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Concentrations of dioxins and furans in breast milk of women living near a hazardous waste incinerator in Catalonia, Spain

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ABSTRACT

Since 1999, a hazardous waste incinerator (HWI) is operating in Constantí (Tarragona County, Catalonia, Spain). In 1996–1998, when the facility was being built, we started a monitoring program aimed at evaluating the impact of the emissions of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) by the HWI on the environment and the human health. This study aimed at determining the current concentrations of PCDD/Fs in breast milk samples of women living nearby the HWI and at comparing these levels and profiles with those obtained in the baseline (1996–1998) and previous surveys (2002, 2007 and 2012). Furthermore, the association between the dietary intake of PCDD/Fs and the congener profiles in breast milk was also explored. Twenty milk samples were collected from women living in Tarragona downtown and near the industrial area where the HWI is placed. The content of PCDD/Fs was analyzed by following a procedure derived from the US EPA methods 1613 and 8290A. The mean concentration of PCDD/Fs was 2.26 pg WHO-TEQ/g fat. No significant differences were found between women living in industrial and urban areas (1.67 pg vs. 2.48 pg WHO-TEQ/g fat). Interestingly, a notable significant reduction (81%) was observed with respect to the concentrations found in the baseline study. The profiles of PCDD/Fs in breast milk were similar independently on the area and period of collection, being mainly influenced by the intake of fish, meat, oils and fats. The decreasing trend of PCDD/Fs in human milk agrees with the reduction observed in the dietary intake of these pollutants. It was also concluded that the current levels of PCDD/Fs in human milk levels are not influenced by the HWI stack emissions.

1. Introduction

Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) are lipophilic ubiquitous pollutants with a considerable toxicity, environmental persistence, potential for long-range atmospheric transport, and capacity for bioaccumulation in the food chain. Once in the human body, PCDD/Fs are slowly eliminated and may elicit adverse effects including neurodevelopmental impairment, immune and hormonal toxicity, cancer and endocrine disruption (Eskenazi et al., 2018; Guo et al., 2018; Hui et al., 2016; Vinceti et al., 2018).

Although PCDD/Fs have been measured in a number of human tissues including kidney, liver, lung, pancreas, and adipose tissue (Domingo et al., 2017; Iida et al., 2007), plasma/blood and breast milk are the most widely used biomonitors (Antignac et al., 2016; Bianco et al., 2013; Boda et al., 2018; Brajenović et al., 2018; Focant et al., 2013; Schuhmacher et al., 2013). Monitoring PCDD/Fs in breast milk is interesting because it is a non-invasive method representing human exposure. For this reason, since 1987 WHO and UNEP are undertaking global PCDD/Fs breast milk surveys in many countries, in order to evaluate the trends across the world, as well as the effectiveness of measures implemented under the Stockholm Convention (van den Berg et al., 2017).

In the past, incinerators were catalogued as important sources of PCDD/Fs (Hutzinger and Fiedler, 1989). However, as a consequence of the development of new Air Pollution Control Technologies to comply with the strict legislations (PCDD/F emissions from waste incinerators are regulated in the European Union by the 2000/76/CE Directive to maximum levels of 0.1 ng TEQ/Nm^3), a substantial reduction of the levels of PCDD/Fs has been observed in environmental matrices, as well as in foodstuffs during the last 20 years (Perelló et al., 2015; Vilavert et al., 2015).

In 1999, the first, and up until now the only, hazardous waste incinerator (HWI) in Spain started regular operations in Constantí (Tarragona County, Catalonia). A monitoring program (baseline or background) was designed during the period of construction

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(1996–1998) of the facility in order to assess its subsequent impact on the environment and the public health. Within that program, PCDD/F concentrations were measured in breast milk samples of primiparae mothers living in the area in order to establish the baseline levels of exposure to these pollutants (Schuhmacher et al., 1999). PCDD/Fs were again analyzed in breast milk samples of mothers living in the same area in 2002, 2007 and 2012 (Schuhmacher et al., 2004, 2009, 2013). A significant decrease of the concentrations of PCDD/Fs in breast milk was observed with time.

