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Temporal trends of polychlorinated dibenzo-*p*-dioxins and dibenzofurans and dioxin-like polychlorinated biphenyls in mothers' milk from Sweden, 1972–2011 ☆

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ABSTRACT

Temporal trends of polychlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (DL-PCBs) in mothers' milk are still quite rare. Data are particularly scarce when it comes to concentrations from the last decade, 2000 and onwards. The aims of the present study were to assess temporal trends of PCDD, PCDF and DL-PCB in mothers' milk from Stockholm, 1972–2011 and to compare the results with previous analysis of some of the older samples.

The samples were analyzed by high resolution GC/MS and results were statistically evaluated for the periods, 1972–2011 and 2002–2011. The rate of which ∑PCDDs, ∑DL-PCBs and the ∑TEQ are decreasing (on pg/g fat WHO-TEQ2005) is higher in the last decade compared to the 40 year period, 1972–2011. A similar trend is indicated, but not confirmed, for ∑TEQ of PCDFs, probably due to too many PCDF congeners below LOQ in the period 2002–2011. Concentrations of ∑PCDDs, ∑PCDFs, ∑DLPCBs and ∑TEQ, all expressed as pg/g fat on TEQ-WHO2005-basis, show a statistically significant decline over time, 5.8–6.8% per year, 1972–2011. The last ten years the annual declines for ∑PCDDs, ∑DL-PCBs and ∑TEQ are 9.2–11% and for ∑PCDF, 5.4%. Congener specific trend analysis, 2002–2001, of PCDDs and DL-PCBs showed the same pattern, while the PCDF congeners showed no such general trend. The results from the re-analysis showed good agreement with slightly lower ∑TEQ1998 pg/g fat concentrations in six out of seven samples and mean difference of 13% in ∑TEQ1998. The study shows that time series can be elongated from previous studies, as long as the sample population remains the same.

1. Introduction

WHO initiated biomonitoring of persistent organic pollutants (POPs) in mothers' milk in 1976 and so far five rounds of the global survey have been carried out during 1987–2010 (UNEP, 2012; WHO, 2009). The aim of the global survey is to assess the concentrations of POPs, so far with emphasis on polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs) and dioxin-like (DL) biphenyls (DL-PCBs), hereafter referred to as "dioxins" in this article. The mothers' milk program is now part of the Stockholm Convention (Stockholm Convention). Apart from on the Stockholm Convention website, dioxin concentrations in mothers' milk around the world have been summarized in several publications (LaKind, 2007; Srogi, 2008; Tanabe and Minh, 2010). In particular, LaKind (2007) has made a comprehensive compilation and analyzed global data on $\sum TEQ_{1998}$ concentrations, including temporal trends. To summarize the findings by LaKind, the concentrations are decreasing globally (1975–2005). However, the study did not report a decline in the last years, 2003–2005. National/regional time trend studies show similar decreasing trends of "dioxins", including studies from Australia (Harden et al., 2004), Russia (Mamontova et al., 2005), Norway (Becher et al., 2002), Sweden (Lignell et al., 2009), and Japan (Hori et al., 1999). In a review from 1996, temporal trends up to that point are summarized and in short, studies from Germany, The Netherlands, Norway and Sweden all show the same general declining trend of ∑TEQ values (Alcock and Jones, 1996). Croes and coworkers summarized the results from a WHO mothers' milk survey from the European countries which show decreasing trends of ∑TEQ concentrations (Croes et al., 2013). In contrast, a study from Japan reports *status quo* of the "dioxin" concentrations, 1998–2004 (Kunisue et al., 2006). Studies with samples from the last decade are more limited but show decreasing "dioxin" concentrations in Belgium (Croes et al., 2012), Ireland (Pratt et al., 2012) and Spain (Schuhmacher et al., 2009). In Sweden, Norén and coworkers started monitoring of mothers' milk already in 1970. A large number of articles/reports concerning levels and time trends of POPs in mothers' milk from this monitoring program are summarized (with some new original data included) in a review article from the year 2000 (Norén and

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Table 1
Data on sampling year, number of donating mothers in each pool, which samples that were previously analyzed for PCDD/Fs and DL-PCBs and double samples analyzed.

Year	Mothers	Mean age (years)	*Primiparae* (%)	Previously analyzed[a]	Two samples
1972	75	27–28	NA[b]	YES	
1974	90	27–28	NA[b]	YES	
1976	78	27–28	NA[b]	YES	
1978	87	27–28	NA[b]		
1980	116	27–28	NA[b]	YES	
1988/89	140	30	58		
1990	60	30	65	YES	
1991	60	28	56	YES	
1992	40	29	65	YES	
1995	20	30	65		
1997	40	31	65	YES	
1999	20	31	70		
2000	10; 10	30	75		YES
2001	20	30	80		
2002	10; 10	30	80		YES
2003	15	31	67		
2004	10; 10	30	80		YES
2007	10; 10	27	100		YES
2008	9; 9	28	100		YES
2009	10; 10	31	100		YES
2010	10; 9	30[c]	100		YES
2011	11; 11	30	100		YES

[a] Norén and Meironyte (2000).
[b] Not available.
[c] Only available for 5 out of 19 mothers.

Meironyte, 2000), which reports decreasing levels of "dioxins" over time. This is supported by Lignell et al. (2009), who report decreasing levels of POPs, including "dioxins", in mothers' milk from Sweden during 1996–2006.

Only a few time series with multiple year sampling of mothers' milk exists, especially with samples from the last decade. In this study we re-analyze a set of samples from the original (composite) time trend study (Norén and Meironyte, 2000), to test comparability, as well as new samples from 1999 to 2011. This will help us answer if the decreasing concentrations of "dioxins" are leveling off, i.e. what is the trend for the first decade of the 21st millennia, and if it is possible to compare the established concentrations from previous studies directly. Hence, the aims of the present study were to assess temporal trends of PCDD, PCDF and DL-PCB in mothers' milk from Stockholm, 1972–2011, and to compare the results with previous analyses of some of the older samples.

2. Materials and method

Three major concerns were considered when choosing mothers' milk samples; i) to ensure comparability between the new and the previous analyses of Swedish mothers' milk; ii) to add samples taken in the past to fill gaps in the previous time trend and iii) to expand the aforementioned time trend study ending in 1997 (Norén and Meironyte, 2000) to obtain data ranging from 1972 to 2011. In total, 30 samples were analyzed and eight of these were non-identical samples from a given year. The samples consisted of pooled mothers' milk from multiple donors, all healthy native Swedish, but were not exclusively from *primiparae*. Further information concerning sample composition is presented in Table 1.

