg TEQm^{-3}. In contrast, the concentrations of $\sum$dl-PCBs were not significantly higher on weekdays (median: 1.47 fg TEQm^{-3}) than on weekends (median: 1.01 fg TEQm^{-3}). However, certain PCB congeners (77, 81, and 169) exhibited significantly higher concentrations on weekdays versus weekends. Consequently, the sum of all dioxin-like compounds was significantly higher during weekdays (median: 13.47 fg TEQm^{-3}) than on weekends (median: 7.59 fg TEQm^{-3}) (Table 2).

Detailed concentrations of each congener of the pollutants and their spatio-temporal distribution in the study area can be observed in Supplementary material Table S2a-f.

3.2. Composition profiles of PCDD/Fs and dl-PCBs

The analysis of contribution profiles revealed that the concentrations of PCDD/F congeners were comparable in both seasons (Fig. 2), with OCDD and 1,2,3,4,6,7,8-HpCDD being the major contributors. However, the contributions were higher in autumn-winter compared to spring-summer, with OCDD contributing 40% and 25%, and 1,2,3,4,6,7,8-HpCDD contributing 18% and 14%, respectively. The rest of the congeners contributed slightly more in spring-summer. The main contributors to TEQ profiles in autumn-winter were 2,3,4,7,8-PeCDF (22%), 1,2,3,7,8-PeCDD (20%), and 2,3,7,8-TCDD (13%), while in spring-summer, they were 1,2,3,7,8-PeCDD (23%), 2,3,7,8-TCDD (22%), and 2,3,4,7,8-PeCDF (20%). No differences were observed in dl-PCB congener profiles between seasons.

When comparing contribution profiles between weekdays (Fig. 3), PCDD/F congener concentration profiles were almost identical in both weekdays and weekends, with OCDD contribution being slightly higher in weekends (37%) than weekdays (32%). Similar results were observed in TEQ profiles, with the only differences being higher contribution of 2,3,4,7,8-PeCDF and lower contribution of 2,3,7,8-TCDD in weekdays than weekends. No differences were observed in dl-PCB congener profiles during weekdays (Fig. 3b).

The composition profiles of PCDD/F and dl-PCB congeners were similar in both zones (Fig. 4). The main contributors to $\sum$PCDD/F concentrations were OCDD (47.2% in zone 1 and 38.8% in zone 2), 1,2,3,4,6,7,8-HpCDD (20.6% in zone 1 and 19.2% in zone 2), and 1,2,3,4,6,7,8-HpCDF (5.65% in zone 1 and 8.78% in zone 2). However, few differences were observed between the zones, with dioxin congeners contributing slightly more in zone 1 than in zone 2, and furan congeners contributing more in zone 2. In the case of TEQ values, the main contributors in both zones were 1,2,3,7,8-PeCDD and 2,3,4,7,8-PeCDF, with contribution values of around 20%, and the congener 2,3,7,8-TCDD with a contribution between 11 and 14%. For dl-PCB congeners, the main contributor to $\sum$dl-PCB concentrations in both zones was the congener PCB 118, contributing more than 60% on average, followed by PCB 105 (around 20%) and PCB 77 (around 8%). However, the sum of TEQ values was dominated by the congener PCB 126 (90% or more).

3.3. Influence of spatio-temporal variables in PCDD/F and dl-PCB concentrations in air

According to the results of the GLM analysis, the concentrations of PCDD/Fs were influenced by zone, seasonality, and day of the week, as shown in Table 3. Zone had the greatest effect on the model, followed by season and day of the week. High concentrations of PCDD/Fs were positively related to Zone 1, the autumn-winter season, and weekdays. On the other hand, sampling year did not have a significant effect, suggesting that other variables may be more influential in this trend. Regarding dl-PCB concentrations, only zone had a significant effect, with Zone 1 showing a positive relationship with high concentrations. For the sum of PCDD/Fs and dl-PCBs, zone, seasonality, and day of the week were all significant factors. Zone had the greatest effect again, followed by seasonality and day of the week, but with less significance in this case.

Table 2

Minimum (Min) and maximum (Max) values, arithmetic means (CI 95%), geometric means (GM) (CI 95%) and medians with the 25th and 75th percentiles of the sum of PCDD, PCDFs, PCDD/Fs, dl-PCB and PCDD/Fs + dlPCBs TEQ equivalencies (fg TEQm^{-3}) in air samples of Gipuzkoa for the years 2017–2018 and 2019–2020, for the autumn-winter (from October to March) and spring-summer (from April to September), and for weekdays and weekends. Mann-Whitney test results (p-values) comparing the years were also reported, significant p-values being indicated in bold.

