Brominated Flame Retardants in Drammens River and the Drammensfjord, Norway

Martin Schlabach[1], Eirik Fjeld[2] and Anders R. Borgen[1]

[1]Norwegian Institute for Air Research, Instituttveien 18, P.O. Box 100, N-2027 Kjeller, Norway
[2]Norwegian Institute for Water Research, Brekkeveien 19, 0884 Oslo, Norway

Introduction

The focus on brominated flame retardants as environmental pollutants, has in the last decade increased substantially. The reported levels of these substances have led to a general concern to both the environment and human health. In 2002, the Norwegian State Pollution Control Authority (SFT) initiated a screening survey to get an overview of the contamination of brominated flame retardants (BFRs)and chlorinated paraffins (CPs) in different parts of the Norwegian environment. The focus was on the levels in soil and sediment samples from landfills and industrial sites; in marine and freshwater sediments; and in freshwater fish, cod liver and blue mussels. The results of this first survey led to a more detailed investigation to make a broader documentation of the BFR- and CP levels, and to localize areas with point sources. This survey was done in 2003, and this paper will present the results from Drammens River and the Drammensfjord, which are located in an industrialized area in the southeast of Norway.

Materials and methods

Sample collection

The average discharge of the Drammens River is about 300 m^3/s, and it runs from the outlet of Lake Tyrifjorden to the Drammensfjord. Sediment samples from 7 stations in the river were collected. Four sediment samples (0-2 cm) were collected in the Drammensfjord, one in the main basin and three close to industrial sites. Homogenated fish samples (tissue from 5-20 individuals per pooled sample; muscle fillets) were prepared from fish caught in the Drammensfjord. The species were anadromous brown trout (*Salmo trutta*), perch (*Perca fluviatilis*), orfe (*Leuciscus idus*), cod (*Gadus morhua*), flounder (*Platichthys flesus*) and eel (*Anguilla anguilla*).

Extraction and clean up

All the samples were added internal standards (^{13}C-PBDEs, ^{13}C-TBBPA and ^{13}C-PCB 118) prior to the sample preparation. The sediment samples were filtered, and then Soxhlet extracted two times. First with acetone and second with acetone/hexane. The biological samples were homogenised with Sodium sulphate prior to cold extraction with hexane/acetone and ethyl acetate/cyclohexane respectively. All the samples were further cleaned on a GPC system. For PBDE, TBBPA and CP analyses the samples were sulphuric acid treated and then concentrated prior to the GC/MS analyses. In addition TBBPA was derivatised using MSTFA. The solvent in the extracts for HBCD analysis were after GPC and sulphuric acid treatment shifted to methanol prior to analysis by LC/MS.

Analysis

An HP5890 GC coupled to a VG AutoSpec, high resolution mass spectrometer was used for all of the GC/MS analyses. For PBDE and TBBPA the MS was operated in EI mode, and for the CPs the MS was operated in ECNI mode. For the HBCD analyses an Agilent 100 HPLC was coupled to a Micromass LCT in electrospray mode, negative ions.

Results and discussion

Sediments

The contamination of PBDEs in sediments from Drammens River and the Drammensfjord are dominated by the fully brominated BDE-209. The highest concentration was found at the station highest up in the river at the outlet of lake Tyrifjorden, in a presumptive rather unpolluted area. This station should be resampled to confirm this level. In the Drammensfjord the highest level of PBDE was found outside a quay for shipping of materials (shredding) from recycled automobiles. BDE-209 dominated the concentrations in both river and marine sediments (80–99%). Sediments from the Drammens River had concentrations of TBBPA in the range of 0.02–10 ng/g d.w., with the highest concentration close to an industrial area. Sediments from the Drammensfjord had concentrations of TBBPA in the range of 0.3–39 ng/g d.w., with the highest level close to an industrial area. Detectable concentrations of α-HBCD (0.9–1.5 ng/g d.w.) and γ-HBCD (0.3–3.1 ng/g d.w.) were found in the Drammens River. In the Drammensfjord, detectable concentrations of all three isomers were found at one station close to an industrial area (concentration of α-, β-, and γ-HBCD were 10.2, 0.7 and 3.3 ng/g, respectively). In the Drammens River, the concentrations of SCCP+MCCP varied between 10–7,400 ng/g d.w., with increasing concentrations downstream. In the Drammensfjord the concentrations were in the range of 750–7,750 ng/g d.w., w ith the highest concentrations close to a floating dock. The concentrations of PBDEs, TBBPA, HBCDs and CPs in sediments from Drammen River and the Drammensfjord are shown in table 1.

Table 1. The concentrations of PBDEs, TBBPA, HBCDs and CPs in sediments from Drammens River and the Drammensfjord (downstream, top to bottom). The concentrations are reported in ng/g dry weight.