The samples, 50 g each, were provided by the Swedish Environmental Specimen Bank, Department of Environmental Research and Monitoring, Swedish Museum of Natural History. The samples were prepared in house before they were shipped, on dry ice, to Eurofins GfA Lab Service GmbH, Hamburg, Germany, for analysis according to the method described by Reis et al. (2007). In brief the method could be described as follows: ^{13}C-labeled surrogate standards were added to the samples followed by liquid–liquid extraction and subsequent gravimetric lipid determination prior to multiple column clean-up, including carbon column purification. The purified extracts were analyzed by GC/HRMS.

2.1. Statistical methods

To test for significant log-linear trends for PCDDs, PCDFs and DL-PCBs, log-linear regression analysis was performed for the entire investigated time period and for the most recent 10 years using the yearly arithmetic mean values. In cases where the regression line had a poor fit, a 3-point running mean smother was checked for statistical significance in comparison with the regression through an ANOVA (Nicholson et al., 1998). Potential outliers in the temporal trends were detected using a method described by Hoaglin and Welsch (1978). The suspected outliers are merely indicated in the figures and were included in the statistical calculations. Values below level of quantification (LOQ) were replaced by LOQ/2 prior to the statistical analyses. Power analysis was also carried out. The power was fixed to 80% and the minimum possible trend to be detected during a monitoring period of 10 years at a significant level of 5% was estimated. A significance level of 5% was used for all tests.

3. Results

Individual PCDD and PCDF congener concentration data are presented in Table 2, for each of the pooled mothers' milk samples analyzed, and with concentrations given on a weight basis per gram fat. Table 2 also includes ∑PCDD/PCDF concentrations, but expressed on basis of WHO-TEQ$_{1998}$ and WHO-TEQ$_{2005}$, in pg/g fat (Van den Berg et al., 1998; Van den Berg et al., 2006). The corresponding data are reported in Table 3 for DL-PCBs, ∑DL-PCBs and ∑TEQ (WHO$_{1998}$ and WHO$_{2005}$).

Based on the results presented in Tables 2 and 3, it is possible to calculate and present temporal trends of the analytes as determined in Stockholm mothers' milk from 1972 to 2011. Time series analyses were performed for all analytes and selected temporal trend data are presented as graphs in Figs. 1–4.

Temporal trends, 1972–2011, for ∑PCDDs, ∑PCDFs, ∑DL-PCBs and ∑TEQ (i.e. the sum of ∑PCDDs, ∑PCDFs and ∑DL-PCBs), based on pg/g fat WHO-TEQ$_{2005}$ concentrations, are presented in Fig. 1a–d). The relative annual decrease over the 40 year period for PCDDs, PCDFs, DL-PCBs and ∑TEQs are 6.1%, 6.1%, 6.9% and 6.5% respectively, with $p < 0.001$ in each case. The relative annual decreases over the last ten years for PCDDs, PCDFs, DL-PCBs and ∑TEQs are 10% ($p < 0.001$), 7.3% ($p < 0.001$), 12% ($p < 0.012$) and 10% ($p < 0.002$), respectively. The number of years required to detect an annual change of 10% varied between 6 and 10 years for the groups in Fig. 1a–d). The power to detect a 10% annual change was 100% for all of the full time series. The smallest possible trend to detect varied between 3.7 and 9.4% change per year during a decade.

Temporal trends, 1972–2011, for 2,3,7,8-TCDD, 1,2,3,7,8-PCDD and 1,2,3,6,7,8-HCDD, based on concentrations in pg/g fat, are presented in Fig. 2a–c). The relative annual decrease over the 40 year period for 2,3,7,8-TCDD, 1,2,3,7,8-PCDD and 1,2,3,6,7,8-HCDD are 6.1%, 5.9% and: 6.0% with $p < 0.001$ in each case. The annual relative decrease over the last ten years for 2,3,7,8-TCDD, 1,2,3,7,8-PCDD and 1,2,3,6,7,8-HCDD are 11%, 10% and: 10%, respectively, with $p < 0.001$ in each case. The number of years required to detect an annual change of 10% varied between 9–11 years for the three PCDD congeners and the power to detect a 10% annual change was 100% for the full time series. The smallest possible trend to detect varied between 6.9–19% change per year during a decade.

Temporal trends, 1972–2011, of 2,3,7,8-TCDF, 2,3,4,7,8-PCDF, 1,2,3,7,8-PCDF and 2,3,4,6,7,8-HCDF, based on concentrations in pg/g fat, are presented in Fig. 3a–d). The relative annual decrease over the 40 year period for 2,3,7,8-TCDF, 2,3,4,7,8-PCDF, 1,2,3,7,8-PCDF and 2,3,4,6,7,8-HCDF are 6.5%, 6.1%, 5.7% and 6.7%, respectively, with $p < 0.001$ in each case. The annual relative decrease over the last ten

Table 2
Concentrations (pg/g fat) of seven PCDD and ten PCDF congeners are presented. Also, WHO-TEQ$_{1998}$ and WHO-TEQ$_{2005}$ are presented for the sum of PCDDs and PCDFs (Van den Berg et al., 1998, 2006).