	$\sum$PCDDs	$\sum$PCDFs	$\sum$PCDD/Fs	Σdl-PCBs	ΣPCDD/Fs + dlPCBs
BY YEAR					
2017–2018 N = 47					
Min	1.07	0.51	2	0.49	2.49
Max	21.95	26.66	41.41	4.49	43.12
Mean [CI 95%]	5.74 [4.42, 7.07]	8.41 [6.54, 10.29]	14.15 [11.15, 17.16]	1.57 [1.33, 1.82]	15.73 [12.58, 18.88]
GM [CI 95%]	4.32 [1.29, 14.06]	6.02 [1.30, 19.77]	10.6 [2.81, 31.84]	1.38 [0.58, 3.15]	12.17 [3.45, 33.91]
Median [P25–P75]	4.2 [2.42, 8.42]	6.09 [3.46, 12.96]	9.87 [6.10, 21.07]	1.37 [1.01, 1.92]	11.26 [6.94, 23.77]
2019–2020 N = 66					
Min	0.92	0.3	1.33	0.04	1.61
Max	29.41	33.15	43.12	9.68	45.62
Mean [CI 95%]	6.06 [4.65, 7.46]	4.91 [3.59, 6.22]	10.96 [8.55, 13.37]	1.68 [1.26, 2.09]	12.64 [9.96, 15.32]
GM [CI 95%]	4.12 [1.22, 17.22]	3.1 [0.49, 11.79]	7.48 [1.67, 32.96]	1.1 [0.34, 5.26]	8.78 [2.03, 35.35]
Median [P25–P75]	3.67 [2.05, 8.44]	3.64 [1.80, 5.93]	7.79 [3.87, 13.68]	1 [0.52, 2.54]	8.82 [4.42, 16.48]
p-value	0.399	0.001	0.023	0.064	0.022
BY SEASON					
Autumn-Winter N = 72					
Min	1.08	0.33	1.41	0.32	1.73
Max	29.41	33.15	43.12	3.47	45.62
Mean [CI 95%]	6.59 [5.28, 7.89]	7.38 [5.84, 8.91]	13.96 [11.5, 16.42]	1.45 [1.26, 1.64]	15.41 [12.84, 17.97]
GM [CI 95%]	4.9 [4.1, 5.85]	5.24 [4.3, 6.38]	10.55 [8.81, 12.62]	1.23 [1.08, 1.41]	11.97 [10.1, 14.2]
Median [P25–P75]	4.63 [2.56, 9.25]	5.17 [3.14, 10.17]	10.42 [5.82, 19.45]	1.25 [0.88, 1.79]	11.59 [6.81, 21.32]
Spring-Summer N = 41					
Min	0.92	0.3	1.33	0.04	1.61
Max	17.22	20.84	34.87	9.68	44.54
Mean [CI 95%]	4.77 [3.35, 6.18]	4.59 [3.14, 6.04]	9.36 [6.62, 12.09]	1.96 [1.32, 2.6]	11.31 [8.01, 14.62]
GM [CI 95%]	3.22 [2.46, 4.23]	2.65 [1.87, 3.76]	6.11 [4.56, 8.19]	1.18 [0.84, 1.65]	7.42 [5.55, 9.93]
Median [P25–P75]	2.52 [1.58, 6.85]	2.77 [0.97, 6.09]	6.61 [2.56, 12.72]	1.11 [0.52, 2.89]	8.09 [3.26, 15.36]
p-value	0.008	0.005	0.004	0.867	0.009
BY WEEKDAY					
Weekdays N = 66					
Min	0.92	0.51	1.48	0.12	1.61
Max	21.95	33.15	43.12	9.68	45.62
Mean [CI 95%]	6.9 [5.63, 8.18]	7.93 [6.33, 9.52]	14.83 [12.19, 17.47]	1.83 [1.44, 2.21]	16.66 [13.79, 19.52]
GM [CI 95%]	5.07 [1.33, 16.79]	5.49 [0.82, 20.05]	10.9 [2.23, 34.77]	1.37 [0.46, 4.46]	12.47 [2.72, 41.54]
Median [P25–P75]	6.02 [2.45, 10.21]	6.01 [3.26, 11.31]	11.33 [6.00, 21.10]	1.47 [0.80, 2.42]	13.47 [6.79, 24.74]
Weekends N = 47					
Min	1.02	0.3	1.33	0.04	1.73
Max	29.41	26.66	34.93	5.76	36.15
Mean [CI 95%]	4.55 [3.08, 6.03]	4.17 [2.84, 5.50]	8.72 [6.42, 11.03]	1.36 [1.04, 1.68]	10.08 [7.61, 12.56]
GM [CI 95%]	3.24 [1.12, 13.1]	2.7 [0.42, 11.95]	6.25 [1.74, 27.20]	1.02 [0.34, 3.37]	7.45 [2.03, 29.92]
Median [P25–P75]	2.63 [1.85, 4.74]	3.28 [1.42, 4.86]	6.21 [3.62, 11.05]	1.01 [0.64, 1.67]	7.59 [4.34, 12.50]
p-value	0.017	0.001	0.006	0.203	0.01

4. Discussion

This study provided a characterization of the baseline levels of PCDD/Fs and dl-PCBs in the Gipuzkoa region of the Basque Country (Spain) between 2017 and 2020. Overall, the results indicated that the levels were comparable to, and even lower than, those reported in other European studies. The study found that seasonality, day of the week, and zone were significant factors influencing the concentrations of these pollutants in the air and their variability.