In 2017, breast milk samples were again collected in order to measure the levels of PCDD/Fs in mothers living nearby the HWI of Tarragona after 18 years of regular operations. The current concentrations and profiles of PCDD/Fs were compared with those obtained in the baseline and previous surveys (2002, 2007 and 2012). Finally, the associations between the dietary intake of PCDD/Fs and the congener profiles in breast milk were also assessed.

2. Materials and methods

2.1. Breast milk samples collection

During 2017, 20 human milk samples were obtained in the Bank of Blood and Tissues of Catalonia, which is the entity of the Catalan Department of Health whose mission is to guarantee the supply and proper use of human blood and tissues in Catalonia. The criteria for donor selection were the same as in our previous surveys: area, parity and sampling time (Schuhmacher et al., 2004, 2009, 2013). Eighteen samples belonged to primipara mothers, while the remaining two corresponded to mothers of a second baby. The age of the participants ranged between 27 and 40 years (mean: 34 years). All of them had lived in Tarragona County, in zones under potential influence of the emissions of the HWI, at least the last 5 years. Fourteen samples corresponded to women living in urban zones (Tarragona downtown), while six samples belonged to women living near the important industrial area of Tarragona where the HWI is placed. The time elapsed between delivery and sampling was between one and two months. Milk samples of each participant (50–100 mL) were stored frozen (−20 °C) until PCDD/F analyses. The study protocol was reviewed and approved by the Ethical Committee for Human Studies of the School of Medicine, "Rovira i Virgili" University, Reus/Tarragona, Spain.

2.2. Analytical method

Analysis of PCDD/Fs was conducted according to a procedure derived from the US EPA methods 1613 and 8290A. The methodology was previously reported (Schuhmacher et al., 2009). Briefly, fat from breast milk samples was extracted with a mixture of diethyl ether and hexane after addition of sodium oxalate and ethanol. Extraction solvent was exchanged to hexane only, and the fat content was gravimetrically determined (Mari et al., 2017) after drying (Boda et al., 2018). A mixture of $^{13}C_{12}$-PCDD/F standards was spiked to control potential losses during the extraction and clean-up processes. The clean-up procedure and fractionation was carried out by adsorption chromatography as multi-step clean-up using silica and alumina columns. Lipids were removed in a silica gel column with sulfuric acid and initially purified on an activated carbon column. Further clean-up of the sample was achieved with an activated aluminum column. The PCDD/F fraction was collected and concentrated to near dryness with a nitrogen flux. Finally, 25 μL of $^{13}C_{12}$-PCDD/F injection standards were added. The analysis of PCDD/Fs was carried out by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) on an Agilent 6890 gas chromatograph equipped with a ZB5-MS capillary column and coupled to a Waters Autospec Ultima mass spectrometer. The chromatographic process separated the 17 toxic 2,3,7,8-substituted congeners from each other. The mass spectrometer measured (via "selected ion recording" at a resolution of N10000) two selected ions per congener group for both the native and labeled compounds. Conventional procedures of quality assurance/quality control (QA/QC) were employed. Blank, replicate and reference samples were analyzed for every batch of samples, proving the method displayed good repeatability. The calculation of the concentrations was done by using the corresponding ^{13}C congener level, automatically correcting according to the recovery percentage specific for each congener. In addition, the relative standard deviation (RSD) was calculated as a measure of the uncertainty. In all cases, the RSD of the control sample was lower than 10%. The recovery percentages ranged 45–75%, being the recoveries for each individual congener listed in Table S1 of Supplementary information.

2.3. Data treatment

Two different sets of toxic equivalency factors (TEFs) were used for PCDD/F toxic equivalents (TEQs): NATO factors for I-TEQs (NATO/CCMS, 1988), and the factors recommended by WHO in 2005 for WHO-TEQs (van den Berg et al., 2006). For TEQ calculations, and in line of our previous studies, when a result was below the limit of detection (LOD), that value was assumed to be one-half of that limit (ND = 1/2 LOD). Statistical analysis was carried out by means of the statistical software package SPSS Statistics 22.0. The level of significance was considered as 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. Furthermore, ANOVA or Kruskal-Wallis tests were executed to normally distributed or no normally distributed data, respectively.