	1972	1974	1976	1978	1980	1988/89	1990	1991	1992	1995	1997	1999	2000:1	2000:2	2001
Fat content (%)	2.5	3.2	2.9	3.0	2.9	2.4	2.6	2.6	2.9	3.1	2.9	3.1	3.0	2.7	3.0
PCDD															
2,3,7,8-TetraCDD	<2.8	3.5	5.2	3.0	3.4	2.4	1.8	7.5	1.7	1.5	1.2	1.1	0.89	1.1	0.90
1,2,3,7,8-PentaCDD	9.4	7.2	7.3	7.8	7.1	5.2	4.8	4.1	3.8	3.6	3.3	2.7	2.0	2.2	2.3
1,2,3,4,7,8-HexaCDD	3.5	3.1	2.4	3.0	3.4	2.3	1.9	1.7	1.6	1.3	1.4	1.1	0.82	0.86	0.79
1,2,3,6,7,8-HexaCDD	28	23	24	27	25	20	20	15	16	14	12	9.8	7.3	8.1	8.3
1,2,3,7,8,9-HexaCDD	3.1	1.9	1.7	2.0	5.6	2.3	2.3	3.0	2.1	2.5	2.0	1.3	1.2	1.5	1.0
1,2,3,4,6,7,8-HeptaCDD	95	80	78	79	69	48	42	31	27	25	24	17	13	16	13
OctaCDD	430	340	320	380	330	230	240	170	140	110	110	96	74	80	77
PCDF															
2,3,7,8-TetraCDF	3.0	2.1	2.1	2.4	2.3	1.5	1.3	1.0	0.78	0.64	0.68	0.57	0.47	0.53	0.45
1,2,3,7,8-PentaCDF	1.3	0.84	0.76	1.0	0.66	0.46	0.43	0.39	0.30	0.26	0.28	0.24	0.23	<0.26	0.23
2,3,4,7,8-PentaCDF	31	23	25	26	22	14	13	10	10	10	8.7	7.2	5.5	6.1	6.3
1,2,3,4,7,8-HexaCDF	14	9.1	8.5	8.5	6.7	3.8	3.5	2.7	2.6	2.2	2.0	1.9	1.6	1.6	1.5
1,2,3,6,7,8-HexaCDF	7.7	5.5	5.4	5.6	4.7	3.1	2.8	2.4	2.3	1.9	1.9	1.7	1.4	1.5	1.4
1,2,3,7,8,9-HexaCDF	<0.28	<0.21	<0.27	<0.24	<0.22	<0.28	<0.28	<0.26	<0.24	<0.22	<0.24	<0.22	<0.25	<0.29	<0.22
2,3,4,6,7,8-HexaCDF	3.2	2.5	2.2	2.1	1.8	1.3	1.2	1.0	0.93	0.79	0.76	0.70	0.59	0.69	0.59
1,2,3,4,6,7,8-HeptaCDF	35	25.0	18	16	12	4.9	5.5	3.7	4.1	2.4	3.0	2.2	2.4	2.3	2.1
1,2,3,4,7,8,9-HeptaCDF	0.69	0.40	0.43	0.43	0.43	<0.27	<0.27	<0.26	<0.23	<0.21	<0.24	<0.21	<0.24	<0.28	<0.22
OctaCDF	1.9	1.2	1.6	0.81	1.0	2.2	<0.83	<0.79	<0.71	<0.66	<0.73	<0.65	<0.75	<0.88	<0.67
∑*PCDD/F*															
∑PCDD/F (WHO-TEQ$_{1998}$)[a]	32	28	31	30	27	19	17	20	14	13	11	9.3	7.2	8.0	7.9
∑PCDD/F (WHO-TEQ$_{2005}$)[a]	26	24	26	25	23	16	14	18	12	11	9.5	7.9	6.1	6.8	6.7

	2002:1	2002:2	2003	2004	2007:1	2007:2	2008:1	2008:2	2009:1	2009:2	2010:1	2010:2	2011:1	2011:2
Fat content (%)	3.4	3.6	2.8	3.7	3.9	3.9	4.1	3.5	4.0	3.0	4.0	3.8	3.2	3.7
PCDD														
2,3,7,8-TetraCDD	0.87	0.85	0.86	0.68	0.39	0.59	0.38	0.34	0.33	0.34	0.32	0.44	0.38	0.33
1,2,3,7,8-PentaCDD	2.3	1.9	2.1	1.7	1.2	1.5	1.1	0.78	1.1	0.87	0.92	1.1	1.0	0.85
1,2,3,4,7,8-HexaCDD	0.84	0.67	0.88	0.62	0.53	0.67	0.38	<0.34	0.39	0.40	0.30	0.51	0.42	0.36
1,2,3,6,7,8-HexaCDD	7.3	6.2	7.2	5.1	4.5	5.1	3.3	2.4	4.2	2.5	2.3	3.5	3.4	2.8
1,2,3,7,8,9-HexaCDD	1.1	1.0	0.94	0.80	0.96	1.3	0.67	0.74	0.71	0.68	0.55	0.70	0.73	0.69
1,2,3,4,6,7,8-HeptaCDD	14	9.2	12	7.2	6.1	8.6	5.8	4.0	4.8	3.8	4.2	4.2	5.8	6.2
OctaCDD	60	54	64	48	42	56	39	31	30	25	27	32	38	34
PCDF														
2,3,7,8-TetraCDF	0.41	0.60	0.62	0.38	<0.40	0.58	0.49	<0.47	<0.37	<0.50	<0.38	<0.40	<0.45	<0.40
1,2,3,7,8-PentaCDF	<0.19	0.26	0.27	<0.18	<0.28	<0.28	<0.28	<0.32	<0.26	<0.35	<0.26	<0.28	<0.31	<0.28
2,3,4,7,8-PentaCDF	6.1	5.4	5.7	4.6	3.2	4.7	3.4	2.5	2.8	3.0	3.0	3.9	3.1	2.9
1,2,3,4,7,8-HexaCDF	1.5	1.3	1.5	1.2	1.2	1.3	1.1	1.0	0.83	1.0	0.78	1.2	1.0	0.92
1,2,3,6,7,8-HexaCDF	1.4	1.3	1.4	1.1	1.0	1.1	1.0	0.85	0.81	0.89	0.76	1.1	1.0	0.84
1,2,3,7,8,9-HexaCDF	<0.21	<0.20	<0.26	<0.20	<0.31	<0.31	<0.31	<0.36	<0.29	<0.39	<0.29	<0.31	<0.35	<0.31
2,3,4,6,7,8-HexaCDF	0.70	0.54	0.54	0.52	0.45	0.63	0.61	0.53	0.48	0.49	0.37	0.51	0.52	0.51
1,2,3,4,6,7,8-HeptaCDF	9.5	1.6	1.6	1.6	2.7	3.4	1.8	1.9	1.0	1.1	1.1	1.1	2.2	1.2
1,2,3,4,7,8,9-HeptaCDF	<0.21	<0.19	<0.25	<0.19	<0.30	<0.30	<0.30	<0.35	<0.28	<0.38	<0.28	<0.30	<0.34	<0.30
OctaCDF	<0.63	<0.59	<0.78	<0.59	<0.93	<0.93	<0.92	<1.1	<0.86	<1.2	<0.87	<0.92	<1.0	<0.92
∑*PCDD/F*														
∑PCDD/F (WHO-TEQ$_{1998}$)[a]	7.8	6.7	7.3	5.8	4.2	5.6	4.1	3.0	3.6	3.4	3.3	4.3	3.7	3.3
∑PCDD/F (WHO-TEQ$_{2005}$)[a]	6.6	5.7	6.1	4.9	3.6	4.7	3.4	2.5	3.0	2.8	2.7	3.6	3.1	2.7

[a] Sums are calculated using LOQ/2 for analytes below LOQ.

years for 2,3,7,8-TCDF and 2,3,4,7,8-PCDF and 2,3,4,6,7,8-HCDF are 11% ($p < 0.002$) 7.9% ($p < 0.001$) and 5.3% ($p < 0.001$) respectively. No temporal concentration trend could be discerned for 1,2,3,7,8-PCDF, during the last ten years. The number of years required to detect an annual change of 10% varied between 7–9 years for the PCDF congeners and the power to detect a 10% annual change was 100% for all of the full time series. The smallest possible trend to detect varied between 3.4–7.9% change per year during a decade.