4.1. Comparison of results with those published in other study areas

We utilized TEQ values as they are an essential tool for characterizing contaminant levels and comparing our findings with those from other studies. Our study found average TEQ values for PCDD/Fs, dl-PCBs, and all dioxin-like compounds to be 12.3 fg TEQm^{-3}, 1.6 fg TEQm^{-3}, and 13.9 fg TEQm^{-3}, respectively, which fall within the low concentration range or the same order of magnitude as recent data presented in Table 4 of the comprehensive review on national and international studies. In previous national studies conducted in Valencia and Catalonia, the geometric mean for the sum of all dioxin-like compounds ranged between 2.97 fg TEQm^{-3} and 17.18 fg TEQm^{-3} (López

et al., 2021). Our findings were consistent with this range. However, in some of the studies of Catalonia (Mari et al., 2008a, 2008b; Martínez et al., 2010; Domingo et al., 2015, 2017), the TEQ values for PCDD/Fs in industrial areas or close to a MSWI at Barcelona were much higher than the ones obtained in our study, between 18 and 121 fg TEQm^{-3}. TEQ values for PCDD/Fs similar to our results were measured in three areas of Catalonia (background area, close to a cement plant area and close to the MSWI of Mataró) (Mari et al., 2008a, 2008b; Rovira et al., 2014, 2015), not exceeding the 18 fg TEQm^{-3}, in general. Besides, our TEQ values of PCDD/Fs were higher than the ones measured close the MSWI in Tarragona (3.56 fg TEQm^{-3}) (Vilavert et al., 2015). Regarding the TEQ values for dl-PCB, there are only two national studies that describe these values, one in Valencia (López et al., 2021) and another in Catalonia (Martínez et al., 2010). Both describe concentration ranges higher than those of this study, 1.18–10 fg TEQ/m^{-3} and 9.7–26.8 fg I-TEQ/m^{-3} respectively.