On the other hand, Principal Component Analysis (PCAs) was executed to get some information about the PCDD/F congener profiles in relation to the area of residence, the period of sampling, as well as the influence of dietary intake. The objective of a PCA is to derive a few new components (Principal Components) as a linear combination of the original variables, which provides a description of the data structure with a minimum loss of information.

3. Results and discussion

3.1. Levels of PCDD/Fs in breast milk

The concentrations of PCDD/Fs in breast milk samples obtained in 2017 from mothers living near the HWI of Constantí are summarized in

Table 1
Concentrations (in pg/g fat) of PCDD/Fs in human milk samples of women living near the HWI of Constantí (Tarragona County, Catalonia, Spain).

Congener	Mean	SD	Min.	Max.
2,3,7,8-TCDD	0.29	0.33	< 0.10	1.50
1,2,3,7,8-PeCDD	0.81	0.42	< 0.19	1.60
1,2,3,4,7,8-HxCDD	0.50	0.26	< 0.26	1.10
1,2,3,6,7,8-HxCDD	2.61	2.03	0.49	8.40
1,2,3,7,8,9-HxCDD	0.46	0.35	< 0.20	1.30
1,2,3,4,6,7,8-HpCDD	2.80	1.55	0.96	7.30
OCDD	15.7	6.11	7.70	30.0
2,3,7,8-TCDF	0.18	0.08	< 0.15	0.34
1,2,3,7,8-PeCDF	0.14	0.10	< 0.09	0.47
2,3,4,7,8-PeCDF	1.92	1.11	0.47	4.20
1,2,3,4,7,8-HxCDF	0.60	0.39	< 0.26	1.40
1,2,3,6,7,8-HxCDF	0.64	0.35	< 0.59	1.50
2,3,4,6,7,8-HxCDF	0.35	0.21	< 0.26	0.84
1,2,3,7,8,9-HxCDF	< 0.25	–	< 0.17	0.34
1,2,3,4,6,7,8-HpCDF	0.92	0.80	< 0.38	3.50
1,2,3,4,7,8,9-HpCDF	< 0.25	–	< 0.18	0.51
OCDF	< 0.86	–	< 0.58	2.90
PCDDs + PCDFs	28.8	9.48	ND	48.5
I-TEQ	2.26	1.04	0.84	4.14
WHO-TEQ	2.26	1.02	0.73	4.19

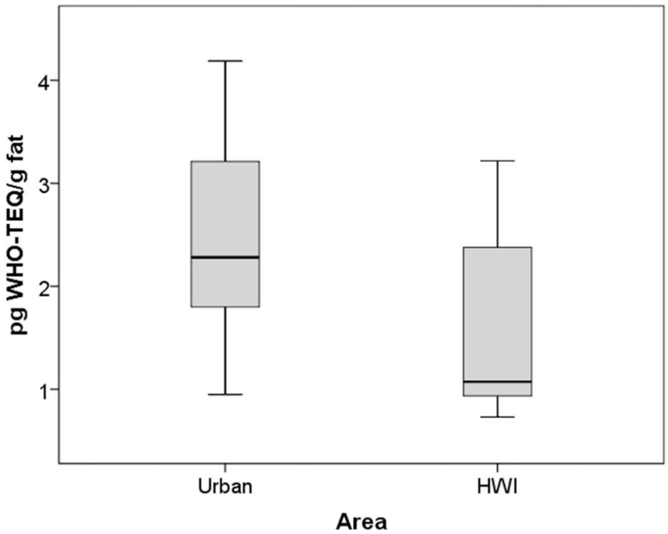

Fig. 1. PCDD/F concentrations (median and quartiles) in breast milk from women living in the vicinity of the HWI ($n = 6$) and in control/urban ($n = 14$) areas.

