LEVELS OF POLYCHLORINATED BIPHENYLS AND BROMINATED FLAME RETARDANTS IN AIR FILTERS FROM NORWAY, 1957-2004

Rossland HK, Søbye E, Engøy T

Protection Division, Norwegian Defence Research Establishment, P.O. Box 25, 2027 Kjeller, Norway

Introduction

Norwegian Defence Research Establishment (FFI) has since 1954 measured radioactive fallout from several different air sampling stations in Norway. Air filters have been collected daily at four to eleven different locations. Measurements after 1957 were nondestructive and a nearly complete collection of these filters have been archived and stored at room temperature. Historical records like this are rare and can contain valuable information about the past. In 2003 a selection of air filters was analyzed in an attempt to assess the temporal and spatial variation in concentration of polychlorinated biphenyls (PCBs) and brominated flame retardants (BFRs). Reconstructed contaminant trends have been reported earlier both in UK and US using various matrixes like air filters, sediment, soil, peat, herbage.[1,2,3] However, both local and global contribution to the atmospheric concentrations could be different in Norway due to factors like usage, production, temperature and wind direction.

Materials and Methods

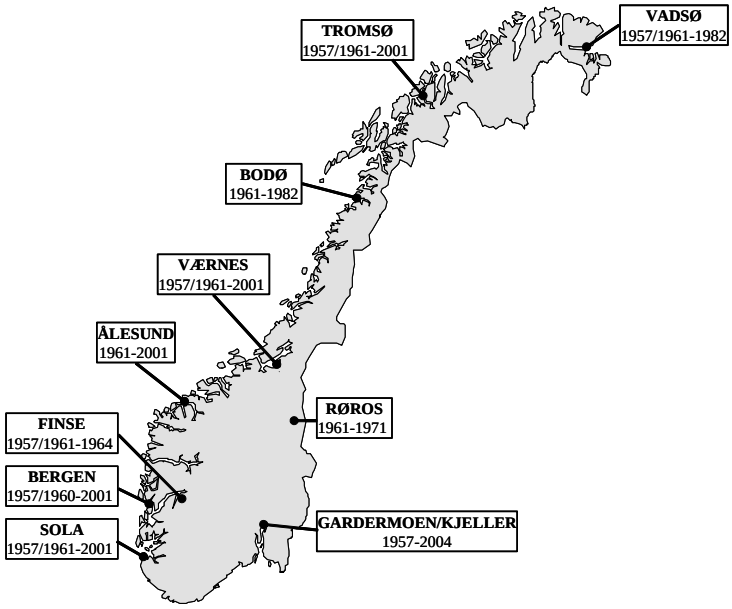

Fig 1 Location and operational period of the air sampling stations

From 1957 to 1975 samples were obtained by drawing air through an 8 cm (diameter) asbestos filter at an average flow rate of 430 m^3/24 h. In 1975 the asbestos filters were replaced by 9 cm (diameter) GFA glass fibre filters. Samples obtained from asbestos filters in February 1975 and glass fibre filters from July the same year, showed no significant measurable differences in the concentration of PCB. The sampling procedure was compared in 2004 against a commonly used high-volume sampler fitted with a 15 cm glass fibre filter and two polyurethane foam (PUF) plugs with a flow rate of 600 m^3/24 h operated by Norwegian Institute of Air Research (NILU). Concentrations of both PCB and BFR samples were near the quantification limit, preventing a clear discernible difference between the two sampling techniques. The particulate phase (glass fibre) of PCBs is only 7 % of the total concentration on average.[3]

Air filters were exchanged daily from 1957 to 1985 and 3 days per week up till 2001. Due to differences in sampling time and because the extraction procedure is destructive, a batch of filters was chosen, and a quarter of each filter was pooled in different ways depending the aim of the study.
Both filter and PUF samples were extracted using microwave assisted extraction (MAE) with heptane, acetone and water. Cleanup was performed with sulphuric acid supplemented with gel permeation chromatography (GPC) as additional cleansing step if the extracts were contaminated with high amounts of soot. A congener specific gas chromatography method, with an electron capture detector (GC/ECD) and internal standard calibration, was performed to determine the concentration of PCB-28, 52, 101, 118, 138 and 180 (Seven Dutch). BFR analysis was conducted using a gas chromatography method, with a mass selective detector (GC/MS) at NILU.
Samples from Bergen in 1980 were bulked to study seasonal and weekly variations of PCB concentration. Filters were bulked from February and September in 1957, 1962, 1964, 1970, 1972, 1974, 1976, 1980, 1981/82, 1993, 1995 and 2001 to study temporal trends. Geographical variation was studied by selecting eight different stations from the south to the north of Norway in 1980 and analyzing a bulk of filters from February and September. BFR and PCB concentrations within a year were studied in air filters from Værnes, Bergen and Kjeller in 2001 and in spring 2004 at Kjeller.