Our TEQ values for PCDD/Fs were compared to those of other studies at the European level. Higher values were observed in urban areas of Switzerland (32–190 fg TEQm-3), Poland (20–375 fg I-TEQm^{-3}), and Italy (65 fg TEQm^{-3}) (Bogdal et al., 2014; Dziubanek et al., 2016; Menichini et al., 2007). In Italy, high values were measured near a modern MSWI (22–125 fg I-TEQm^{-3}) and even higher near an old MSWI
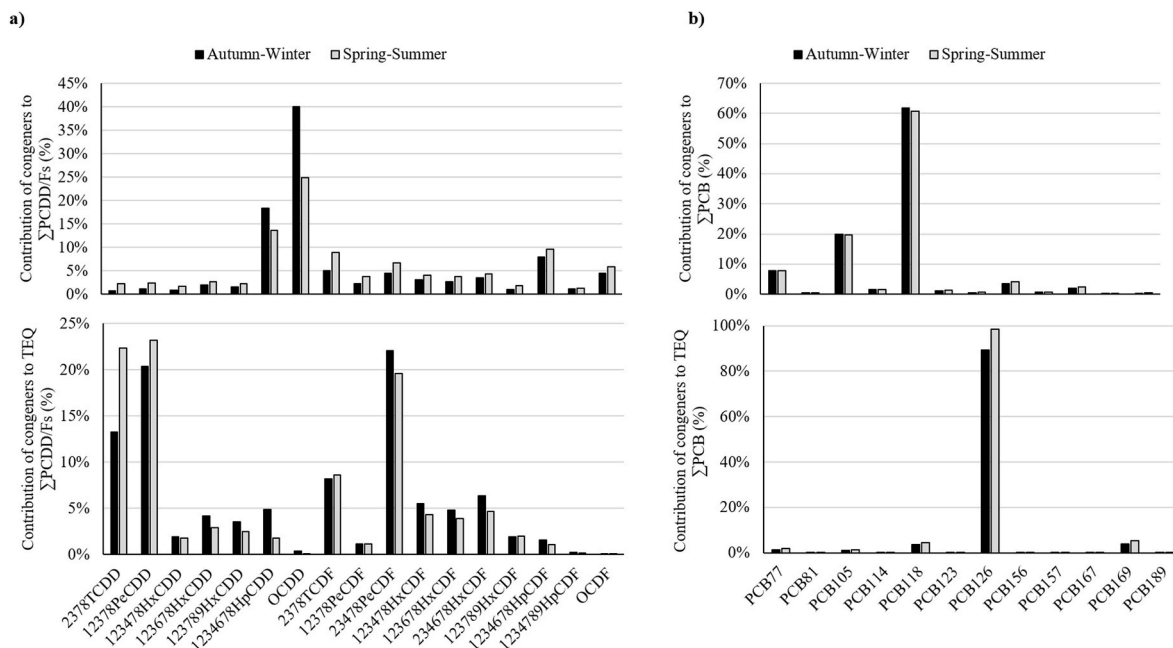
Fig. 2. Composition profiles based on the relative contribution (%) of each PCDD/Fs congener to ∑PCDD/Fs and dl-PCB congeners to ∑dl-PCB in terms of a) concentrations and b) TEQ$_{WHO2005}$ values for the different seasons (Autumn-winter and spring-summer).
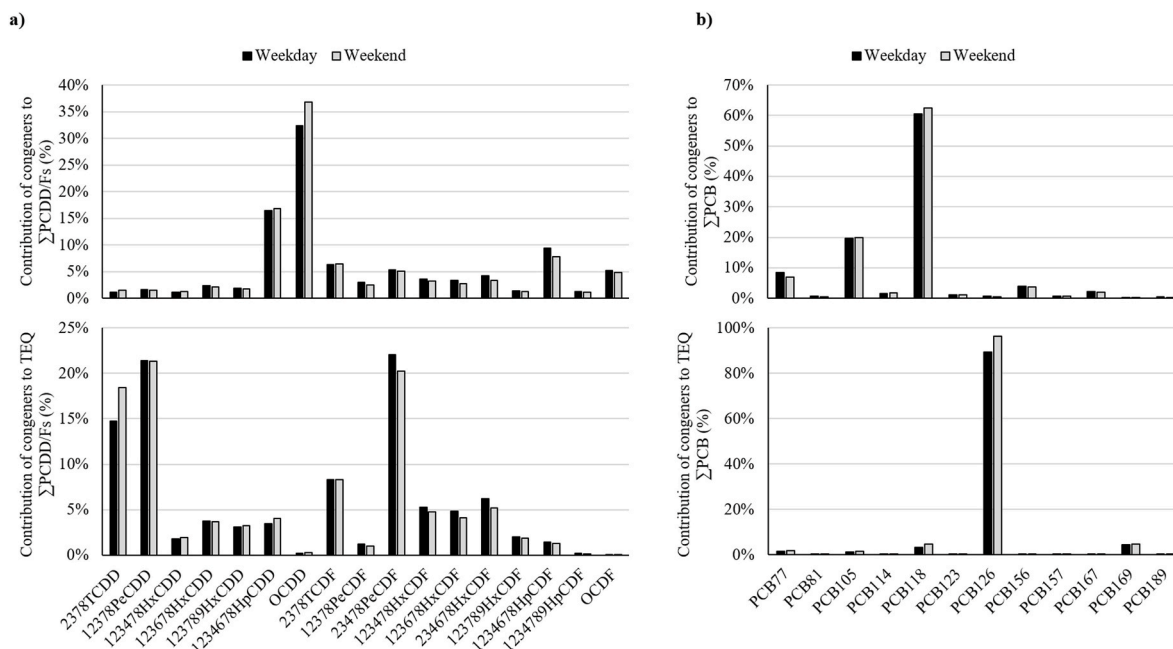

Fig. 3. Composition profiles based on the relative contribution (%) of each PCDD/Fs congener to ∑PCDD/Fs and dl-PCB congeners to ∑dl-PCB in terms of a) concentrations and b) TEQ$_{WHO2005}$ values for the different days of the week (Weekday and weekend).

(144–337 fg I-TEQm^{-3}) (Caserini et al., 2004). However, in the industrialized cities of Brescia and Trieste in Italy, the measured levels (10–19 fg TEQm^{-3} and 5–38 fg TEQm^{-3}, respectively) were in the same range as those obtained in our study (Colombo et al., 2013), as well as in a recent study conducted in a background area of the Czech Republic (0.2–61.1 fg TEQm^{-3}) (Degrendele et al., 2020). Nonetheless, Antunes et al. (2012) reported extremely high values of TEQ for PCDD/Fs (0–0.94 ng I-TEQm^{-3}) and dl-PCBs (0–0.081 ng I-TEQm^{-3}) in an industrial area of Portugal.

