

Rapport Report

Screening studies of POP levels in bottom sediments from selected lakes in the Paz watercourse



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Screening studies of POP levels in bottom sediments from selected lakes in the Paz watercourse

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Sammendrag / Summary

This screening study of POPs in bottom sediments carried out in the Paz watercourse reveal higher levels of all environmental contaminants studied in the bottom sediments from Lake Kuetsjarvi. There was a clear trend that the contamination levels decreased with increasing distance from the smelters. The levels of PCB and DDT in sediments from the Paz watercourse were high compared to levels measured in surface sediments from other lakes in Northern Norway. There was no clear trend on the distribution of PBDE in the Paz watercourse compared to the reference lakes. It is strongly recommended that POPs in sediments are included in future monitoring programmes.

Emneord:	Key words:
Pasvik vassdraget	Paz watercourse
Sedimenter	Sediments
Miljøgifter	Contaminants
PCB	PCB

Prosjektleder / Project manager

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Screening studies of POP levels in bottom sediments from selected lakes in the Paz watercourse

1 Introduction

Discharges from smelting industry of copper-nickel ore at Kola Peninsula have significant pollution effects on the environment in the border areas between Russia, Finland and Norway. Investigations carried out in the early 1990s revealed numerous acidified and heavy metal polluted lakes in the border areas (Traaen *et al.*, 1991; 1992; Moiseenko *et al.*, 1994; Dauvalter and Rognerud, 2001). Water quality monitoring carried out in eastern Finnmark, Norway has shown that the heavy metal concentrations in the lakes have remained high through the 1990s (SFT, 2001). However, smelting processes are the potential source of many different contaminants, including persistent organic pollutants (POPs) and polycyclic aromatic hydrocarbons (PAHs).

Traditionally, management of aquatic resources in freshwater ecosystems have primary focused on water quality and less on sediment quality. Sediments represent essential elements of freshwater ecosystems and available information on sediment quality conditions indicates that sediments throughout the border area are contaminated by a wide range of toxic and bioaccumulative substances, including metals, PAHs, polychlorinated biphenyls (PCBs), organochlorine pesticides and polychlorinated dibenzo-p-dioxins and furans (PCDDs and PCDFs) (Dauvalter and Rognerud, 2001; Skotvold and Savinov, 2003).

Contaminated sediments represent an important environmental concern for several reasons. First, contaminated sediments have been demonstrated to be toxic to sediment-dwelling organisms and fish. As such, exposure to contaminated sediments can result in increased mortality, reduced growth, or impaired reproduction in benthic invertebrates and fish. Additionally, certain sediment-associated contaminants (termed bioaccumulative substances) are taken up by benthic organisms and transferred further up the food chain. Many POPs are characterized by lower water solubility and high lipid solubility, leading to their bioaccumulation in the food chain. Contaminated sediments can also compromise human health due to direct exposure or through the consumption of contaminated fish and shellfish.

2 Aim of the study

The aim of this study was to analyse freshwater sediments from lakes in the border area of Russia and Norway for persistent environmental contaminants and trace elements. Also some lakes from non industrialized areas in Norway and Finland were included in the study. These data, along with results of benthic and ichthyologic studies, carried out in the same areas forms the basic for an evaluation of the current environmental status in the region.

3 Quality Assurance Project Plan

The project also suppose to:

1) In addition to assessing environmental status in the border area, the project was to serve an educational purpose. One aim was to instruct and train personnel in sediment sampling for analyses of POPs. The training program included the following aspects:

• Quality assurance objectives and methods for assessing precision, accuracy, completeness, representativness, and comparability of the data generated;

- Sampling procedures, including sampling equipment, decontamination of equipment, collection of field duplicates, generation of field blanks, collection of positional data, sample containers, sample identification and labeling, sample preservation and holding times, fields documentation, and field data sheets;
- Sample custody and transportation, including field custody procedures, sample packaging and transport.

2) In addition carry out intercalibration exercise on contaminant determination between analytical laboratories involved in the project.

