PCDD/Fs, PCBs, PBDEs, TBBPA and HBCD in compost and digestate

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Introduction

About 17 million tons of organic household and green waste are collected annually in the EU resulting in 9 million tons of compost. Composting and compost application to the soil follow the principle of recycling and sustainability. Compost can also have a positive effect on physical, chemical, and biological soil parameters. In order to improve knowledge on persistent organic pollutants (POPs) in compost and digestate and to contribute to a safe application of compost in agriculture, a wide-ranging project entitled 'Organic pollutants in compost and digestate in Switzerland' was launched. Within this project, a monitoring network of some 50 composting and digestion plants in Switzerland has been established. Sampling accounts for processes that might be of relevance for the fate and behavior of POPs such as different feedstock material (organic household waste, green waste), treatment processes (composting, digestion), catchment areas (urban, rural), and seasons (summer, winter). POP data gathered from six composting facilities are presented in this preliminary study. The environmental contaminants determined in these samples included polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F), polychlorinated biphenyls (PCB), tetrabromobisphenol A (TBBPA), polybrominated diphenyl ethers (PBDE) and hexabromocyclododecane (HBCD).

Methods and Materials

Samples: Samples were collected in six Swiss compost facilities (see Table 1).

Analytical method for PCDD/F, PCB and PBDE: About 70 g compost dried at room temperature was soxhlet extracted with toluene for 24 hours. The extracts were filtered (Na_2SO_4) and adjusted to a volume of 250 ml. An aliquot of 40 ml was spiked with $^{13}C_{12}$-labeled PCDD/F, PCB, and PBDE. Clean-up of the samples included gel permeation chromatography, treatment with concentrated sulphuric acid, chromatography on multilayer silica, alumina, and carbon AX-21 as described in the literature[1,2]. The PBDE were collected as fraction passing the carbon AX-21 column, whereas the PCDD/Fs and the non-*ortho*-substituted PCB (77, 81, 126 and 169) were collected after the back flush of the carbon AX-21 column with toluene. Analysis of PCDD/F, PCB and dioxin-like PCB (DL-PCB) was carried out using GC/HRMS on a 60 m × 0.25 mm J&W DB-Dioxin capillary column (film thickness 0.15 µm). Analysis of PBDE, except decabromodiphenyl ether (BDE-209), was carried out on a 30 m × 0.25 mm RTX-5 Sil MS capillary column (film thickness 0.10 µm). The analysis of BDE-209 was carried out by on-column injection on a 10 m × 0.28 mm capillary column coated with 0.10 µm polydimethylsiloxane.

Analytical method for TBBPA and HBCD: About 50 g compost dried at room temperature was soxhlet extracted with acetone/n-hexane (1:1 v/v) for 24 hours. The extracts were filtered (Na_2SO_4) and adjusted to a volume of 100 ml. A 10 ml aliquot was spiked with $^{13}C_{12}$-labeled TBBPA and $^{81}Br_6$-labeled HBCD. The analysis of TBBPA was carried out after acetylation with acetic anhydride and cleanup over silica by GC/HRMS on a 30 m × 0.25 mm RTX-5 Sil MS capillary column (film thickness 0.10 µm). After clean-up over silica, total HBCD concentrations were determined by GC/HRMS using the same capillary column as for TBBPA. More details on clean-up and the analytical method used are given in the literature[2].

Results and Discussion

The results of the investigation are summarized in Table 1.

Table 1: POP concentrations in urban compost samples (ng/kg dw, all values rounded to two significant digits).