Temporal trends, 1972–2011, of the DL-PCB congeners, CB-118, CB-126 and CB-156 based on concentrations in pg/g fat are presented in Fig. 4a–c). The relative annual decrease over the 40 year period for CB-118, CB-126 and CB-156 are 7.6%, 7.0% and 5.8%, respectively, with $p < 0.001$ in each case. The annual relative decrease over the last ten years for CB-118, CB-126 and CB-156 are 9.7% ($p < 0.001$), 12% ($p < 0.015$) and 8.1% ($p < 0.003$), respectively. The number of years required to detect an annual change of 10% was 7–10 years, and the power to detect a 10% annual change was 100% for the full time series. The smallest possible trend to detect varied between 5.2%-9.0% change per year during a decade.

4. Discussion

The present study confirms decreasing temporal trends of the ∑TEQ of ∑PCDDs, ∑PCDFs and ∑DL-PCBs assessed herein (Table 2, Fig. 1). Likewise, it confirms significant concentration declines of the individual PCDD, PCDF and DL-PCB congeners analyzed. This was to be expected as the time series covers 40 years. The data are in accordance with previously obtained data for ∑PCDDs, ∑PCDFs and ∑DL-PCBs in mothers' milk from Stockholm, 1972–1997 (Norén and Meironyte, 2000). However, it is striking to see a steeper rate of decline over the most recent years,

Table 3
Concentrations (pg/g fat) of 12 DL-PCB congeners and the TEQ levels of each milk sample, using both the WHO TEQ_{1998} and TEQ_{2005} are shown (Van den Berg et al., 1998, 2006).

	1972	1974	1976	1978	1980	1988/89	1990	1991	1992	1995	1997	1999	2000:1	2000:2	2001
Fat content (%)	2.5	3.2	2.9	3.0.	2.9	2.4	2.6	2.6	2.9	3.1	2.9	3.1	3.0	2.7	3.0
PCB															
PCB 77	150[a]	33	21	28	28	21	36	120[a]	15	<9.8	<11	<9.7	<11	<13	<10
PCB 81	17	6.2	6.3	6.6	6.9	4.0	3.0	13	2.1	<1.3	1.5	1.7	<1.5	<1.8	1.5
PCB 105	14000	12000	13000	12000	9400	5200	5000	3900	3700	3400	2700	2200	1600	1900	1600
PCB 114	1900	1600	1700	2100	1600	1100	1000	860	790	780	670	490	350	490	480
PCB 118	64000	53000	56000	55000	43000	26000	25000	19000	18000	17000	14000	11000	8100	9400	8100
PCB 123	680	540	560	570	450	260	260	200	170	160	130	100	83	92	92
PCB 126	240	220	230	180	160	82	89	60	69	79	71	35	42	48	39
PCB 156	20000	15000	17000	19000	16000	12000	11000	9300	9300	8100	7700	6400	4900	6000	5400
PCB 157	3300	2800	3000	3400	2900	2200	2000	1700	1700	1500	1300	1200	880	1100	1000
PCB 167	7500	6000	6700	6800	5700	3900	3700	3000	2800	2600	2100	1900	1400	1500	1400
PCB 169	92	69	63	74	63	51	44	41	41	40	35	33	27	30	26
PCB 189	1600	1300	1400	1600	1300	940	1000	810	830	700	670	640	410	510	560
∑DL-PCB (WHO-TEQ_{1998})[b]	46	39	42	38	32	20	20	15	16	16	14	9.3	8.6	10	8.7
∑DL-PCB (WHO-TEQ_{2005})[b]	30	26	28	24	21	11	12	8.4	9.3	10	9.0	5.2	5.5	6.3	5.2
∑TEQ															
∑TEQ (WHO-TEQ_{1998})[b]	78	67	73	68	60	38	37	35	29	28	25	19	16	18	17
∑TEQ (WHO-TEQ_{2005})[b]	56	50	54	48	44	27	26	26	21	21	19	13	12	13	12

	2002:1	2002:2	2003	2004	2007:1	2007:2	2008:1	2008:2	2009:1	2009:2	2010:1	2010:2	2011:1	2011:2
Fat content (%)	3.4	3.6	2.8	3.7	3.9	3.9	4.1	3.5	4.0	3.0	4.0	3.8	3.2	3.7
PCB														
PCB 77	<9.5	<8.9	<12	<8.9	<14	<14	<14	<16	<13	<17	<13	<14	<16	<14
PCB 81	1.5	<1.2	1.8	1.3	<1.8	<1.9	<1.8	<2.2	<1.7	<2.3	<1.7	<1.8	<2.1	<1.8
PCB 105	1500	1700	1700	1400	930	1600	840	660	770	880	830	1100	680	810
PCB 114	430	360	450	300	190	300	200	150	150	200	220	280	180	150
PCB 118	8100	8100	8800	6400	4600	7000	4400	3400	3800	3700	3900	5100	3400	3900
PCB 123	78	89	94	66	45	79	47	38	51	45	43	62	35	43
PCB 126	34	54	38	32	28	43	13	10	20	12	19	20	17	17
PCB 156	4500	4100	4600	3200	2600	3700	2600	1900	2300	1800	2500	2900	2500	1800
PCB 157	880	680	880	640	460	650	460	330	360	330	450	540	430	320
PCB 167	1300	1200	1400	970	710	910	610	460	570	460	540	630	520	480
PCB 169	24	23	21	17	16	18	14	<10.8	13	<11.6	13	13	16	<9.2
PCB 189	390	360	410	300	220	340	190	150	220	130	190	230	200	140
∑DL-PCB (WHO-TEQ1998)[b]	7.6	9.2	8.1	6.3	5.2	7.6	3.6	2.6	4.0	2.8	4.1	4.6	3.8	3.3
∑DL-PCB (WHO-TEQ2005)[b]	4.7	6.6	5.0	4.1	3.6	5.2	2.0	1.2	2.6	1.4	2.5	2.7	2.4	1.9
∑TEQ														
TOTAL-TEQ (WHO-TEQ_{1998})[b]	15	16	15	12	9.4	13	7.7	5.6	7.6	6.1	7.4	8.9	7.5	6.6
TOTAL-TEQ (WHO-TEQ_{2005})[b]	11	12	11	8.9	7.2	9.9	5.4	3.7	5.7	4.2	5.2	6.2	5.5	4.6