4 Sampling program

Sampling program was carried in cooperation with Norwegian College of Fishery Science (NCFS), University of Tromsø and Institute of Industrial Ecology, Kola Scientific Center of Russian Academy of Sciences.

Three sites (Kuetsjarvi) on the Russian side and 4 sites (Pasvik area) on the Norwegian side have been chosen for sampling of sediments (*Figure 1*; *Table 1*). Moreover, sediment samples were also collected in two lakes located at non-industrial areas of Norway (Stuorajavri) and Finland (Inarijarvi).

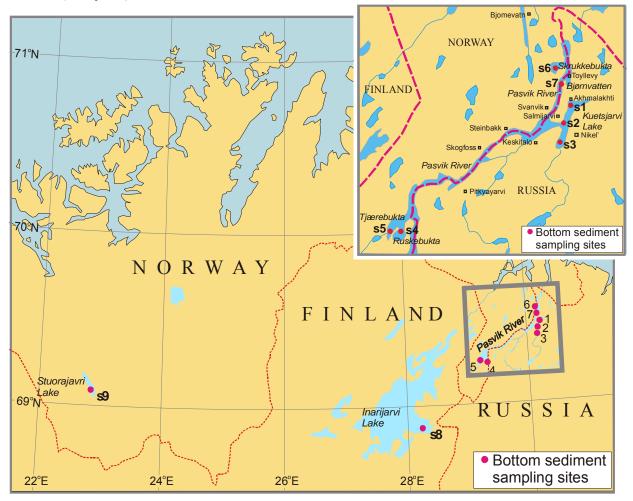


Figure 1. Map of the studied area and bottom sediment sampling site locations (2003-2005).

Date	Station number	Latitude (N)	Longitude (E)	Depth, m	Location
14.08.03	1	69°28.644′	30°11.469′	23	Kuetsjarvi Lake (Golfstream)
14.08.03	2	69°26.052′	30°09.447′	10	Kuetsjarvi Lake (Salmijarvi)
14.08.03	3	69°23.936′	30°08.228′	12	Kuetsjarvi Lake (Kolosjoki)
17.09.03	6	69°33.296′	30°07.302′	31	Pasvik River (Skrukkebukta)
18.09.03	7	69°31.213′	30°06.569′	24	Pasvik River (Bjørnvatten)
04.08.04	8	68°51.941′	28°16.259′	42	Inarijarvi Lake
13.09.04	4	69°12.604′	29°14.773′	15	Pasvik River (Ruskebukta)
13.09.04	5	69°12.750′	29°10.760′	10	Pasvik River (Tjærebukta)
30.06.05	9	68°06.416′	22°50.345′	21	Stuorajavri Lake

Table 1. Location of bottom sediment sampling sites, 2003-2005.

4.1 Sampling procedure

To ensure comparability of the data, internationally accepted sampling methods were used to collect samples from all sampling stations within the assessment area.

Recommendations of the Arctic Monitoring and Assessment Program (AMAP, 2000), Canadian and US Environmental Protection Agencies (US EPA, 2002) for core sampling were used during the fieldwork.



Figure 2. Sampling of bottom sediments, Kuetsjarvi, August 2003.

These recommendations include:

- knowledge of lake bathymetry is necessary in order to select deep sedimentary basin within the lake;
- using 7.5-10 cm diameter cores in small lakes;
- slices at 0.5 or 1.0 cm intervals in top 5 to 10 cm depending on sedimentation rate;
- outer 0.5 cm of core should be removed to reduce effect of smearing from the walls of core;
- the sliced samples should be stored in precleaned glass jars at 4 °C until analyses.

The surface (0-1 cm) sediment samples were collected from the deepest part of each lake with modified Kajak-Brinkhurst gravity corer (Mudroch and Azcue, 1995). Two deeper slices (15-18 cm and 22-23 cm) were also collected in Inrijarvi and Stuorajavri lakes respectively.

