

INCREASING CONCENTRATIONS OF DECABROMODIPHENYL ETHER (DecaBDE) IN SWISS SEWAGE SLUDGE SINCE 1993

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Introduction

Polybrominated diphenyl ethers (PBDE) are a class of flame retardants for which ubiquitous occurrence and increasing levels in the environment have been observed¹. PBDE are released into the environment mainly from plastic materials and textiles where they are used as flame retardants. Endocrine disrupting effects triggered by these and other chemicals are currently discussed to be responsible for various disorders and the diminution of fish populations. Sewage sludge is an important material to monitor the mass fluxes of PBDE from settlement areas to agricultural fields onto which sewage sludge may be applied in Switzerland. In the light of the controversial discussion on the environmental fate of decabromodiphenyl ether (DecaBDE, BDE-209) and the ban of pentabromodiphenyl ether (PentaBDE) within the EU starting in 2003, temporal concentration trends of PBDE in sewage sludge were investigated based on samples from eight sewage treatment plants taken in the greater Zürich area in 1993 and 2002.

*Methods and Materials*²

Sewage sludge samples were centrifuged, dried at room temperature, ground, and stored in the dark. Samples were extracted for 24 h with toluene (soxhlet). An aliquot of each extract was spiked with the internal standard mixture (¹³C₁₂-labeled BDE-28, -47, -99, -100, -153, -183 and -209, 5 to 25 ng per congener), treated with concentrated sulfuric acid, desulfurated with mercury, and purified by liquid chromatography (multi layer silica gel column followed by a column containing basic alumina). Samples were analyzed using gas chromatography / electron ionization high resolution mass spectrometry.

Results and Discussion

Concentrations of BDE-28, -47, -99, -100, -153, -154 and -183 in sewage sludge from the sewage treatment plants A-H in 1993 and 2002 are shown in Figure 1. In all cases, levels were higher in 1993 than in 2002. The average sum of these BDE congeners dropped from 150 to 69 ng/g dw, corresponding to an average reduction of 51 % (Table 1). The congener patterns for BDE-28, -47, -99, -100, -153, -154 were similar to the congener pattern of Bromkal 70-5DE, a commercial PentaBDE product³ (Table 2). Concentrations of BDE-183, a heptabromodiphenyl ether indicative for the commercial OctaBDE product, were in the same range or slightly higher than BDE-154 levels. Since the levels of all these BDE-congeners have been decreasing, we assume that the application of these products has been reduced in Switzerland between 1993 and 2002. In contrast to most biological materials (e.g. fish tissue), the BDE-99/BDE-47 concentration ratio in all sewage sludge samples was larger than one. Qualitative analysis of the mass chromatograms of all tri- to decabromodiphenyl ether congeners revealed no significant differences between the congener patterns of the 1993 and 2002 samples, with the exception of BDE-209. In contrast to the levels of the lower brominated BDE congeners, concentrations of DecaBDE were considerably higher in the samples of 2002 than in 1993 (except for the sewage treatment plant H, see Figure 2).

The average DecaBDE concentration increased from 220 to 1100 ng/g dw, corresponding to an average increase of 560% (see Table 1) .

PBDE concentrations of 20-30 ng/g dw (sum of BDE-28, 47 and 100) were reported in sewage sludge samples collected in Sweden (Gothenburg) in 1988⁴. In Germany, Hagenmaier and coworkers⁵ reported levels of Tetra- and PentaBDE of 0.4-15 ng/g in 1992. Compared to our 1993 data, these levels are clearly lower. However, a more recent Swedish study reports concentrations of BDE-47, BDE-99 and BDE-100 in sewage sludge samples (Stockholm) between 13-100 ng/g dw in 1997-1998⁶, being in the same range as the concentrations found in our 1993 samples. The reported DecaBDE levels of 170-270 ng/g dw are in the same range as those detected in our samples from 1993. In sewage sludge samples taken in the Netherlands in 1999, de Boer and coworkers⁷ report concentrations of DecaBDE up to 190 ng/g dw. In sewage sludge from the United States, levels of 1370 ng/g dw (sum BDE-47 to BDE-154) and 1470 ng/g dw for DecaBDE were reported by Hale and coworkers⁸ in 2002.

In 1999, 979 sewage treatment plants were servicing 95% of the Swiss population, producing 209000 t (dw) of sewage sludge annually. Based on the average concentrations for BDE-28 to BDE-183, the annual load of these compounds in sewage sludge was estimated to about 14 kg. For DecaBDE, the estimated annual load was 230 kg. Compared to the material flows occurring via regular waste disposal and other pathways, these numbers are low. A recent material flow analysis⁹ estimates that 30 t of PentaBDE and 370 t of DecaBDE are disposed of in Switzerland each year.

Despite its very low water solubility and vapor pressure, DecaBDE is released to the environment at an increasingly fast rate. The question if and to what extent DecaBDE is debrominated in environmental systems is discussed controversially, since debromination of DecaBDE would lead to the occurrence of lower brominated diphenylethers with known adverse effects for the environment. The consequences of the rapid increase of the concentration of DecaBDE in sewage sludge for the environment are still unknown.

Acknowledgments

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Figure 1: Concentrations of BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154 and BDE-183 in sewage sludge from the sewage treatment plants A-H in 1993 and 2002 ([ng/g] dry weight).