[a] Values contain a degree uncertainty due to poor recovery of the corresponding ^{13}C-labeled surrogate standard.
[b] Sums are calculated using LOQ/2 for analytes below LOQ.

2002–2011 for the ∑PCDD and ∑DL-PCB TEQs, than for the full period. In contrast, the steepness of the ∑PCDF TEQ decreasing time trend has not changed much over time. Several of the PCDFs are below LOQ during the latter 10 years, allowing no trend analysis, while 2,3,7,8-TCDF and 2,3,4,7,8-PCDF (WHO-TEF_{2005} = 0.1 and 0.3) both show stronger and significant declines over the recent 10 years. However, 1,2,3,4,7,8-HCDF and 1,2,3,6,7,8-HCDF (WHO-TEF_{2005} = 0.1 and 0.1) show a similar significant decrease as over the 40 year period. 2,3,4,6,7-HCDF and 2,3,4,6,7,8-HCDF show no statistical significant trend ($p > 0.05$) for the last decade. Still, a majority of the PCDD, PCDF and DL-PCB congeners decrease faster during the last decade than during the whole 40 year period and the congeners that do not decrease are difficult to assess since they all have several concentration points below LOQ. Altogether we therefore conclude that the "dioxins" decline faster today than previous decades. This is to be regarded as a positive outcome of the management of dioxin sources and the official advice given to pregnant and nursing women in Sweden (NFA, 2013). The results reported herein are particularly good news for nursing mothers and their children, both in Sweden and beyond. The latter, because the steeper decline of dioxins in mothers' milk over the last decade confirms that it is possible to make a change through strict management of dioxin sources.

It is previously reported that certain, in particular PCDF, congeners do not show decreasing time trends (Lignell et al., 2009; Pratt et al., 2012; Solomon and Weiss, 2002). In these reports no statistically significant decreases of temporal trends were observed for 2,3,7,8-TCDF, 1,2,3,7,8-PCDF and 2,3,4,6,7,8-HCDF, between 1996 and 2006. The increase in concentration of 2,3,4,7,8-PCDF between sampling times reported in Irish mothers' milk (Pratt et al., 2012) could not be observed in the present study. In fact, a tenfold decrease for the whole series and a halving of the concentrations between 2002 and 2010, see Table 2, duplicate samples for 2002: 5.4; 6.1 and 2010: 3.0; 3.9 pg/g fat, for the same sampling years as the Irish study. The authors of the Irish study explain the increase of 2,3,4,7,8-PCDF as a result of the selected sampling groups, changing from a rural to a more urban population.

When looking into the actual concentrations of "dioxins" in mothers' milk reported in recent years (milk that includes samples from 2008 and later) the ∑TEQ_{2005} place the Swedish concentrations (this study) in the lower end of dioxin exposures (Table 4). This is supported by the ∑TEQ_{1998} concentrations, all of which are higher than the Swedish concentrations. The ∑PCDD/Fs (both TEQ_{1998} and TEQ_{2005}) concentrations reported in the current study are comparatively low, but still

Table 4
Concentrations of "dioxins" reported in selected, recent studies with concentrations expressed in pg/g fat (Van den Berg et al., 1998, 2006).

Country	Year	∑PCDD/F (mean) TEQ_{1998}	∑PCDD/F (mean) TEQ_{2005}	∑PCDD/F (median) TEQ_{2005}	∑DL-PCB (mean) TEQ_{1998}	∑DL-PCB (mean) TEQ_{2005}	∑TEQ (mean) TEQ_{1998}	∑TEQ (mean) TEQ_{2005}	Reference
Africa	'05–'11			3.6					UNEP (2011)
Antigua & Barbuda	'07–'09							4.3	UNEP (2009)
Asia & the Pacific	'05–'11			4.5					UNEP (2011)
Belgium	'09–'10	8.4[a]	6.9[a]		5.8[a]	3.7[a]	14[a]	11[a]	Croes et al. (2013)
Central & Eastern Europe	'05–'11			5.9					UNEP (2011)
Chile	'07–'09							9.7	UNEP (2009)
Ghana	'07–'09							3.2	UNEP (2009)
GRULAC[b]	'05–'11			5.6					UNEP (2011)
Ireland	2010	6.32			3.34		9.66		Pratt et al. (2012)
Italy	'08–'09	4.6–6.1	3.8–4.9		6.2–6.9	4.8–5.7	11–13	8.6–11	Ulaszewska et al. (2011)
Italy	'08–'09							4.3–15[c]	Bianco et al. (2013)
Korea	'07–'09							4.0	UNEP (2009)
Nigeria	'07–'09							3.1	UNEP (2009)
Senegal	'07–'09							7.2	UNEP (2009)
Sweden	2011	3.3; 3.7	2.7; 3.1		3.3; 3.8	1.9; 2.4	6.6; 7.5	4.6; 5.5	Current study
Uruguay	'07–'09							6.9	UNEP (2009)
Western Europe & other States	'05–'11			6					UNEP (2011)
Vietnam	2008			2.7; 6.6					Nhu et al. (2011)
Vietnam	2008			5.2					Manh et al. (2013)

[a] Geometric mean concentrations.
[b] Group of Latin America & Caribbean Countries.
[c] TEQ not specified.

it is a limited data set to compare with. Only a few studies report concentrations of ∑DL-PCBs, but the concentrations obtained in this study are low to medium. The study from Croes et al. (2013) also includes concentrations obtained from CALUX-assays. These are not included in Table 4 since more comparable, GC–MS analysis derived, results from the same samples are available.

