

CIRCUMPOLAR INVESTIGATION OF BROMINATED DIPHENYL ETHERS -CONNECTING RESEARCH AND EDUCATION

Eldbjørg S. Heimstad¹, Dorte Herzke¹, Geir Endregard² and Karl T. Hetland³

1 NILU, Polar Environmental Centre, NO-9296 Tromsø, Norway

2 NILU, NO-2027 Kjeller, Norway

3 Vest Telemark Ressurssenter, NO-3880 Dalen, Norway

Introduction

Wind and sea currents transport organic chemicals from the high industrialised parts of the globe to the more pristine Arctic regions. Many of these chemicals exert toxic effects, are not easily water soluble and degradable, and may persist in the polar environment for long periods of time. These are known as persistent organic pollutants (POPs). Due to their lipophilic character they tend to accumulate in lipid-rich organs of fish and animals.

Polybrominated diphenyl ethers (PBDEs), widely used as flame retardants have been well studied in southern part of Europe and America, but not in same extent in the Arctic. PBDEs have in general been increasing in human milk and environmental samples during the last decades¹, while for instance PCBs have levelled off or decreased. Studies have revealed that these compounds are potential endocrine disruptors. There is therefore a need for both temporal and spatial trends of these compounds in the Arctic in order to assess distant and local sources, distribution and potential increase with time, and thus the risk of long term exposure of wildlife and humans, especially the children.

A circumpolar project was initiated in 2001 with the aim to analyse so called “new POPs” such as PBDEs in the Arctic and to enlarge the knowledge and interest of basic and environmental sciences in schools within the Arctic at the same time. With the use of pre-cleaned equipment and a sampling protocol for fish, the students were doing scientifically correct cutting of fish organs such as liver or fillet. Datasheets with important data such as sampling date, description of sampling location including GPS co-ordinates, type of fish species, Latin name, fish weight, fish length, gender and maturity were also filled out. PBDE47 and PBDE99 were analysed in all fish samples. PCB153 was analysed as a reference persistent organic pollutant as well.

In this project 15 GLOBE (Global Learning and Observations to Benefit the Environment) schools from 7 Arctic countries participate. Information about the project, including fish sampling protocols, can be found at the project web-site www.nilu.no/web/arcticpops.

This article covers only a scientific evaluation of the results so far. It is planned to evaluate the value of using students in such sophisticated sampling at the end of the project. Furthermore the educational benefits of the project are to be evaluated at a later stage. The project as now planned is ending in summer 2004.

Methods and Materials

The students sampled two parallels during fall 2001, spring 2002 and fall 2002. NILU analysed 34 samples of Atlantic and Pacific cod liver, 10 samples burbot liver, 4 samples haddock liver, 5 samples of whitefish liver, 4 whitefish fillets, and 16 samples of Arctic char, Atlantic and Pacific salmon and Brown trout fillets using the method described in³, briefly by extracting the Na₂SO₄-homogenate, GPC to remove lipids, florisil chromatography for further clean up prior to GC/EI-MS.

GC/MS investigations:

Quantification was carried out with low resolution Finnigan MD800 quadrupole mass spectrometry (LRMS) as detector in selected ion monitoring mode (SIM). Electron impact (EI) was used as ionisation method for the determination of PCB and PBDE.

Table 1: Fish species sampled fall 2001, spring 2002 and fall 2002. (– : no sampling).

Country	Location of school	ID	Fish species ¹ fall 2001	Fish species spring 2002	Fish species fall 2002
Alaska	<i>Anchorage</i>	A-A	Coho salmon fillet	Pacific cod liver	Coho salmon fillet
	<i>Kodiak</i>	A-K	Pacific cod liver	Pacific cod liver	Pacific cod liver
Canada	<i>Old Crow</i>	C-O	Broad whitefish liver	-	-
	<i>Inuvik</i>	C-I	Burbot liver	-	-
	<i>Nunavut</i>	C-N	Arctic char fillet	Arctic char fillet	-
Finland	<i>Tornio</i>	F-T	Common whitefish fillet	Burbot liver	Burbot liver
	<i>Akureyri</i>	I-A	Atlantic cod liver	Atlantic cod liver	Atlantic cod liver
Iceland	<i>Vestmannaeyjar</i>	I-V	Haddock liver	Haddock liver	Atlantic cod liver
	<i>Kjøllefjord</i>	N-K	Atlantic cod liver	Atlantic cod liver	Atlantic cod liver
	<i>Vannareid</i>	N-V	Atlantic cod liver	Atlantic cod liver	Atlantic cod liver
Norway	<i>Leknes</i>	N-L	Atlantic cod liver	Atlantic cod liver	Atlantic cod liver
	<i>Apatity</i>	R-A	Lake whitefish liver	Lake whitefish liver	Lake whitefish fillet
Russia	<i>Kiruna</i>	S-K	Brown trout fillet	Brown trout, Whitefish fillet ²	Brown trout fillet
	<i>Pajala</i>	S-P	Atlantic salmon fillet	Burbot liver	Burbot liver