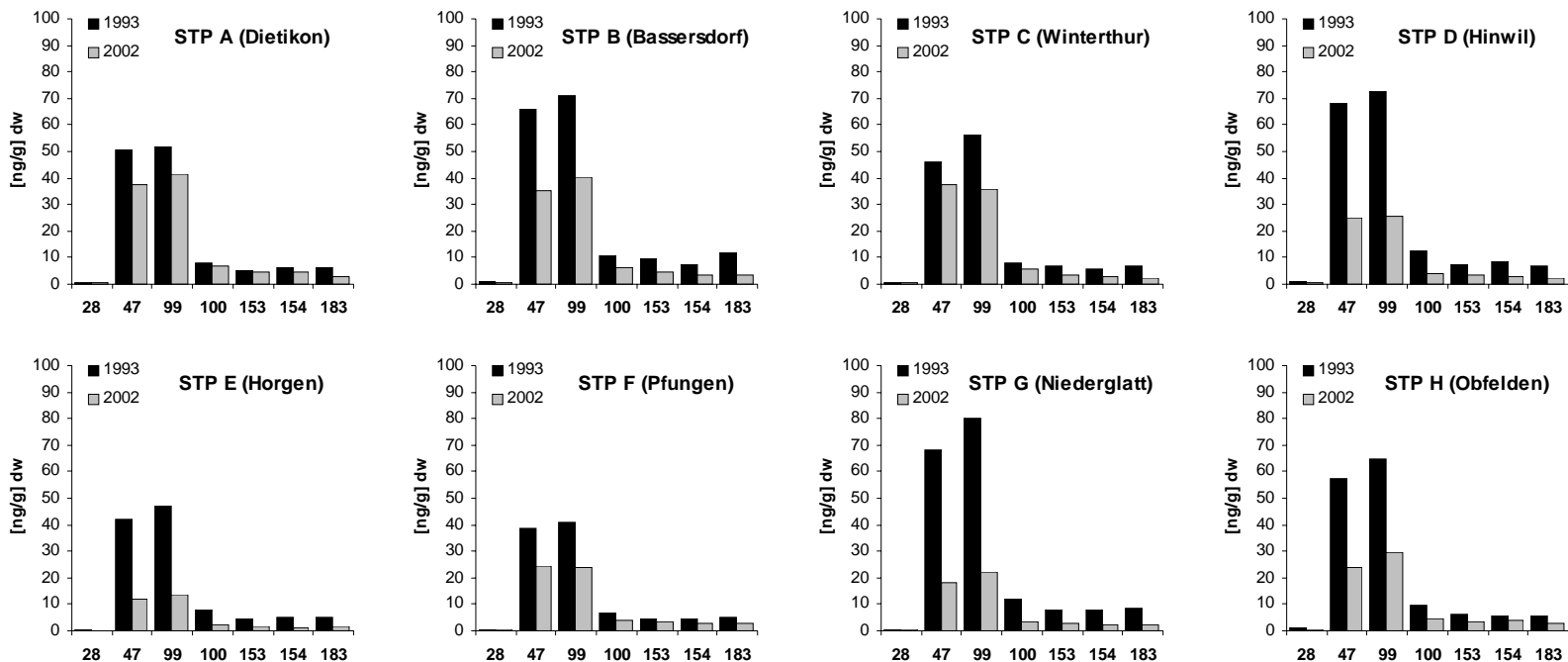


Figure 2: Concentrations of DecaBDE (decabromodiphenyl ether) in sewage sludge from sewage treatment plants A-H in 1993 and 2002 ([ng/g] dry weight).

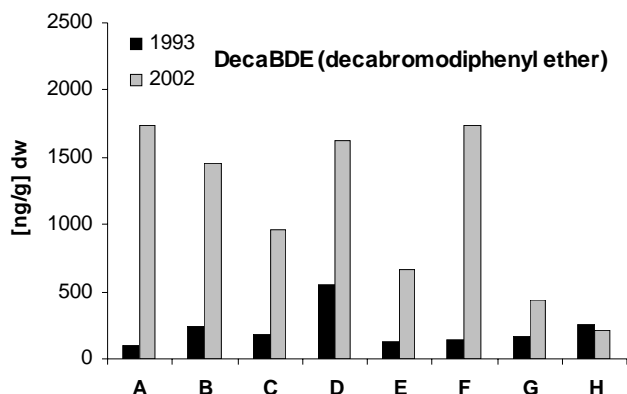


Table 1. PBDE concentrations in sewage sludge from sewage treatment plants A-H in 1993 and 2002 ([ng/g] dry weight).

Sewage Treatment Plant	A	B	C	D	E	F	G	H	Average
1993 [ng/g dw]									
Σ (BDE-28 to BDE-183)	130	180	130	180	110	100	190	150	150
DecaBDE	99	240	190	550	120	140	180	260	220
2002 [ng/g dw]									
Σ (BDE-28 to BDE-183)	98	94	88	63	32	62	50	68	69
DecaBDE	1700	1500	970	1600	660	1700	440	220	1100
change from 1993 to 2002 [%]									
Σ (BDE-28 to BDE-183)	-23	-47	-32	-64	-71	-39	-73	-55	-51
DecaBDE	1700	500	410	200	450	1100	150	-17	560

Table 2. Comparison of the averaged PBDE congener patterns of the sewage sludge samples 1993 and 2002 and the pattern of a commercial PentaBDE product (Bromkal 70-5DE, calculated based on Sjödin et al. 1998³).

BDE	Sewage Sludge 1993 [%]*	Sewage Sludge 2002 [%]*	Bromkal 70-5DE [%]*
28	0.6	0.7	0.1
47	39	40	41
99	44	43	43
100	6.8	6.9	8.0
153	4.7	5.1	4.6
154	4.6	4.4	2.9

*Sum of congeners BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154 = 100%.