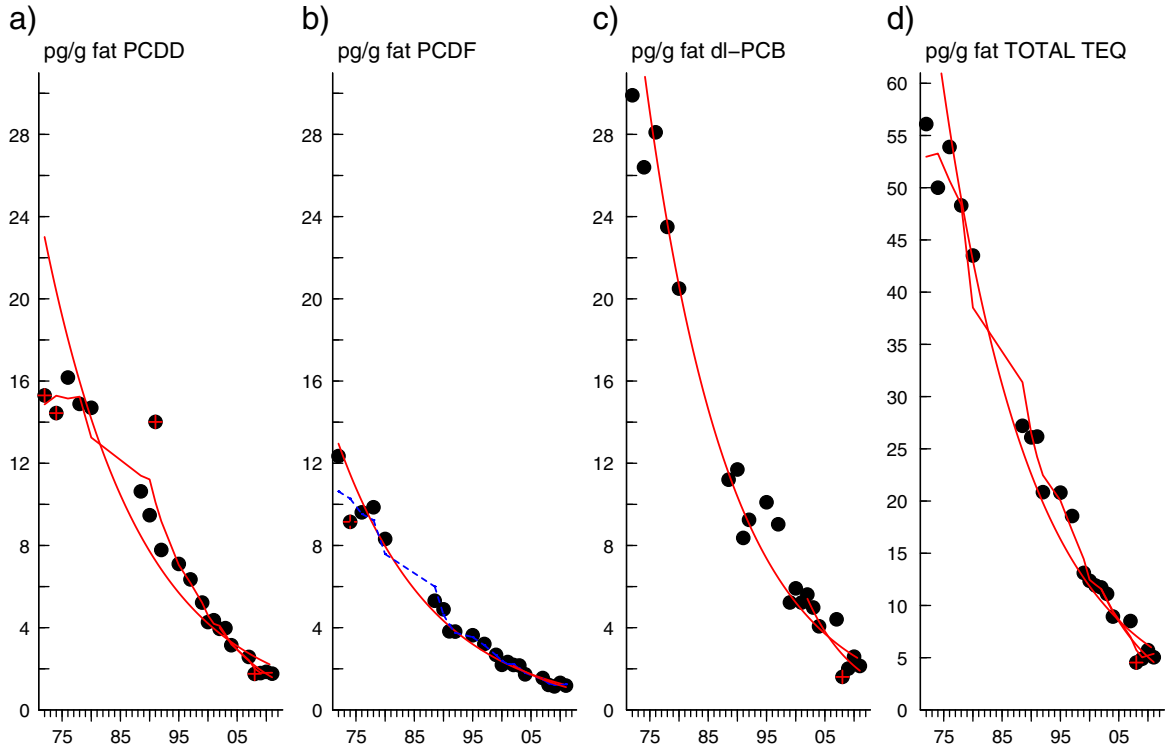

Fig. 1. Temporal trends of $TEQ_{(WHO-2005)}$ for PCDDs, PCDFs, DL-PCBs and ∑TEQ (∑TEQ PCDDs + ∑TEQ PCDFs + ∑TEQ DL-PCBs) (pg/g fat) in mothers' milk from Stockholm, 1972–2011. The linear red lines ($p < 0.05$) are based on log-linear regression analyses. The red, as well as the blue dotted, non-linear lines ($p < 0.05$ and $0.05 < p < 0.1$, respectively) are smoothers fitted to the annual mean values. A red cross represents a suspected outlier.

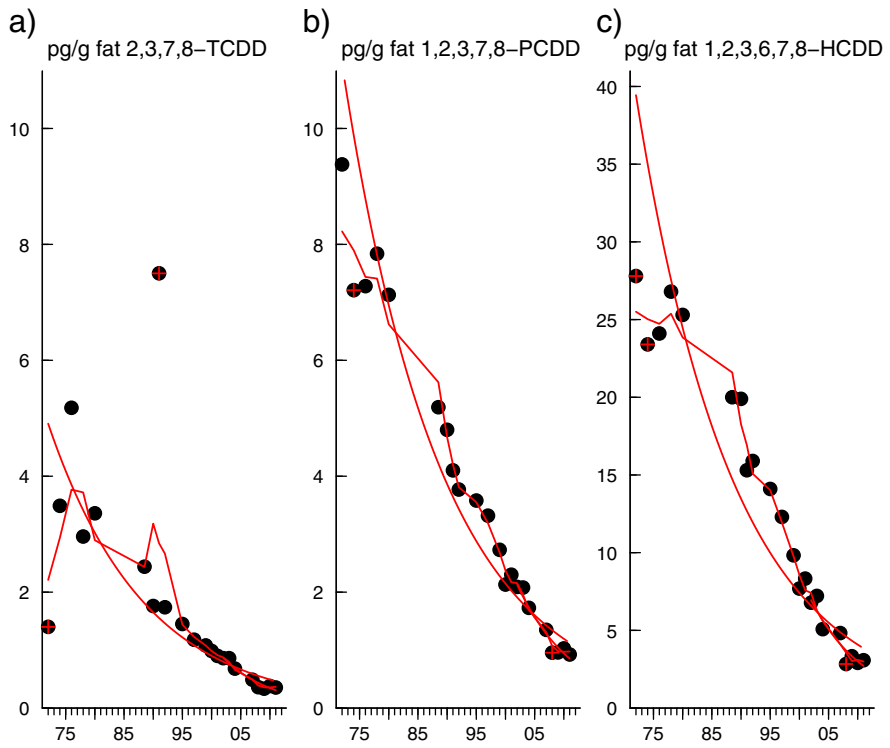

Fig. 2. Temporal trends of 2,3,7,8-TCDD, 1,2,3,7,8-PCDD and 1,2,3,6,7,8-HCDD (pg/g fat) in mothers' milk from Stockholm, 1972–2011. The linear red lines ($p < 0.05$) are based on log-linear regression analyses. The red non-linear lines ($p < 0.05$) are smoothers fitted to the annual mean values. A red cross represents a suspected outlier.