¹List of Latin names:

Atlantic cod: *Gadus morhua*, Pacific cod: *Gadus macrocephalus*, Haddock: *Melanogrammus aeglefinus*
 Burbot: *Lota lota*, Atlantic salmon: *Salmo salar*, Coho salmon (Pacific salmon): *Onocorhynchus kisutch*, Brown trout: *Salmo trutta*, Arctic char: *Salvelinus alpinus*, Broad whitefish: *Coregonus nasus*, Lake whitefish: *Coregonus clupeaformis*, Common whitefish: *Coregonus lavaretus*, ²Most probably *Coregonus acronis* or *Coregonus nilssonii*

Results and Discussion

Results from the analyses of the three sampling campaigns in fall 2001, spring 2002 and fall 2002 are shown for liver and fillet samples in table 2 and 3, respectively. Levels of PCB153 in liver from Atlantic cod (*Gadus morhua*) from Norway and Iceland are comparable with levels in liver from Pacific cod (*Gadus macrocephalus*) in Alaska, although with a tendency of higher values in the European Arctic. The median values including minimum and maximum values of PBDE47 in cod liver are higher in the European part of the Arctic (Norway and Iceland) compared to Alaska, and in average lower than levels detected in cod from the North Sea^{1,2}. Similar trends can also be seen by comparing the levels of PCB153 and PBDE47 in salmonid fish (Table 1 and 2), although less verified due to a smaller amount of samples.

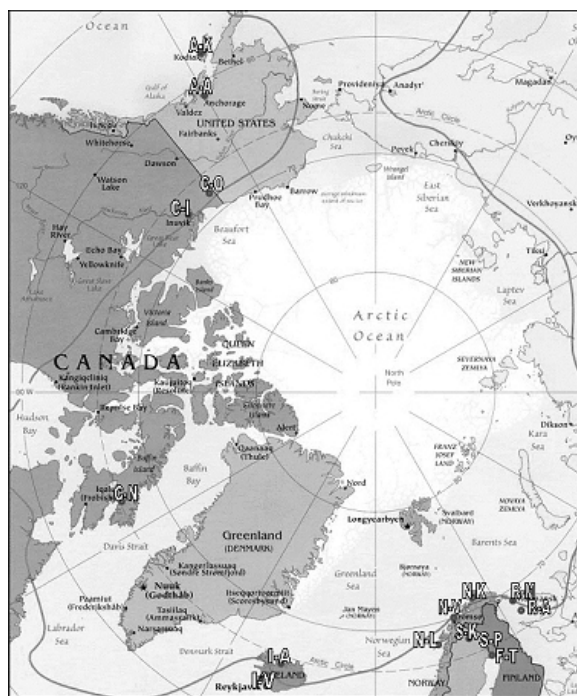


Figure 1: Map showing the locations of the participating schools. The name of the schools and the ID's are shown in table 1.

The fish species burbot (*Lota lota*) from Sweden and Finland are characterised by the highest levels of PCB153 and PBDE47, both on wet and lipid based weight (see comparison of lipid based concentrations of PBDE47 in cod, haddock and burbot livers in Figure 2). As a fish-eating predator it may have higher levels compared to fish lower in the food-chain. Since burbot is a limnic cod specie and a bottom feeder, it may be influenced by local pollution of these freshwater systems. Very high levels of PBDE47 in burbot liver from the Lake Mjøsa in southern part of Norway have been detected supporting this theory (Mariussen et al., this issue). More data are needed in order to evaluate this further. The haddock is also a bottom feeder and the two samples in this study show relatively higher values of PCB153 and PBDE47 than the cod.

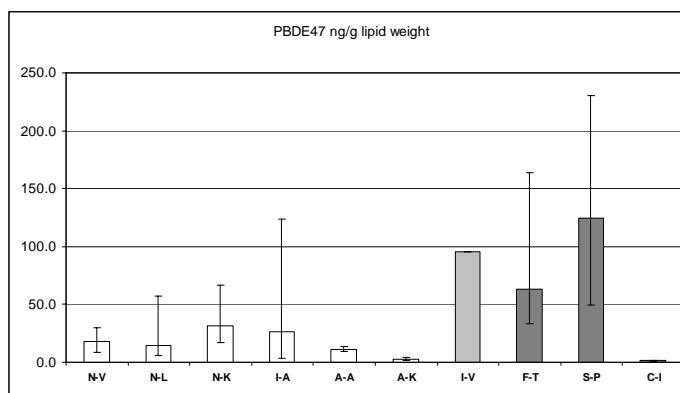
Table 2: Median concentrations (ng/g wet weight) of PCB153 and PBDE47 in fish livers with minimum (Min) and maximum (Max) values. Number of samples is given as N. The median value of extractable organic material (% EOM) in the samples with minimum and maximum is also given. Concentrations that are lower than detection of limit (LOD) are given as <LOD.