At international level, the air quality monitoring programs of Mexico, the United States, and Canada (MDAMN, NDAMN and NAPS,

respectively) reported PCDD/F values of 0.2 fg TEQm^{-3} (period 2008–2012), 0.6–43.1 fg TEQm^{-3} (period 1999–2004) and 1–1419 fg TEQm^{-3} (period 1989–2009) respectively (Wöhrnschimmel and Yao, 2014). The levels observed in this study were in the range of those three nations. Similarly, dl-PCB and all dioxin-like compound values measured recently in Lebanon were below our measured average values, the area not being a background area, but an urban one with moderate industrial activity (Fadel et al., 2022). In studies carried out in an urban area of Istanbul, an industrialized city in Korea, and two MSWIs in Taiwan, high values of PCDD/Fs (52–229 fg I-TEQm^{-3}, 0.052 pg TEQm^{-3}, 39–88 and 33.5–105 fg TEQm^{-3}; respectively) were observed
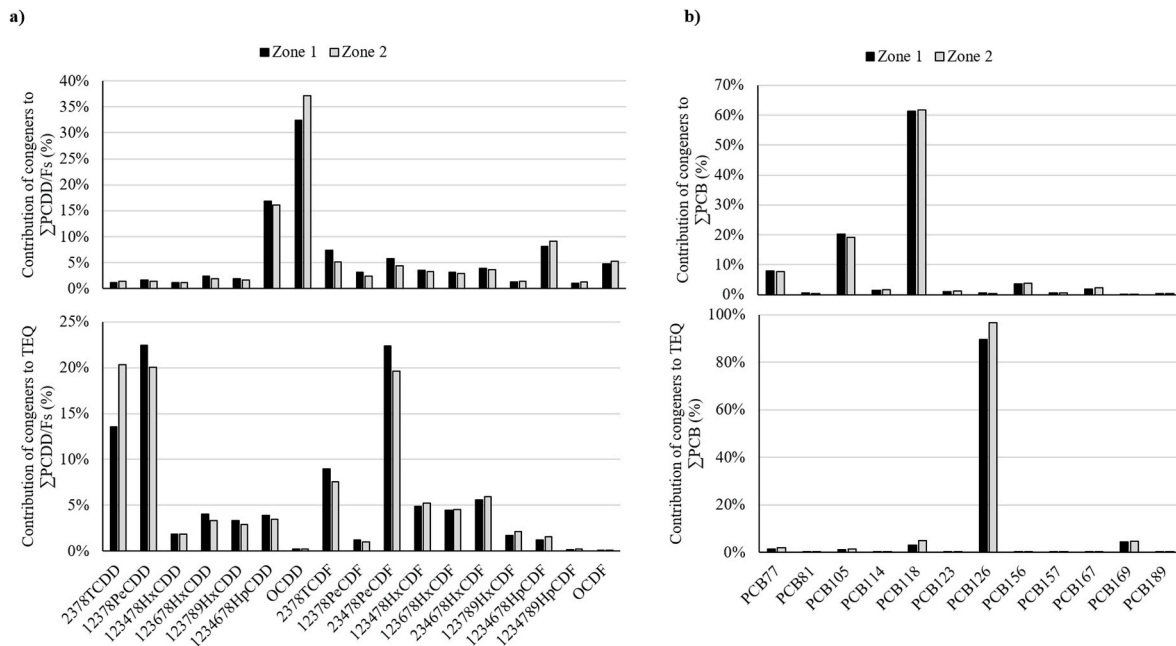
Fig. 4. Composition profiles based on the relative contribution (%) of each PCDD/Fs congener to ∑PCDD/Fs and dl-PCB congeners to ∑dl-PCB in terms of a) concentrations and b) TEQ$_{WHO2005}$ values for the different zones (Zone 1 and 2).

Table 3

Results of the GLM analysis using sampling year, zone, season and weekday as fixed factors and pollutant concentrations as response variable. Values in bold indicate statistical significance.

Factors	Response variables		
	PCDD/Fs Estimate (CI); p	dl-PCB Estimate (CI); p	PCDD/Fs + dl-PCB Estimate (CI); p
Zone 2	1	1	1
Zone 1	**1.00 [0.75,1.26]; <0.001**	**1.04 [0.82,1.27]; <0.001**	**1.01 [0.76,1.26]; <0.001**
Spring-Summer	1	1	1
Autumn-winter	**0.42 [0.15,0.68]; 0.002**	–	**0.34 [0.08,0.60]; 0.010**
Weekend	1	1	1
Weekday	**0.28 [0.03,0.53]; 0.030**	–	**0.25 [0.01,0.50]; 0.041**
Year 2018	1	1	1
Year 2017	0.34 [−0.21,0.88]; 0.219	–	0.30 [−0.23,0.82]; 0.262
Year 2019	0.08 [−0.19,0.35]; 0.555	–	0.08 [−0.19,0.34]; 0.569
Year 2020	−0.27 [−0.80,0.25]; 0.302	–	−0.18 [−0.68,0.32]; 0.481
R^2/R^2 adjusted	0.485/0.456	0.435/0.430	0.487/0.458

(Chen et al., 2011; Gunes et al., 2014; Kim and Yoon, 2014; Wang et al., 2010). In China, PCDD/F values measured by Hu et al. (2014) were extremely high, being the minimum values obtained almost ten times higher than the maximum values observed in this study (320–1360 fg TEQm^{-3}).