In order to certify the analytical results between previously reported data (Norén and Meironyte, 2000) and the results presented herein, several samples were selected for reanalysis. The results from the two occasions for analyses, 2000 and 2013, respectively, are visualized in Fig. 5. The concentration differences are rather small, with the highest discrepancy observed for the sample taken in 1972 (Fig. 5). Also, the

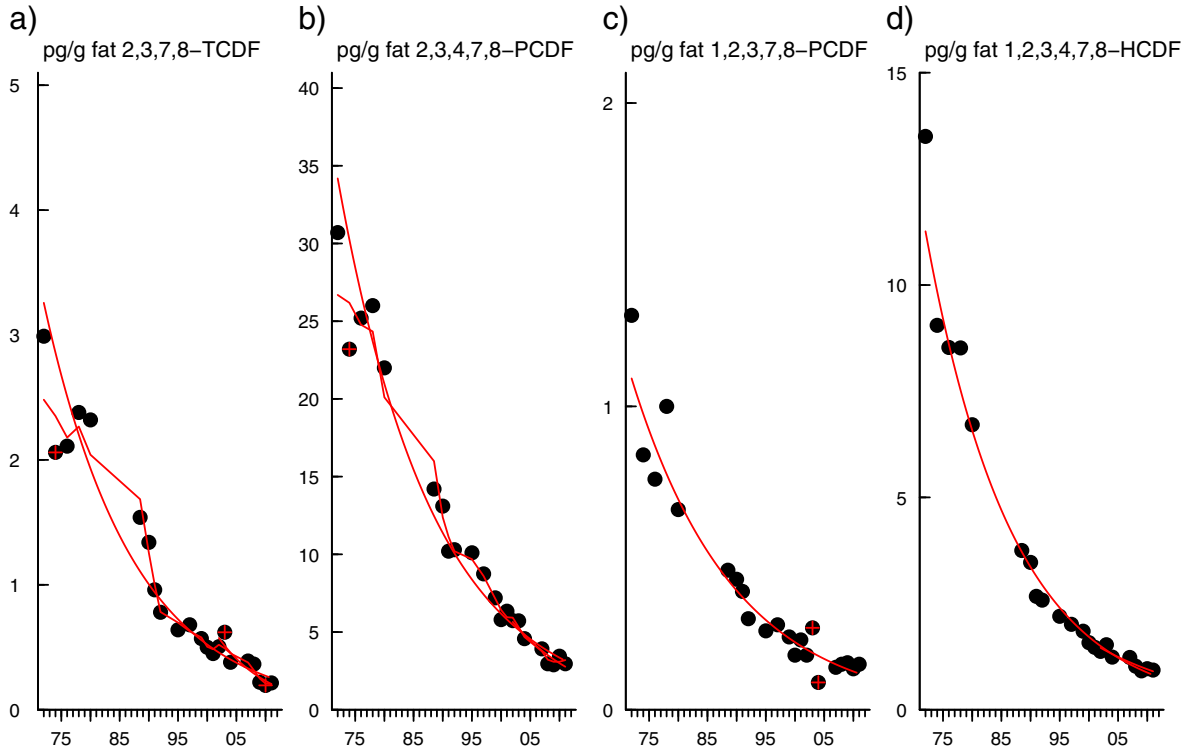

Fig. 3. Temporal trends of 2,3,7,8-TCDF, 2,3,4,7,8-PCDF, 1,2,3,7,8-PCDF and 1,2,3,4,7,8-HCDF (pg/g fat) in mothers' milk from Stockholm, 1972–2011. The linear red lines ($p < 0.05$) are based on log-linear regression analyses. The red non-linear lines ($p < 0.05$) are smoothers fitted to the annual mean values. A red cross represents a suspected outlier.

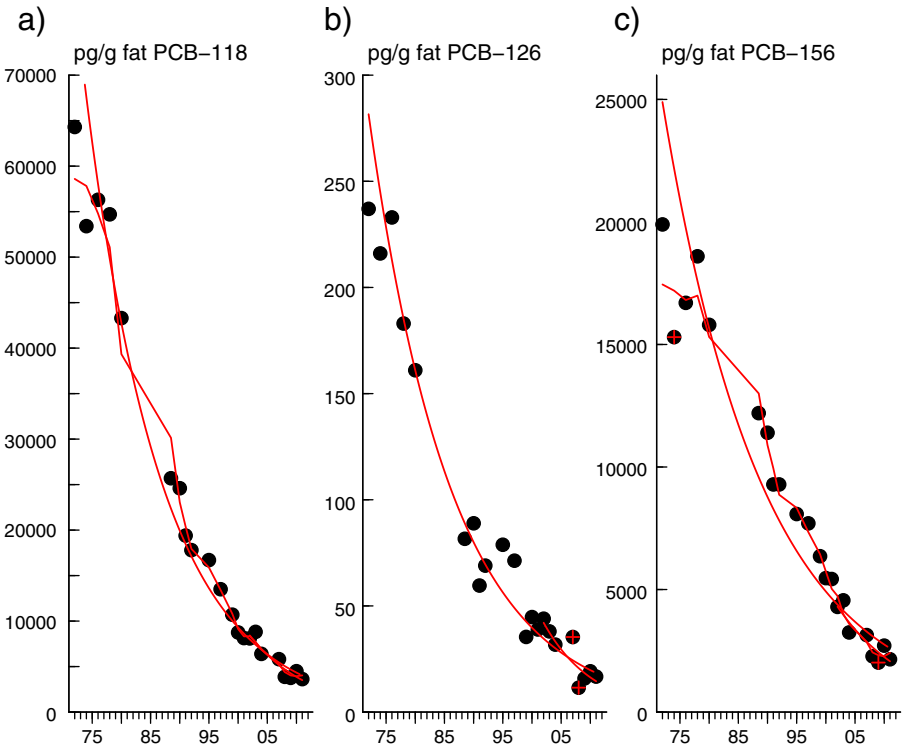

Fig. 4. Temporal trends of CB-118, CB-126 and CB-156 (pg/g fat) in mothers' milk from Stockholm, 1972–2011. The linear red lines ($p < 0.05$) are based on log-linear regression analyses. The red non-linear lines ($p < 0.05$) are smoothers fitted to the annual mean values. A red cross represents a suspected outlier.

relative proportions of ∑PCDDs, ∑PCDFs and ∑DL-PCBs, are in rather good agreement for all years. In some further detail, the previous analysis seems to have yielded a somewhat higher result on pg/g fat $\sum TEQ_{1998}$ basis compared to the current study with the exception of one of the samples, the one from 1980. Further, the mean and median differences between the studies were 13 and 15%, respectively, on $\sum TEQ_{1998}$ basis. The largest difference was found for ∑PCDDs, mean and median difference of 20% and 25% respectively. The differences for ∑DL-PCBs and ∑PCDFs were lower, approximately 10% mean and median difference for both groups of compounds. The result of this part of the present study shows that direct comparison between historical data and new data is possible for monitoring of PCDDs, PCDFs and DL-PBCs by applying the methodology described herein. Accordingly, it is possible to elongate existing time trends with new samples.