5 Results and discussion

5.1. Analyses

The following contaminants were analyses in the sediment samples:

Trace elements (Cd, Cu, Ni, Hg)

Polycyclic aromatic hydrocarbons (PAHs) – 21 compounds

Basic POPs

PCBs (50 ortho-substituted congeners; including all congeners recommended by AMAP), DDT-family (6 isomers), chlorobenzenes, (tetra-, penta- and hexachlorobenzene), hexachlorocyclohexane (HCH; α -, β - and γ -isomers), chlordane compounds (heptachlorepoxide, oxychlordane, cis- and trans-chlordane, trans- nonachlor, heptachlor)

New compounds

Coplanar PCBs, brominated flame retardants (PBDEs), chlorinated phenols, polychlorinated naphthalenes (PCNs) and dioxins/furans (PCDD/PCDF).

Analyses were carried out at Typhoon Analytical Centre (Obninsk, Russia). The laboratory has national accreditation within the framework of Russian Analytical Laboratories Accreditation System (ALAS) for POPs and mercury in abiotic and biotic environmental media (fresh- and seawater, air, soil, bottom sediments, biological material, including human tissues). The laboratory has also successfully participated in the QUASIMEME International interlaboratory study on POPs and heavy metals in biological samples (2000-2002). Moreover, in 2001-2002 the laboratory took part in the intercalibration analyses started by Department of Energy DOE (MAPEP-2001-2002), USA; NIST/NOAA-NS&T/EPA-EMAP QA Program; AMAP Ring Test (Round 1-2 at 2002 and Round 1 at 2002; 6-th and 7-th Round International Intercalibration Study by MTM Research Center Orebro University, Sweden (for DIOXIN 2001 and 2002); Second Italian Free Intercalibration Round. Detailed method description are given in *Appendix 1*.

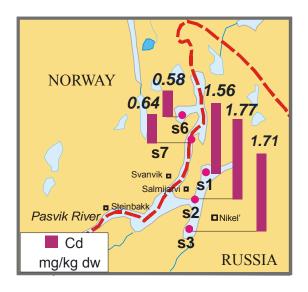
Additional quality assurance was provided by Akvaplan-niva and University of Michigan on a subset of samples.

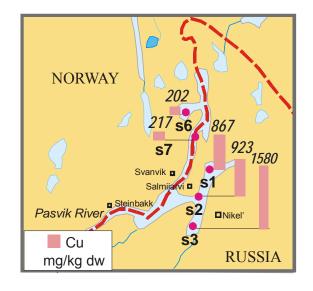
5.2. Trace elements

Table 2 summarize the results of trace element analyses in bottom sediment samples. Geographical distribution of the trace element concentrations are shown in and *Figure 3*.

Table2. Trace element concentrations (mg/kg dry weight) in surface bottom sediments from Kuetsjarvi Lake and Paz watercourser, August-September 2003.

			Elen	nents	
Station	Lake	Cadmium	Copper	Nickel	Mercury
number		(Cd)	(Cu)	(Ni)	(Hg)
1	Kuetsjarvi	1.56	867	2030	0.12
2	Kuetsjarvi	1.77	923	2500	0.47
3	Kuetsjarvi	1.71	1580	2390	0.73
6	Skrukkebukta	0.58	202	322	0.20
7	Bjørnvatn	0.64	217	419	0.12





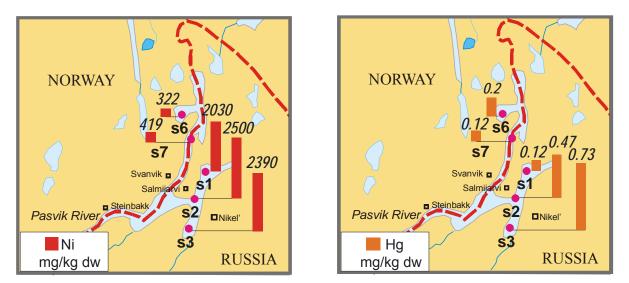


Figure 3. Trace elements (mg/kg dry weight) in surface (0-1 cm) bottom sediments. Numbers above bars represent concentrations of the elements.