4.2. Seasonality

The results of this study demonstrate a significant difference in PCDD/F levels between seasons, with higher levels observed in autumn-winter compared to spring-summer. These seasonal variations may be attributed to season-dependent sources, such as heating systems, or temperature-related factors. Autumn-winter conditions create stable atmospheres, particularly during nocturnal thermal inversions, resulting in lower pollutant dispersion and potential accumulation in specific areas (Lohmann and Jones, 1998). The differences observed in this study are likely due to heating systems used in winter, consistent with previous research (Coutinho et al., 2007; Degrendele et al., 2020; Dziubanek et al., 2016; Muñoz-Arnanz et al., 2018). Although the observed differences between seasons in this study were not as significant as those observed in Portugal (Coutinho et al., 2007) and Poland (Dziubanek et al., 2016), they were comparable to those reported by Muñoz-Arnanz et al. (2018) in two locations in Spain with similar climates, Azpeitia (In Gipuzkoa) and La Coruña.

The findings of this study indicated that the season did not have a significant impact on dl-PCB levels, although the concentrations were slightly higher in spring-summer compared to autumn-winter. The literature on the seasonality of dl-PCBs presents conflicting results. While some studies, such as that of Dziubanek et al. (2016), found higher levels of dl-PCBs in winter than in summer, others reported the opposite, observing significantly higher levels in warm seasons than in cold seasons (Degrendele et al., 2020; Melymuk et al., 2012; Menichini et al., 2007). Positive correlations between dl-PCBs and temperature have been observed in Spain (Barbas et al., 2018; Muñoz-Arnanz et al., 2018), but other studies did not find significant changes between seasons (Mari et al., 2008a; Vilavert et al., 2015). Since the production and use of dl-PCBs ceased in Spain between 1984 and 1986 (Directive 85/467/EEC, 1985; Royal Decree 1406/89, 1989), the presence of these contaminants in the air could be primarily linked to volatilization and leaching from landfills and the incineration of materials containing dl-PCBs (Abad et al., 2006; Weber et al., 2001; Brubaker and Hites, 1998).

Our results show differences between PCDD/F and dl-PCB levels observed on weekdays and during the weekend. The concentration of these compounds was higher during weekdays, almost double, coinciding with industrial activity and traffic, including the movement of people and the transport of goods. To our knowledge, we did not find any prior literature on this topic.

4.3. Comparison of pollutants between the two zones

The study revealed that zone 1 had higher average concentrations of

Table 4

Arithmetic mean or range for the total PCDD/Fs, dl-PCB and PCDD/Fs + dl-PCB TEQ values obtained in this study for the area of Gipuzkoa and others worldwide with active air samplers. Note that the units for each reference are different.