Table 1. In turn, Fig. 1 depicts the boxplots of PCDD/F concentrations in human milk classified according to the place of residence of the mothers: urban (Tarragona downtown) and industrial (where the HWI is placed) areas. Table 2 shows the levels of PCDD/Fs in breast milk samples obtained in the baseline (1996) and previous (2002, 2007 and 2012) surveys together with those obtained in recent years worldwide. In the current study, the mean concentration of PCDD/Fs was 2.26 pg WHO-TEQ/g fat (2.26 pg I-TEQ/g fat), ranging from 0.73 to 4.19 pg WHO-TEQ/g fat (0.84 to 4.14 pg I-TEQ/g fat). No significant differences were observed between the results corresponding to mothers living in the industrial (1.67 pg WHO-TEQ/g fat; 1.57 pg I-TEQ/g fat) and urban (2.48 pg WHO-TEQ/g fat; 2.51 pg I-TEQ/g fat) areas ($p > 0.05$). A significant reduction (81%) ($p < 0.001$) was noted when the current PCDD/F concentrations (2.26 pg I-TEQ/g of fat) were compared with those found in the baseline study (12.2 pg WHO-TEQ/g fat; 11.8 pg I-TEQ/g of fat). In fact, as it can be observed in Table 2, a progressive decrease in the total PCDD/Fs breast milk levels has been noticed in the study area over the time, being the concentrations 10.6, 7.6 and 4.8 pg WHO-TEQ/g of fat, in 2002, 2007 and 2012, respectively (Schuhmacher et al., 2004, 2009, 2013). The decrease in the levels of PCDD/Fs in breast milk has also been reported in other countries (Focant et al., 2013; van den Berg et al., 2017; Wittsiepe et al., 2007), being in agreement with the reduction of PCDD/Fs observed from the nineties in environmental and biological samples in most developed countries, where strict industrial emission legislations have been continuously implemented (Domingo et al., 2017). For example, recently Bruckmann et al. (2013) reported a decrease of at least one order of magnitude in PCDD/F in air concentrations in Germany, Augusto et al. (2015) found a decrease of PCDD/Fs in lichens of approximately 70% (from 2000 to 2011) in Portugal, while Bjurlid et al. (2018) reported decreasing concentrations in seals from the Baltic Sea. However, in those zones where non-industrial PCDD/Fs sources are high contributors, or where PCDD/F industrial emission legislations are not so strict, the downward trend is not being so evident (Dopico and Gómez, 2015). For example, a recent study by Zhang et al. (2016) reported an increase of PCDD/Fs in human milk, which was associated with the increase of PCDD/Fs emissions in China.

When our data are compared with the concentrations of PCDD/Fs in a number of countries (Table 2), the current levels of PCDD/Fs in breast milk of women living near the HWI of Constantí, were in the lowest part of the range. In order to make easier the comparison, details on the factors that may affect the concentration of PCDD/Fs in human milk, such as parity, age of the mother, time of collection after delivery, number of individual samples (or pools) or type of collection area, are also shown in Table 2 (Rawn et al., 2017; Vigh et al., 2013). In general, the highest values corresponded to Vietnam, a country where several authors have investigated the human health effects in Agent Orange dioxin hotspots (Hue et al., 2014; Kido et al., 2016; Manh et al., 2015; Nghi et al., 2015).

For the general population, exposure to PCDD/Fs occurs mainly though food intake (Linares et al., 2010; Sirot et al., 2012). Hence, the decrease of PCDD/F levels in breast milk of women living in the vicinity of the HWI of Constantí coincides with the spectacular reduction observed in the dietary PCDD/Fs intake in the same area since 1996–1998 (Fig. 2). In the baseline study, the total dietary intake in this area was 210 pg I-TEQ/day (Domingo et al., 1999), while in subsequent surveys conducted in 2002, 2006, 2012 and 2018, the dietary intake of PCDD/Fs was 63.8, 27.8, 33.1 and 8.54 pg WHO-TEQ/day, respectively (Bocio and Domingo, 2005; González et al., 2018; Perelló et al., 2012). The slight increase noted in 2012 was mainly associated with the inclusion of two new food groups which were not included in the previous surveys. In turn, in 2018 the great differences in the total dietary exposure to PCDD/Fs were explained not only by the reduction of PCDD/Fs in foodstuffs, but also by the notable differences in consumption data used. In any case, the decrease in the PCDD/F intake in the study area is in agreement with the trends observed at European level where the dietary exposure were reduced between 16.6% and 79.3% in the period 2002–2010 (Malisch and Kotz, 2014).