Sample no.	**1**	**5**	**10**	**16**	**17**	**19**	**Blank**
Characterization of compost	Organic household waste[a] (winter)	Digestate (winter)	Organic household waste[a] (winter)	Organic household waste[a] (autumn)	Green waste[b] (autumn)	Digestate (autumn)	
Sum PCDD	20	270	520	620	1100	820	1.0
Sum PCDF	58	78	94	110	450	150	1.1
Sum PCDD/F	1200	340	610	730	1500	970	2.1
PCDD/F WHO-TEQ	1.6	2.5	3.7	4.4	20	6.0	<0.37
DL-PCB WHO-TEQ	1.7	3.6	4.4	5.4	4.7	6.1	0.014
PCB-28	240	500	990	600	400	510	11
PCB-52	1100	2100	2300	2400	1700	3100	19
PCB-101	2400	4900	5300	5300	4600	8000	22
PCB-138	3600	8700	7200	7900	6700	13000	17
PCB-153	3100	7400	6400	6700	5300	10000	17
PCB-180	1500	4900	3100	3500	2400	5900	8.3
Sum indicator PCB	12000	29000	25000	26000	21000	41000	94
BDE-28	12	21	27	45	100	28	0.19
BDE-47	540	590	740	1300	1100	1100	9.5
BDE-99	720	640	740	560	720	1200	7.4
BDE-100	160	140	160	260	230	280	1.8
BDE-153	61	97	66	90	110	150	6.2
BDE-154	73	76	80	130	130	150	0.80
BDE-183	45	81	50	93	94	94	29
BDE-209	4800	9200	12000	10000	5700	20000	460
Sum BDE-28 - 183	1600	1600	1900	2500	2500	3000	54
Sum PBDE incl. BDE-209	6400	11000	14000	13000	8100	23000	500
TBBPA	1300	1400	450	2003	1100	560	40
HBCD	19000	160000	170000	23000	39000	100000	140

a) Mixture of kitchen waste, garden waste and small amounts of paper
b) Organic waste from private gardens and public areas

PCDD/F and PCB: The PCDD/F WHO-TEQ of the six samples were 1.6 to 20 ng/kg dry weight (dw), with an average of 6.4 ng/kg dw and a median of 4.1 ng/kg dw. These values are similar to I-TEQ concentrations in 101 compost samples reported by Fiedler et al. (1994)[3] who observed concentrations between 7.5 and 18 ng I-TEQ/kg dw (median 11.3 ng I-TEQ/kg dw). The homologue profile of the PCDD/F is dominated by the PCDD with a ratio PCDD/PCDF of 4.1 ± 1.5. The PCDD are dominated by OCDD followed by HpCDD and HxCDD. For the PCDF the dominating homologues are TCDF followed by PeCDF and HxCDF.

The DL-PCB WHO-TEQ of the samples were between 1.7 and 6.1 ng/kg dw (average 4.3 ± 1.4 ng/kg dw, median 4.6 ng/kg dw). Total WHO-TEQ (PCDD/F and DL-PCB) of the samples were 3.2 to 25 ng/kg dw, (average 10.7 ± 7 ng/kg dw, median 9 ng/kg dw). The relative contribution of the DL-PCB to the total WHO-TEQ was 48% ± 13. Therefore, dioxin-like PCB should be included in the analysis of compost samples for calculating the total WHO-TEQ. Recently, similar data were published by Kerst et al.[4] who observed a relative contribution of the DL-PCB of up to 50% in 22 samples from composting plants (median 30%, range 20 – 50%). The major contributions to the WHO-TEQ are due to PCB-126 (70% ± 4.5) followed by PCB-118 (11% ± 1.5), PCB-156 (9.2 ± 2), and PCB-105 (4.8 ± 0.7). These four congeners cover up to 95% ± 0.5 of the WHO-TEQ of DL-PCB.

PBDE, TBBPA, and HBCD: The total concentrations of the PBDE congeners 28, 47, 99, 100, 153, 154, and 183