Results and Discussion
Figure 2 summarize the concentrations of individual PCBs and PCB_7 in Bergen 1980. PCB-28 and 52 are the most volatile of the analyzed PCBs and are dominating the results with an average of 1300 and 200 pg/m^3 respectively. The five others are higher chlorinated PCBs and are ten folds lower in concentration ranging from 10-40 pg/m^3. Levels of these five PCBs are stable within the year while the concentration of PCB-28 and 52 have biannual peaks. Maximum are found in February and October and minimum in July and December. Parameters like temperature, wet deposition and wind directions were compared with the variation in concentration of PCB_7 without finding any clear connection.
Weekly atmospheric concentrations of PCBs in February and September 1980 in Bergen are summarized in figure 3. Some variation is found. The same months were chosen to represent the levels of PCBs at eight different locations in Norway. Differences in concentration between the locations are only slight and there are no connection between the latitude and the concentration (figure 4). However, the decline in concentrations going from the station Sola in the south of Norway to the stations Tromsø and Vadsø in the north is noticeable.
Table 1 and figure 5 summarize the temporal trend for atmospheric concentrations of PCBs in Bergen from 1957 to 2001. PCB-28 and 52 are the dominating compounds until 1981. Between 1981 and 1993 the concentrations decline dramatically. After 1993 the higher chlorinated and less volatile PCBs are the only ones to be detected. Norway banned new use of PCB in 1980 when the usage was at its peak. The use was declined with 70 % from 1980 to 1995 and with additional 10 % in 2003.[5] The decline to a minimum concentration is confirmed at the stations Kjeller and Værnes in 2001 (table 2). Assuming that the distribution between the PCB concentrations in the vapor phase and the particulate phase is constant the total atmospheric concentration would change from 23 ng/m^3 PCB_7 in 1980 to 0,02 ng/m^3 in 2001. In comparison, the total atmospheric concentration of PCBs in Birmingham, UK was 0,07 ng/m^3 in 1999/2000.[6]
Air filters from Bergen, Kjeller and Værnes in 2001 were also analyzed for BFRs and the results are summarized in table 3. The concentrations were low compared to reported values from UK and since the assumed peak of usage was similar to the sampling year, the BFR analysis was not conducted any further on the filters in this study.[7]

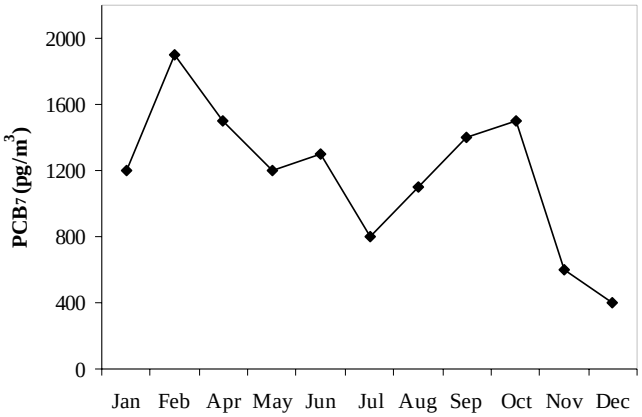

Fig 2 Seasonal atmospheric concentrations of particulate PCBs in Bergen 1980

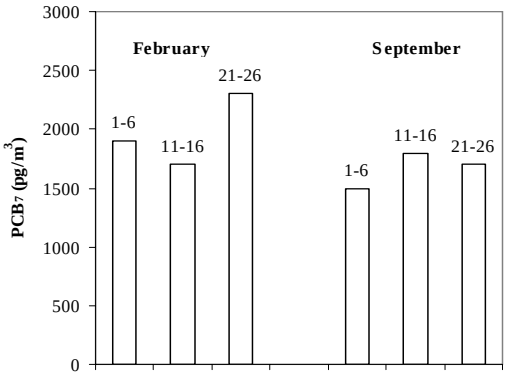

Fig 3 Weekly atmospheric concentrations of particulate PCBs in February and September in Bergen 1980