3.2. Profiles of PCDD/F congeners in breast milk

Figs. S1 and S2 in Supporting Information show the average PCDD/F composition of the samples collected in the urban and industrial areas as well as in the different surveys. OCDD was the most abundant congener in breast milk samples (Table 1), with a mean concentration of 15.7 pg/g of fat. On the other hand, the most toxic congener, 2,3,7,8-TCDD, showed an average concentration of 0.29 pg/g of fat, being detected in 12 of the 20 samples. With respect to furans, the highest average concentration corresponded to 2,3,4,7,8-PeCDF (1.92 pg/g fat). In contrast, most samples showed levels below the respective detection limits for OCDF (17/20), 1,2,3,7,8,9-HxCDF (17/20) and 1,2,3,4,7,8,9-HpCDF (16/20): < 0.86, < 0.25, and < 0.25 pg/g fat, respectively. Table 3 shows the median concentrations of the 17 2,3,7,8-substituted congeners in the period elapsed between 1996–1998 and 2017, as well as the temporal trends. Since the baseline study, the degree of decrease for all PCDD/F congeners has been rather similar (around 80%), indicating that the PCDD/F profile in breast milk also remained similar over time.

A Principal Component Analysis (PCA) was executed to evaluate potential differences in breast PCDD/F profiles collected in the different areas of residence and surveys, as well as to explore the influence of the dietary intake on the PCDD/F profiles in breast milk samples. PCA was executed considering the PCDD/F profiles of the 85 breast milk collected during the 5 surveys conducted between 1996–1998 and 2017, together with the PCDD/F congener profiles from 114 food samples purchased in the period 2007–2018 in the same area (Domingo et al., 2012; González et al., 2018). Food samples consisted of vegetables and tubers, pulses, cereals, fish and seafood, meat and meat products, eggs, milk and dairy products, fruits, oils and fats, and industrial bakery. Since the main objective was to compare profiles, instead of absolute concentrations, the percentages of contribution of each congener to the sum of the 17 2,3,7,8-substituted congeners in the corresponding

Table 2
Concentrations of PCDD/Fs in human breast milk samples: A summary of recent (2013–2018) reports from various countries.

Country	Year of collection	Number of samples	Donors characteristics	Mean TEQ	Reference
Spain	1996	15	Primiparae, 25–35 years, living in the neighbourhood of a HWI	12.2[a]	Schuhmacher et al. (1999)
Spain	2002	15	Primiparae, 25–35 years, living in the neighbourhood of a HWI	10.6[a]	Schuhmacher et al. (2004)
Spain	2007	15	Primiparae, 25–41 years, living in the neighbourhood of a HWI	7.6[a]	Schuhmacher et al. (2009)
Spain	2012	20	Primiparae, 25–41 years, living in the neighbourhood of a HWI	4.8[a]	Schuhmacher et al. (2013)
Spain	2017	20	18 Primiparae and 2 multiparae, 27–40 years, living in the neighbourhood of a HWI	2.3[a]	Current study
Hungary	2007	22	Primiparae, 27.7 ± 4.4 years, days 5, 12, 84 after delivery	2.13[a]; 1.85[a]; 1.65[a]	Vigh et al. (2013)
Italy	2007–2008	95	Primiparae, under 35 years living in areas affected by the illegal dumping of wastes periodically set to fire, collection between the second and eighth week after delivery	6.46[a]	Giovannini et al. (2014)
Germany	2007–2008	273	59% primiparae and 41% multipara, 15–43 years, living in rural and urban, collection 4 to 8 week after birth	5.1[b]	Raab et al. (2013)
France	2007	44	22 Primiparae and secundipara, 12 Tertiparara, and 10 quadripara or more, 24 to 41 years, collection between week 6 and 8 after delivery	11.37[a]	Focant et al. (2013)
Canada	2008–2011	298	141 Primiparae and 150 multipara, 21–46 years, collection between two and ten weeks post-delivery	5.4[a]	Rawn et al. (2017)
New Zealand	2008	39	Primiparae, 25–41 years, living in rural and urban areas, collection during the second and the third month after birth	3.54[a]	Mannetje et al. (2013)
China	2009	137 (4 pools)	Primiparae, 26–33 years, collection 3 to 8 week after birth, living in Hong Jong for at least 10 years	7.48[a]	Wong et al. (2013)
China	2011–2012	150	Primiparae, 18–35 years, settled in Shanghai for 0–3 years before delivery, collection first week postpartum	5.4[a]	Lu et al. (2015)
China	2011	1760 (32 pools)	Primiparae, 25.3 ± 3.9 years, living in 16 different provinces of China	6.7[a]	Zhang et al. (2016)
Vietnam	2012	79	Primiparae, 28 ± 4.6 years, living in Bien Hoa (dioxin hot spot), collection 1 month after delivery	10.5[a]	Nghi et al. (2015)
		131	Multipara, 28 ± 4.6 years, living in Bien Hoa (dioxin hot spot), collection 1 month after delivery	8.93[a]	
France	2011–2014	96	45 primiparae and 27 multipara, 30.3 ± 4.7 years, collected in Nantes Human Milk Biobank, collected between 1 and 2 months after delivery	6.1*[a]	Antignac et al. (2016)