Location	Type of area	ΣPCDD/Fs	Σdl-PCB	ΣPCDD/Fs + dl-PCB	Units	Reference
Gipuzkoa (Spain)	Industrial	12.29 (1.33–43.12)	1.63 (0.04–9.68)	13.92 (1.61–45.62)	fg TEQ$_{WHO\ 2005}$m^{-3}	Present study
Valencia (Spain)	Background	1.72	1.25	2.97	fg TEQ$_{WHO\ 2005}$m^{-3}	López et al., 2021
Valencia (Spain)	Urban	9.26–13.71	2.35–2.83	12.06–17.18	fg TEQ$_{WHO\ 2005}$m^{-3}	López et al., 2021
Valencia (Spain)	Industrial	3.10–9.60	1.34–3.84	4.66–11.61	fg TEQ$_{WHO\ 2005}$m^{-3}	López et al., 2021
Barcelona (Spain)	Industrial	0.018			pg TEQ$_{WHO\ 2005}$m^{-3}	Mari et al., 2008a
Barcelona (Spain)	Background	0.012			pg TEQ$_{WHO\ 2005}$m^{-3}	Mari et al., 2008b
Barcelona (Spain)	MSWI[1]	18.5–38.7			fg TEQ$_{WHO\ 2005}$m^{-3}	Mari et al., (2008b)
Barcelona (Spain)	Background	10.9			fg TEQ$_{WHO\ 2005}$m^{-3}	Mari et al., (2008b)
Barcelona (Spain)	Urban	3.8–36.5			fg TEQ$_{WHO\ 2005}$m^{-3}	Van Drooge et al., (2021)
Barcelona (Spain)	Industrial	18–41			fg TEQ$_{WHO\ 2005}$m^{-3}	Domingo et al., (2015)
Barcelona (Spain)	MSWI[1]	0.042–0.048			pg TEQ$_{WHO\ 2005}$m^{-3}	Domingo et al., (2017)
Mataró (Spain)	MSWI[1]	0.014			pg TEQ$_{WHO\ 2005}$m^{-3}	Rovira et al., (2015)
Sant Vicens dels Horts and Pallejà (Spain)	Industrial	0.009–0.018			pg TEQ$_{WHO\ 2005}$m^{-3}	Rovira et al., (2014)
Tarragona (Spain)	MSWI[1]	3.56			fg TEQ$_{WHO\ 2005}$m^{-3}	Vilavert et al., 2015
Catalonia (Spain)	Industrial	41.4–121.9	20.5–26.8		fg I-TEQ m^{-3}	Martínez et al., (2010)
Catalonia (Spain)	Urban	19.4–45.7	9.7–14.8		fg I-TEQ m^{-3}	Martínez et al., (2010)
Catalonia (Spain)	Industrial	3–228			fg I-TEQ m^{-3}	Parera et al., (2018)
Catalonia (Spain)	Urban	3–126			fg I-TEQ m^{-3}	Parera et al., (2018)
Portugal	Industrial	0–0.94	0–0.081		ng I-TEQ m^{-3}	Antunes et al., (2012)
Brescia (Italy)	Industrial	0.01–0.19			pg TEQ$_{WHO\ 2005}$m^{-3}	Colombo et al., (2013)
Trieste (Italy)	Urban	5.04–33.12			fg TEQ$_{WHO\ 2005}$m^{-3}	Mosca et al., (2012)
Trieste (Italy)	Industrial	7.71–37.82			fg TEQ$_{WHO\ 2005}$m^{-3}	Mosca et al., (2012)
Trieste (Italy)	Background	5.07–18.96			fg TEQ$_{WHO\ 2005}$m^{-3}	Mosca et al., (2012)
Po Valley (Italy)	MSWI[1]	22–125			fg I-TEQ m^{-3}	Caserini et al., (2004)
Rome (Italy)	Urban	65			fg TEQ$_{WHO\ 2005}$m^{-3}	Menichini et al., (2007)
Italy	Background	3			fg TEQ$_{WHO\ 2005}$m^{-3}	Menichini et al., (2007)
Zurich (Switzerland)	Urban	32–190			fg TEQ$_{WHO98}$m^{-3}	Bogdal et al., (2014)
Czech Republic	Background	0.2–61.1			fg TEQ$_{WHO\ 2005}$m^{-3}	Degrendele et al., (2020)
Upper Silesia (Poland)	Urban	19.8–375.8	1.5–31.8		fg I-TEQ m^{-3}	Dziubanek et al., (2016)
Mexico	Overall[2]	0.2–902			fg TEQ$_{WHO\ 2005}$m^{-3}	Wöhrnschimmel and Yao (2014)
United States	Overall[2]	0.6–43.1			fg TEQ$_{WHO\ 2005}$m^{-3}	Wöhrnschimmel and Yao (2014)
Canada	Overall[2]	1–1419			fg TEQ$_{WHO\ 2005}$m^{-3}	Wöhrnschimmel and Yao (2014)
Turkey	MSWI			0.0084–0.0588	pg I-TEQ m^{-3}	Güzel et al., (2020)
Lebanon	Urban		0.02	5.49	fg TEQ$_{WHO\ 2005}$m^{-3}	Fadel et al., (2022)
Lebanon	Urban		0.37	5.67	fg TEQ$_{WHO\ 2005}$m^{-3}	Fadel et al., (2022)
Istanbul	Urban	52–229			fg I-TEQ m^{-3}	Gunes et al., (2014)
Taiwan	MSWI[1]	0.039–0.088			pg TEQ$_{WHO\ 2005}$m^{-3}	Chen et al., (2011)
Southern Taiwan	MSWI[1]	33.5–105			fg TEQ$_{WHO\ 2005}$m^{-3}	Wang et al., (2010)
China	Industrial	0.31–0.84			pg TEQ$_{WHO\ 2005}$m^{-3}	Hu et al., (2014)
China	Industrial	0.32–13.6			pg TEQ$_{WHO\ 2005}$m^{-3}	Hu et al., (2014)
Korea	Industrial	0.052			pg TEQ$_{WHO\ 2005}$m^{-3}	Kim and Yoon (2014)

[1] Municipal solid waste incinerator [2] North American ambient air monitoring network.

all pollutants compared to zone 2, which is not surprising given the presence of PCDD/Fs emitting industries located within 4–5 km from the air samplers in zone 1 (one at 0.5 km from the air sampler 2), according to the Spanish Registry of Polluting Emission Sources (PRTR-Spain). However, maximum values of furan concentrations were higher in zone 2 than in zone 1. Similarly, the composition profiles of the PCDD/Fs showed that furans congeners contributed more in zone 2 than in zone 1. Chlorinated furan congeners are expected to be more prevalent in incinerator flue gases than chlorinated dioxin congeners (Caserini et al., 2004; Xu et al., 2009). However, in zone 2 the industries that emit PCDD/Fs were located more than 10 km from the sampling zone, which probably resulted in greater pollutant dispersion.