		PBDE ng/g dry weight											ng/g dry weight	HBCD ng/g dry weight			CP ng/g dry weight	
Station ID	Station name	BDE-28	BDE-47	BDE49-71	BDE-77	BDE-99	BDE-100	BDE-119	BDE-153	BDE-154	BDE-183	BDE-209	TBBPA	α-HBCD	β-HBCD	γ-HBCD	SCCP	MCCP
DRE-7	Vikersund	<0.01	0.02	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	79.27	0.02	<0.1	<0.08	<0.12	12	0.8
DRE-6	Loselva	0.05	0.91	0.20	0.01	2.04	0.31	0.11	0.91	0.27	0.27	54.44	9.96	0.33	<0.08	0.27	180	280
DRE-5	Hokksund	0.02	0.17	0.03	<0.01	0.19	0.04	0.02	0.03	0.02	0.02	5.59	0.29	0.09	<0.08	0.36	16	6.2
DRE-4	Mjøndalen	<0.01	0.37	0.03	<0.01	0.47	0.09	0.15	0.06	0.03	0.03	4.83	0.81	0.99	0.07	3.08	150	100
DRE-3	Langesøya	<0.01	0.16	0.02	<0.01	0.22	0.05	<0.01	0.02	0.02	0.02	3.55	0.28	0.15	<0.08	0.25	150	380
DRE-2	Politihuset	0.01	0.17	0.03	<0.01	0.32	0.05	0.08	0.05	0.04	0.04	9.36	0.72	1.55	<0.2	0.85	430	1400
DRE-1	Jernbane-brua	0.04	0.68	0.15	<0.01	1.29	0.23	<0.03	0.28	0.15	0.15	32.18	1.59	0.78	<0.2	0.32	1800	5600
DRF-1	Hoved-basseng	0.01	0.14	0.08	<0.01	0.14	<0.01	<0.01	<0.04	<0.03	<0.03	6.89	1.29	<0.3	<0.2	<0.4	94	140
DRF-2	Lierter-minalen	<0.01	0.17	0.04	<0.01	0.36	0.06	0.01	0.06	0.06	0.06	12.61	0.75	10.15	0.65	3.34	440	350
DRF-3	Teigen kaianlegg	0.02	0.41	0.11	<0.01	0.79	0.13	0.03	0.19	0.11	0.11	31.71	39.16	<0.3	<0.2	<0.4	1300	220
DRF-4	Tangen flytedokk	0.01	0.24	0.07	<0.01	0.32	0.05	<0.01	0.04	0.04	0.04	7.47	0.34	<0.3	<0.2	<0.4	250	7500

Fish

In the fish samples from the Drammensfjord, BDE-47 was dominating among the congeners with 41–72%, with BDE-100 as second (9–22%). The percentage of BDE-99 was low in orfe, cod, flounder and eel (0.3–5%), but relatively high in trout and perch (14 and 31%). TBBPA was only detected in one sample (eel) with a concentration just above the detection limit. In fish from the Drammensfjord there were in general low concentrations of α-HBCD (5–23 ng/g lipid). Fish from the Drammensfjord had concentrations of SCCP+MCCP between 46–495 ng/g lipid. The lowest concentration was found in an eel sample, the highest in a sample of flounder liver. The concentrations of PBDEs, TBBPA, HBCDs and CPs in fish from the Drammensfjord are shown in table 2.

Table 2. The concentrations of PBDEs, TBBPA, HBCDs and CPs in fish samples from Drammens River and the Drammensfjord. The concentrations are reported in ng/g lipid weight.

		PBDE ng/g lipid weight							ng/g lipid weight	HBCD ng/g lipid weight			CP ng/g lipid weight	
Sample	% lipid	BDE-47	BDE-49+71	BDE-99	BDE-100	BDE-119	BDE-153	BDE-154	TBBPA*	α-HBCD	β-HBCD	γ-HBCD	SCCP	MCCP
Perch (muscle)	1.19	74.0	26.9	30.4	24.2	1.3	4.0	4.9	-	22.3	<2.5	<3.4	490	<17
Orfe (muscle)	0.89	108.5	5.9	0.5	24.9	1.3	8.6	8.4	<300	14.8	<3.4	<4.5	190	250
Flounder (liver)	7.68	86.8	6.0	7.8	24.4	5.3	3.1	5.0	-	7.2	<0.9	<2.6	530	230
Cod (liver)	43.70	29.0	3.0	1.6	4.5	0.2	0.2	1.1	<9	9.3	<0.9	<0.3	69	<2
Trout (muscle)	6.71	11.7	3.5	3.3	2.2	0.4	0.5	1.2	<5	<1.9	<1.3	<0.2	78	<6
Eel (muscle)	19.80	7.6	0.6	0.4	1.9	0.1	0.3	0.4	0.3	4.7	<0.9	<2.8	41	<9