[a] WHO-TEQ according to van den Berg et al. (2006).
[b] WHO-TEQ according to van den Berg et al. (1998).

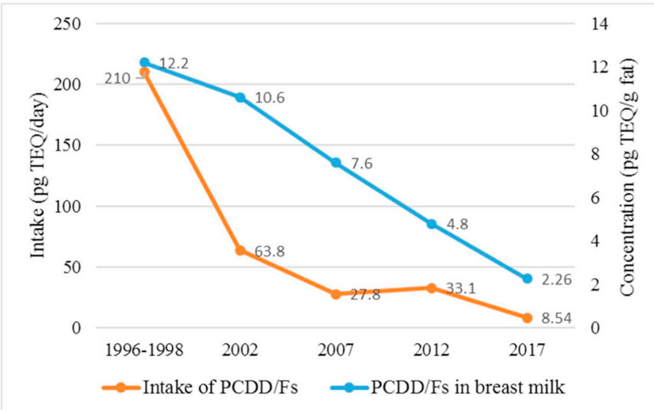

Fig. 2. Trends of the PCDD/Fs intake and human breast milk concentrations in the period 1996–2018. Intake values are expressed in pg I-TEQ/day (1998) or in pg WHO-TEQ/day (2002, 2006, 2012 and 2018). Breast milk concentrations are given in pg WHO-TEQ/g fat.

sample, were calculated. PCA provided a three-dimensional model with 3 principal components (PC1, PC2 and PC3), which explain 32%, 17% and 16% of the variance, respectively. The score plot allows us to rapidly locate similar observations. In order to facilitate the analysis, the scores plots of PC1 vs. PC2, and PC1 vs. PC3 were labeled in different colors considering: a) the area of collection, b) the year of collection, and c) the type of food item. Observations that are similar fall close to each other in the score plot. In our case, all breast milk samples appeared clustered together irrespectively of the area (Fig. 3a) and year (Fig. 3b) of collection. This, together with the fact that profiles have not changed over time, indicates a lack of influence of the HWI on the burdens of PCDD/Fs in the surrounding environment. For the general population, the dietary habits and the levels of food contamination explain the main variations in human exposure to PCDD/Fs (Sirot et al., 2012). Finally, PCA analysis showed that fish, meat, and oils and fats were associated with the breast milk cluster (Fig. 3c) indicating the influence of those food items on the breast milk profiles. A recent study by González et al. (2018) in the area under evaluation, indicates a change in the dietary patterns, with a reduction of the intake of dairy products, pulses, and fish and seafood. However, it was also pointed out that fish and seafood are still among the food groups with the highest contribution in the dietary exposure to PCDD/Fs in the area, since the baseline study (1996–1998). It is in agreement with the lack of changes in the PCDD/F congener profiles in breast milk samples over time, and the predominant influence of fish, meat, and oils and fats in breast profiles (Bocio and Domingo, 2005; González et al., 2018; Perelló et al., 2012). In recent years, a number of studies have assessed the PCDD/F dietary intake in various countries (Diletti et al., 2018; Perelló et al., 2012; Sirot et al., 2012; Wang et al., 2017; Windal et al., 2010). Fish and seafood have been identified as the main contributors to dietary exposure (EFSA, 2012). Papadopoulou et al. (2014) reported that the intake of red and white meat, and lean and fatty fish, was linked to high levels of PCDD/Fs and dioxin-like compounds in maternal blood of European pregnant women. Some studies have addressed a specific signature of each country in the levels of PCDD/Fs and other POPs in breast milk (Antignac et al., 2016; Krysiak-Baltyn et al., 2010; Nadal et al., 2004). Antignac et al. (2016) compared the profiles of an extended range of POPs (including PCDD/Fs, PCBs, PBDEs and pesticides) from human milk of women in Denmark, Finland and France. Regarding PCDD/Fs, they found that the three countries could be discriminated by the PCDD versus PCDF and the 1,2,3,6,7,8-HxCDD versus 1,2,3,4,7,8-HxCDD ratios. The latter ratio was previously identified as country discriminant by Krysiak-Baltyn et al. (2010), with samples of the same cohorts from Denmark and Finland. In turn, Nadal et al. (2004) evaluated the variation of PCDD/Fs in breast milk samples from various countries from Europe, North America and Asia, which were tried to correlate with the dietary habits. Some correlations between PCDD/F congener profiles and a higher consumption of fish were noticed in different countries. However, other factors, such as environmental exposure or fish origin, had also a key role in the PCDD/F congener profiles.