Although zone 1 had higher mean concentrations of all pollutants compared to zone 2, both zones have similar composition profiles of PCDD/Fs, being dominated by OCDD, 1,2,3,4,6,7,8-HpCDD and 1,2,3,4,6,7,8-HpCDF in terms of concentration, and 1,2,3,7,8-PeCDD, 2,3,4,7,8-PeCDF and 2,3,7,8-TCDD in terms of TEQs, thereby, suggesting the existence of similar sources for both zones. The results are consistent with previous studies such as Degrendele et al. (2020), Parera et al. (2018), Trinh and Chang (2018) and Venier et al. (2009). According to Degrendele et al. (2020), these profiles of congeners are compatible with the incineration of hazardous waste and/or ferrous smelters. This is an interesting point, because once the ERP starts working, it will be possible to measure its contribution to air pollutants in zone 1, especially if variations in those congeners contribution are observed. On this matter, Mari et al. (2008a) concluded that the most

abundant congeners in all samples of an industrial area of Catalonia were OCDD, 1,2,3,4,6,7,8-HpCDD and OCDF in terms of concentrations, and 2,3,4,7,8-PeCDF congener in terms of TEQs. Similar congener patterns were also found in other studies (Muñoz-Arnanz et al., 2018; Tominaga et al., 2016), suggesting that it is a typical congener emission from vehicles. However, the profile found in this study does not match exactly; therefore, we could not make the conclusion that the source of pollution in zone 2 is vehicle traffic. Likewise, it has to be taken into consideration that OCDD concentrations in air may stem from a lower atmospheric removal rate compared to that of other congeners (Brubaker and Hites, 1997). Therefore, it seems that different types of pollution sources are affecting the zones of this research.

Regarding dl-PCBs, zone 1 showed higher concentrations (both mean and median) of these compounds, with maximum values of the congeners. The composition profile was similar in both zones, with PCB 118 being the predominant congener in terms of concentration, followed by PCB 105 and PCB 77, and PCB 126 being the dominant congener in terms of TEQs. Degrendele et al. (2020) described similar results, with PCB 118 and PCB 105 as the main contributors in terms of concentration and PCB 126 in terms of TEQ, suggesting that the atmospheric dl-PCB concentrations observed were influenced by metallurgy industries. As mentioned before, zone 1 contains industries working in the sector of production and first transformation of aluminum, steel cold rolling, graphic printing and iron foundry for automotive parts. Although zone 2 does not contain this type of industry, the main economic activity is focused on the iron and steel sector (Goierri, 2022). Nevertheless, other studies where PCB 126 was also the main contributor to toxic content, followed to a lesser extent by PCB 118, concluded that those results are common in most environmental samples, including ambient air (Barbas et al., 2018; Choi et al., 2008; Kerst et al., 2003; Kim et al., 2011; Li et al., 2021; Martínez et al., 2010).

The current study has several strengths such as exhaustive sampling, additive information of several spatiotemporal variables (sampling year, season, weekday and zone) and the analysis of POPs in two important industrial areas in the territory of Gipuzkoa. In addition, we have analyzed the presence of these pollutants in the most unfavorable situation with respect to levels of population exposure. The weaknesses of the study are the size of the sample and the lack of more detailed information on the sources of emissions (profiles of congeners, for example) to be able to know their contribution to the overall pollution of the studies areas.

5. Conclusions

This study aimed to characterize the levels of PCDD/Fs and dl-PCBs in Gipuzkoa, Basque Country (Spain) from 2017 to 2019. The results provide baseline levels of PCDD/F and dl-PCB TEQs prior to the plant operation, serving as a reference for future monitoring programs. Compared to other national and international studies in industrial areas, the PCDD/F levels in this study were similar or lower, while the dl-PCB levels were lower except for a recent study in Lebanon. The study also observed seasonal and weekday patterns in pollutant levels, with higher PCDD/F levels in cold seasons and higher concentrations on working days. This informs us about a time-trend influenced behavior in terms of emissions, which will be helpful when interpreting future results. Additionally, the study found higher levels of pollutants in zone 1 than in zone 2, indicating that the industries emitting PCDD/Fs are closer to zone 1 according to the Spanish Registry of Pollutant Emission Sources. The congener profiles further supported this finding, showing that congeners related to metallurgical industry emissions were the primary contributors to the sum of dioxin concentrations and TEQ values.

Credit author statement

L. Santa Marina: Conceptualization, Methodology, Investigation, Writing – original draft preparation, Formal analysis, Funding

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Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Jesus Ibarluzea reports financial support was provided by Gipuzkoa Provincial Council.

Data availability

The data that has been used is confidential.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envres.2023.115901.

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