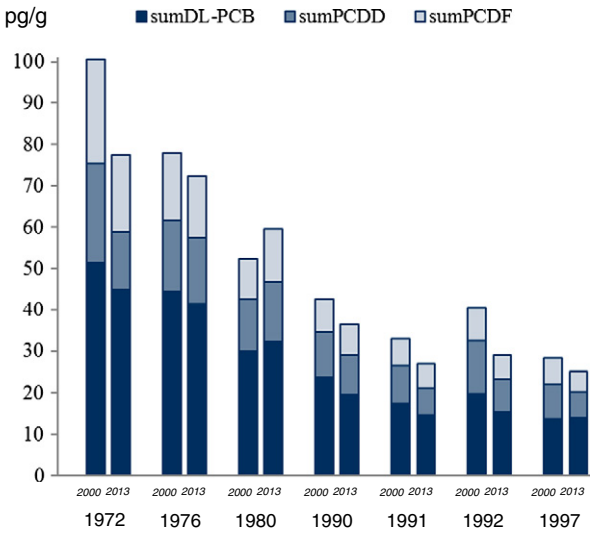

Fig. 5. The concentrations of PCDD, PCDFs and DL-PCBs previously analyzed and reported (Norén and Meironyte, 2000) compared to those presented in this study in the same samples, denoted 2000 and 2013 respectively. The TOTAL-TEQ-value (WHO_{1998}) of each sample is divided in three segments: ∑PCDDs, ∑PCDFs and ∑DL-PCBs.

Fig. 6 shows the quotas of the PCDDs, PCDFs and DL-PCBs of the $TOTAL\text{-}TEQ_{2005}$ for each sample of the time trend, 1972–2011, presented herein. It can be generalized that half of the ∑TEQ is made up of DL-PCBs, and the other half comprise of somewhat more PCDDs than PCDFs. Time trend analyses of the three fractions show a relative annual decrease over the 40 year period for the DL-PCBs, 0.44% per year ($p < 0.49$), but show no statistical significant trend for the last decade. The PCDDs and PCDFs show no statistical significant trend for either time period.

Comparability between studies from the literature, even when it comes to the same matrix — mothers' milk, is strongly hampered by several facts. First, the present lack of original congener specific data, presented either on a weight basis or on a molar basis, that is necessary to allow calculations of TEQs when new TEFs are applied, is not reported. Further, congener specific data are the most reliable data as a base for assessing temporal trends. Sum of analyte data may hide interesting and relevant temporal trends, as discussed for the PCDFs above. Second, the lack of unified sampling strategies influences the results. To promote the best possible sampling strategy it is relevant to apply the instructions from the WHO milk program (UNEP, 2012) or something as close to this as possible. Third, the lack of long term temporal trend analysis strongly hampers spatial comparisons of such trends.

5. Conclusions

The rate of which ∑PCDDs, ∑PCDFs ∑DL-PCBs and the ∑TEQ are decreasing (on pg/g fat $WHO\text{-}TEQ_{2005}$) is steeper in the last decade compared to the 40 year period, 1972–2011. The declines for PCDDs, PCDFs, DL-PCBs and ∑TEQs are 10%, 7.3%, 12% and 10% per year, last decade, compared to 6.1%, 6.1%, 6.9%% and 6.5% per year, 1972–2011. The

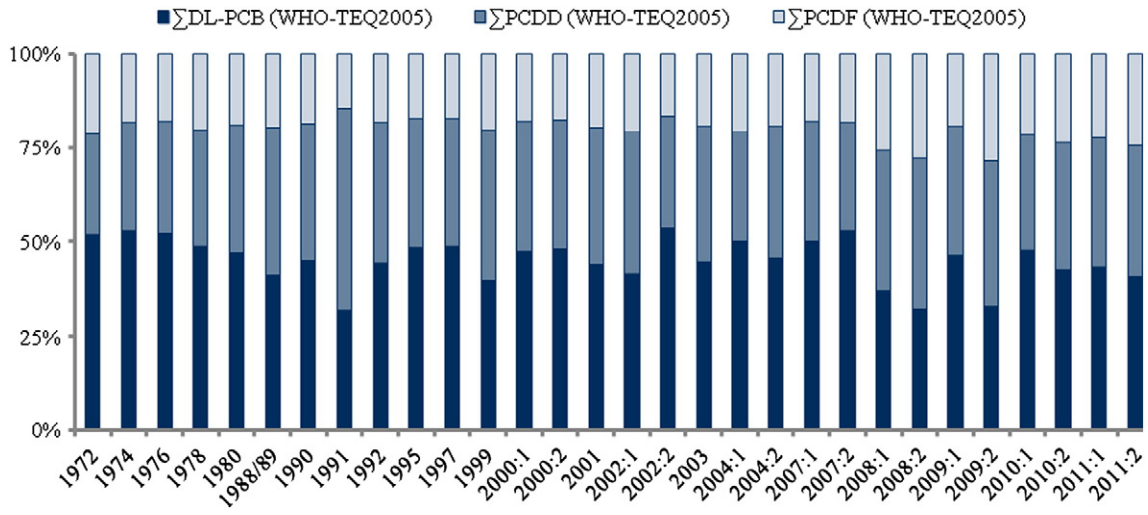

Fig. 6. Composition of the time series from 1972 to 2011. The TOTAL-TEQ-value (WHO_{2005}) of each sample is divided into three segments: ∑PCDDs, ∑PCDFs and ∑DL-PCBs.

difference in steepness, between the whole time period and the last ten years, is much smaller for ∑TEQ of PCDFs than for the other groups, likely due to too many PCDF congeners below LOQ, 2002–2011. The faster rate of decline over this period of time is confirmed by the temporal trends of the individual "dioxins", as determined on a weight basis. The faster drop in "dioxin" concentrations in mothers' milk in Sweden is a mirror of successful measures for lowering dioxin exposures. The good agreement between historical data and new data supports the elongation of existing monitoring series or data points, within the monitoring program. In contrast, it is still very difficult to compare results between monitoring programs due to differences in sampling strategies, reporting and lack of long term temporal studies of dioxins in mothers' milk.

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