Fish species	COUNTRY	ID	N	PCB153 Min	Max	PBDE47 Min	Max	EOM Min	Max
Pacific cod	ALASKA	A-K	6	5.6	3.7	9.1	0.7	0.4	0.9
Pacific cod	ALASKA	A-A	2	31.4	13.8	49.0	2.5	2.1	3.0
Atlantic cod	NORWAY	N-V	5	26.3	12.0	62.3	7.8	3.3	14.3
Atlantic cod	NORWAY	N-L	6	41.3	16.4	97.1	8.7	3.0	18.2
Atlantic cod	NORWAY	N-K	6	78.6	40.2	319.8	15.1	8.7	23.0
Atlantic cod	ICELAND	I-A	6	59.0	24.5	117.8	10.7	1.1	13.4
Atlantic cod	ICELAND	I-V	1	16.3		<LOD			36.0
Haddock	ICELAND	I-V	2	269.8	48.7	490.8	33.9		29.8
Burbot	FINLAND	F-T	4	293.6	196.3	362.2	32.7	15.9	58.5
Burbot	SWEDEN	S-P	4	145.4	116.4	458.0	29.8	21.3	119.4
Burbot (Loche)	CANADA	C-I	2	11.3	9.0	13.7	0.5	0.4	0.6
Lake Whitefish	RUSSIA	R-A	4	25.9	2.5	57.1	0.2	0.1	0.7
Broad Whitefish	CANADA	C-O	1	3.7			0.1		16.8

Table 3: Median concentrations (ng/g wet weight) of PCB153 and PBDE47 in fish fillets with minimum (Min) and maximum (Max) values. Number of samples is given as N. The median value of extractable organic material (% EOM) in the samples with minimum and maximum is also given. Concentrations that are lower than detection of limit (LOD) are given as <LOD.

Fish species	COUNTRY	ID	N	PCB153	Min	Max	PBDE47	Min	Max	EOM	Min	Max
Atlantic salmon	SWEDEN	S-P	2	40.2	17.3	63.2	4.4	2.3	6.5	6.8	4	9.5
Coho salmon	ALASKA	A-A	4	0.3	0.2	0.4	0.04	0.04	0.05	2.5	1	3.5
Brown trout	SWEDEN	S-K	5	3.8	0.3	21.0	0.5	0.4	0.6	1.8	1	7.5
Arctic char	CANADA	C-N	3	2.0	0.9	2.7	0.2	0.2	0.2	7.8	1.9	7.9
Whitefish	SWEDEN	S-K	1	13.9			0.3			7.0		
Lake whitefish	RUSSIA	R-A	2	2.5	0.3	4.6	<LOD			1.3	1	1.6
Common whitefish	FINLAND	F-T	1	5.0			0.5			0.6		

Figure 2: Median values of PBDE47 lipid weight based concentrations with minimum and maximum values in cod liver (non-filled bars), haddock liver (light grey bars) and burbot liver (dark grey bars).



The results from these three sampling campaigns reveal that brominated flame retardants such as PBDE47 is present all over the Arctic. There is a trend of higher levels of POPs in the European Arctic compared to northern part of America. No clear seasonal trend or correlation with fish length or weight is present in this dataset. The levels of POPs indicate that long range air and ocean transport from distant sources are most potential, but some freshwater systems in Scandinavia may be influenced by local pollution from industrial and municipal waste water facilities as well.

Acknowledgements

The authors want to thank Vegard Lyngmo (Unilab Analyse a.s.) for his contribution to the project. A special warm thank to all the teachers and students for their enthusiasm for environmental issues and valuable work in this project. We are very grateful to Astrid Sandås at the Norwegian board for Education, who was crucial in starting the project with her strong believe in science based education. The financial support from the Ministry of Education, Ministry of Environment, Ministry of Foreign Affairs and the Barents Secretariat in Norway, as well as the US embassy in Copenhagen is highly acknowledged.

References

- de Wit, C.A. (2002). An overview of brominated flame retardants in the environment. *Chemosphere* **46**, 583-624
- Boon, J.P.; Lewis, W.E.; Tjoen-A-Choy, M.R.; Allchin C.R.; Law R.J.; de Boer, J.; Ten Hallers-Tjabbes, C.C.; Zegers B.N. (2002). Levels of polybrominated diphenyl ether (PBDE) flame retardants in animals representing different trophic levels of the North Sea food web. *Environ. Sci. Technol.* **36**, 4025-4032.
- Herzke, D.; Gabrielsen, G. W.; Evenset, A.; Burkow I. C.; (2003). Polychlorinated camphenes (toxaphenes), polybrominated diphenylethers and other halogenated organic pollutants in glaucous gull (*Larus hyperboreus*) from Svalbard and Bjornoya (Bear Island). *Environmental Pollution* **121**, 293-300.