4. Conclusions

The current concentrations show that PCDD/Fs have significantly decreased (81%) since the baseline survey, which is in agreement with the trends also noticed in most developed countries. The present PCDD/F concentrations were in the low part of the range in comparison with data from other worldwide studies. Although some changes in dietary habits have occurred in recent years, the congener profiles of PCDD/Fs in breast milk have not changed since the baseline study, being mainly influenced by the intake of fish, meat, oils and fats. The results indicate that human milk levels of PCDD/Fs are not influenced by the HWI stack emissions, and they follow the decrease trend observed in other regions and countries where industrial emission legislations have been implemented.

Table 3
Median levels (pg/g fat) of PCDD/F congeners in human milk samples collected between 1996–1998 and 2017. Temporal trends (%).

Congener	1996–1998	2002	2007	2012	2017	1996/2002	1996/2017	1996/2012	1996/2017
2,3,7,8-TCDD	1.03	0.94	0.97	0.54	0.20	−9	−6	−48	−81
1,2,3,7,8-PeCDD	4.00	2.92	2.64	1.45	0.80	−27	−34	−64	−80
1,2,3,4,7,8-HxCDD	3.03	1.66	1.48	0.72	0.49	−45	−51	−76	−84
1,2,3,6,7,8-HxCDD	28.4	14.9	13.80	4.97	2.20	−47	−51	−83	−92
1,2,3,7,8,9-HxCDD	4.46	1.91	2.08	0.68	0.37	−57	−53	−85	−92
1,2,3,4,6,7,8-HpCDD	34.0	10.8	9.45	3.31	2.30	−68	−72	−90	−93
OCDD	143	42.6	53.2	20.6	15.0	−70	−63	−86	−90
2,3,7,8-TCDF	0.66	0.38	0.34	0.24	0.15	−42	−48	−64	−77
1,2,3,7,8-PeCDF	0.27	0.27	0.09	0.11	0.10	0	−67	−59	−63
2,3,4,7,8-PeCDF	7.92	5.48	4.83	3.63	1.80	−31	−39	−54	−77
1,2,3,4,7,8-HxCDF	3.08	1.88	1.50	0.96	0.66	−39	−51	−69	−79
1,2,3,6,7,8-HxCDF	2.51	1.69	1.48	0.87	0.63	−33	−41	−65	−75
2,3,4,6,7,8-HxCDF	ND	ND	0.14	0.36	0.31	–	–	–	–
1,2,3,7,8,9-HxCDF	0.99	0.68	0.54	0.05	0.12	−31	−45	−95	−88
1,2,3,4,6,7,8-HpCDF	2.17	1.37	1.00	0.05	0.72	−37	−54	−98	−67
1,2,3,4,7,8,9-HpCDF	0.15	ND	0.15	0.07	0.17	–	0	−57	13
OCDF	ND	ND	0.31	ND	0.43	–	–	–	–

ND: Not detected.