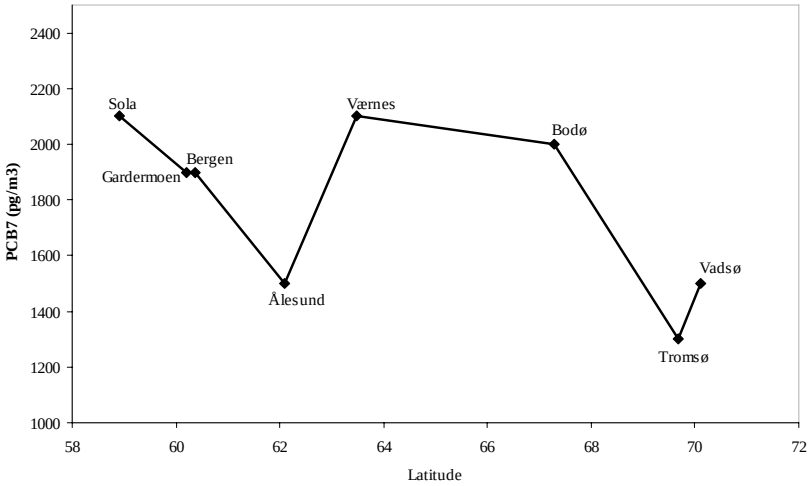

Fig 4 Atmospheric concentrations of particulate PCBs for 8 different locations in Norway 1980

Tab 1 Temporal trend for atmospheric concentrations of particulate PCBs in Bergen 1957-2001

	PCB 28 (pg/m^3)	PCB 52 (pg/m^3)	PCB 101 (pg/m^3)	PCB 118 (pg/m^3)	PCB 153 (pg/m^3)	PCB 138 (pg/m^3)	PCB 180 (pg/m^3)	PCB_7 (pg/m^3)
1957	80	20	20	10	20	30	30	200
1962	40	10	30	20	50	70	60	270
1964	60	10	5	7	10	20	20	130
1970	400	150	40	30	40	80	20	760
1972	270	110	20	20	20	150	20	600
1974	100	30	20	10	2	2	10	170
1976	230	70	30	10	4	5	4	350
1980	1310	200	30	20	20	20	10	1600
1981	950	170	40	10	10	10	1	1200
1993	1	< 0,5	1	2	2	2	2	10
1995	< 0,5	< 0,5	1	3	4	7	5	20
2001	< 0,05	< 0,05	0,2	< 0,05	0,6	0,2	0,4	1,4

Fig 5 Temporal trend for atmospheric concentrations of particulate PCBs in Bergen 1957-2001

Tab 2 Atmospheric concentrations of particulate PCBs for 3 different locations in Norway in 2001

	PCB 28 (pg/m^3)	PCB 52 (pg/m^3)	PCB 101 (pg/m^3)	PCB 118 (pg/m^3)	PCB 153 (pg/m^3)	PCB 138 (pg/m^3)	PCB 180 (pg/m^3)	PCB_7 (pg/m^3)
Kjeller	< 0,05	0,07	< 0,05	< 0,05	0,3	0,1	0,3	0,8
Bergen	< 0,05	< 0,05	0,2	< 0,05	0,6	0,2	0,4	1,4
Værnes	< 0,05	< 0,05	< 0,05	< 0,05	0,1	< 0,05	< 0,05	0,1

Tab 3 Atmospheric concentrations of particulate BFRs for 3 different locations in Norway in 2001

	TBA (pg/m^3)	BDE-28 (pg/m^3)	BDE-47 (pg/m^3)	BDE-99 (pg/m^3)	BDE-100 (pg/m^3)	BDE-153 (pg/m^3)	BDE-154 (pg/m^3)	BDE-138 (pg/m^3)	BDE-183 (pg/m^3)	BFR (pg/m^3)
Kjeller	0,002	0,01	0,27	0,27	0,05	0,04	0,02	< 0,001	0,04	0,7
Bergen	0,003	0,005	0,05	0,09	0,01	0,05	0,02	0,007	0,16	0,4
Værnes	< 0,001	< 0,001	0,06	0,06	0,01	0,03	0,01	< 0,001	0,04	0,2

Acknowledgements
We are grateful to Espen Mariussen (NILU) for contributions to the BFR analysis and the calibration of the air sampler against NILUs high-volume air sampler.

References

1. Jones KC, Duarte-Davidson R, Cawse PA. *Environ Sci Tecnol* 1995;29:272
2. Sanders G, Eisenreich SJ, Jones K. *Chemosphere*, 1994;29:2201
3. Jones KC, Sanders G, Wild SR, Burnett V, Johnston AE. *Nature* 1992;356:137
4. Hung H, Blanchard P, Halsall CJ, Bidleman TF, Stern GA, Fellin P, Muir DCG, Barrie LA, Jantunen LM, Helm PA, Ma J, Konoplev A. *Science of the Total Environment* 2005;342:119
5. State of the Environment Norway. *www.environment.no*
6. Harrad S, Mao H. *Atmospheric Environment* 2004;38:1437
7 Lee RGM, Thomas GO, Jones KC. *Organohalogen Compounds* 2002;58:193