ranged from 1600 to 3000 ng/kg (average 2200 ± 500 ng/kg dw). The Bavarian environmental protection agency reported higher PBDE concentrations (sum of 13 PBDE congeners, without BDE-209) in compost of 6600 to 37000 ng/kg dw (average 12000 ng/kg dw). The concentrations of decabromodiphenyl ether (BDE-209) in our samples were 4800 to 20000 ng/kg dw (average 10000 ± 5000 ng/kg dw). The contribution of PBDE to the total PBDE concentration (sum of BDE-28, 47, 99, 100, 153, 154, 183 and 209) in our samples is 81% ± 6.4. The normalized PBDE congener patterns of the samples are shown in Figure 1. The congener patterns of samples no. 1, 5, 10 and 19 are similar to the technical pentabromodiphenyl ether Bromkal 70-5 whereas the patterns of samples no. 16 and 17 are distinctly different. The different patterns are reflected in the ratio of BDE-47/BDE-99: For Bromkal 70-5 and samples no. 1, 5, 10 and 19 the ratio is 0.92 ± 0.09 whereas for samples no. 16 and 17 the ration increases to 2.3 and 1.5, respectively. This difference may indicate transformation, e.g. biodegradation, of BDE-99 during the composting process: Compost samples no. 16 and 17 were processed for 210 and 127 days, respectively, whereas the processing duration of the remaining samples was between 42 and 105 days, only.

TBBPA was found in all compost samples at concentrations of 450 to 2000 ng/kg dw (average 1100 ± 520 ng/kg dw).

HBCD was the most prominent brominated flame retardant (BFR) in the compost samples with concentrations between 19000 and 170000 ng/kg dw (average 85000 ± 62000 ng/kg dw). The relative contributions of the analyzed BFR are given in Figure 2.

Figure 1: Normalized PBDE congener patterns of technical pentabromodiphenyl ether Bromkal 70-5 and of compost samples (sample number followed by duration of processing and total age of the compost in days).

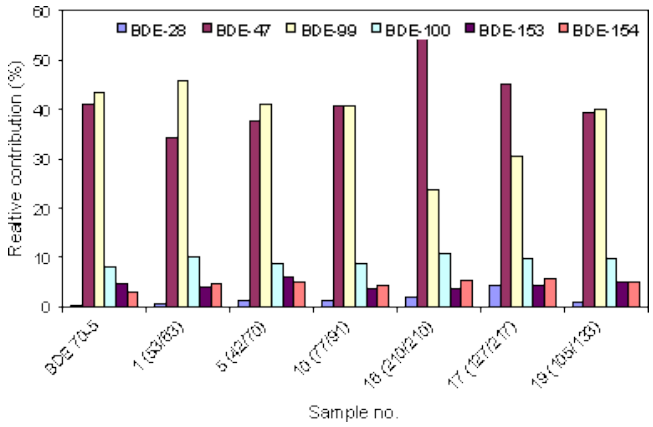
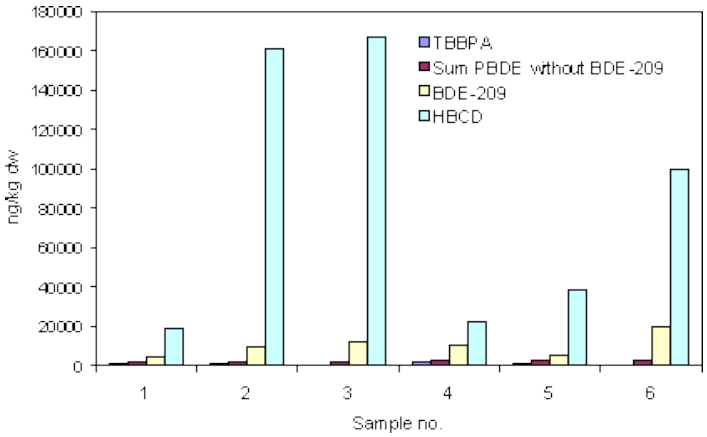


Figure 2: Distribution of the analyzed brominated flame retardants in six compost samples.



Acknowledgements

The following institutions are acknowledged for financial support and collaboration: Swiss Agency for the Environment, Forests and Landscape (BUWAL), Swiss Federal Office of Energy (BfE), Swiss Federal Office for Agriculture (BLW), Office for Waste, Water, Energy and Air, Canton of Zürich (AWEL), Association of Swiss Compost and Methanisation Plants (VKS), Research Institute of Organic Agriculture (FiBL).

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