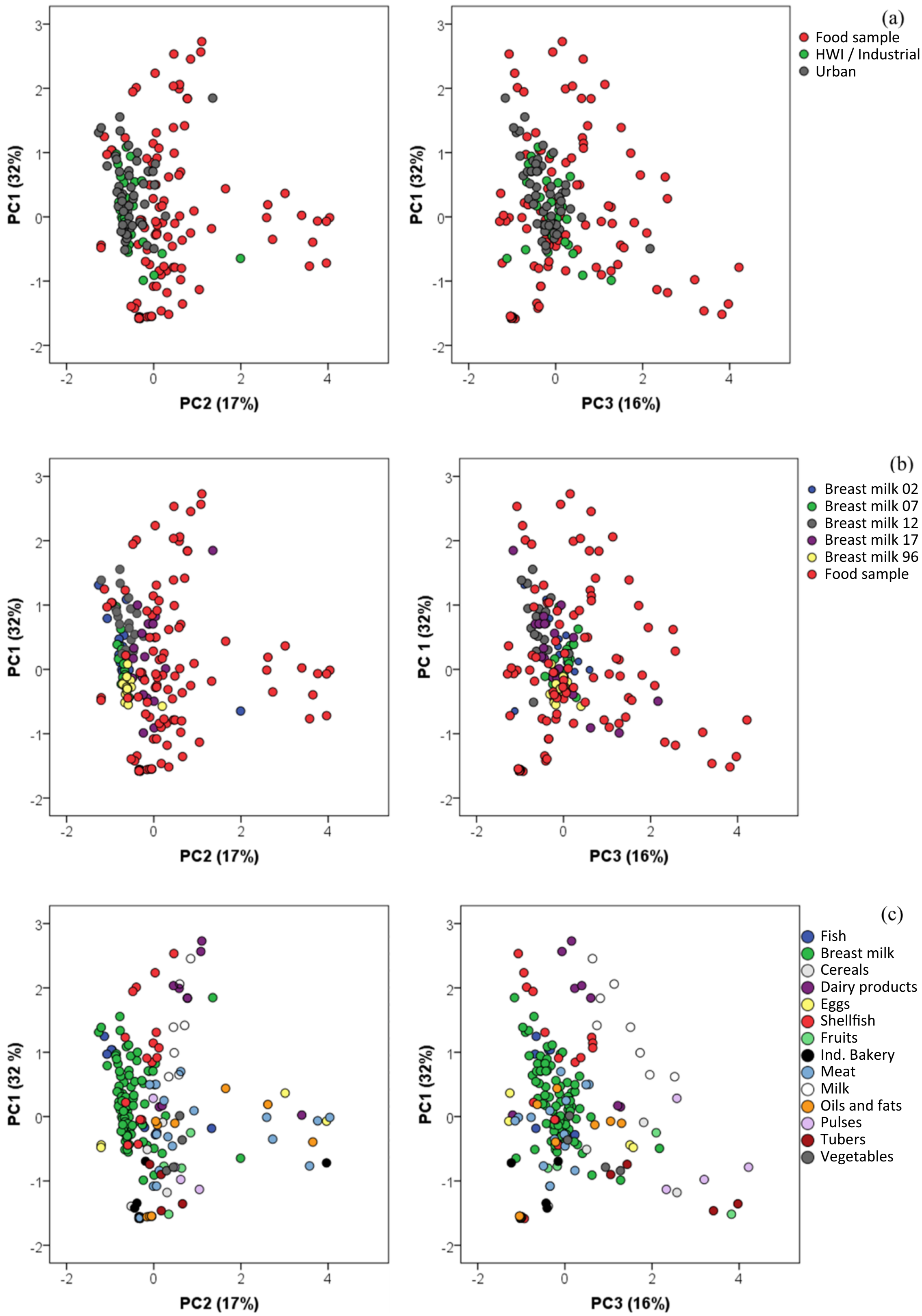

Fig. 3. Score plot of breast milk and food samples. PC1 and PC2, and PC1 and PC3 labeled in terms of a) area, b) period of collection of the breast milk samples, and c) food item.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envint.2019.01.074.

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