All trace element levels decreased with increasing distance from the smelters. According to Norwegian Pollution Control Authorities (SFT) environmental classification (Andersen *et al.*, 1997) of freshwater sediments, Kuetsjarvi Lake sediments can be considered as "strongly contaminated" with Cu and Ni, "markedly contaminated" with Hg, and "moderately contaminated" with Cd.

The Paz-watercourse sediments can be classified as "markedly contaminated" with Ni and Cu, "moderately contaminated" with Cd, while Hg levels were as low as "background" levels (Andersen *et al.*, 1997).

5.3. Polycyclic aromatic hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) belong to one of the most hazardous classes of hydrophobic persistent organic pollutants having high potential for accumulation in biological tissues. Recent studies have examined dioxin-like activity of PAHs and shown that their contribution to total toxicity equivalent value is greater that those by dioxins and dioxin-like polychlorinated biphenyls (Willett et al., 1997; Clemons et al., 1998; Klimm et al., 1999; Kannan et al., 2000; Eljarrat et al., 2001). PAHs are ubiquitous contaminants of lacustrine sediments which arise from incomplete combustion of organic matter in flames, engines, and industrial processes (pyrogenic PAHs) and from emissions of oil-derived products (petrogenic PAHs). PAHs of biogenic origin are generated by biological processes or by the early stages of diagenesis in sediments (e.g. perylene) (Venkatesan, 1988). Therefore the level of perylene is related to the conditions in the catchment area of the lake. A catchment area with a lot of peat and bogs can lead to high levels of perylene in the lake sediments. Perylene is therefore often excluded when levels of PAHs are discussed. The relative amounts of the less stable kinetic PAH isomers compared to the more stable thermodynamic isomers of the same molecular mass (PAH ratios) are temperature dependent (Alberty and Reif, 1988) and they can indicate combustion or anthropogenic inputs (Yunker et al., 1995; 1996).

Table 3 summarize the results of PAH analyses in bottom sediment samples collected in the study area. Geographical distribution of total PAH concentrations (Σ PAH) are presented in *Figure 4*.

PAH related parameters	Abbreviation					Station numb	per and sed	iment slice				
		1	2	3	6	7	4	5	8a	8b	9a	9b
		Kuetsjarvi	Kuetciarvi	Kuetciarvi	Skrukke-	Bjørnvatn	Ruske-	Tjære-	Lake	Lake	Lake	Lake
			Rucisjaivi	Kucisjaivi	bukta	Bjørnvatn	bukta	bukta	Inari	Inari	Stuorajavri	Stuorajavri
		0-1 cm	0-1cm	0-1 cm	0-1 cm	0-1 cm	0-1 cm	0-1 cm	0-1 cm	15-18cm	0-1 cm	22-23cm
Naphthalene	NAP	93.3	79.2	92.3	67.0	36.2	19.2	13.3	73.9	42.5	42.0	26.6
Methylnaphthalene	C1N	170	152	222	160	89	n.a.	n.a.	158	143	172	110
Acenaphthylene	ACL	3.2	2.8	17.0	n.d.	n.d.	0.8	0.7	n.d.	n.d.	n.d.	n.d.
Acenaphthene	ACN	11.7	9.6	33.0	2.0	3.7	1.5	1.2	n.d.	n.d.	n.d.	n.d.
Fluorene	FLN	23.8	23.4	116	11.6	11.9	7.3	6.3	n.d.	n.d.	0.3	n.d.
Phenanthrene	PHE	95.7	116	598	17.3	24.2	40.6	37.9	5.9	1.4	5.1	1.3
Anthracene	ANT	21.6	27.8	278	4.5	6.5	1.1	1.4	2.7	1.1	2.0	0.4
Fluoranthene	FLT	225	259	2590	50.8	65.2	6.2	7.3	10.5	1.2	121	0.6
Pyrene	PYR	155	202	3230	34.5	43.6	13.5	11.2	8.5	5.1	119	0.9
Benzo(a)anthracene	BAA	87.6	111	1400	16.5	25.9	4.2	3.3	9.6	n.d.	9.3	n.d.
Chrysene	CHR	272	264	1390	65.3	62.3	17.6	14.3	10.6	n.d.	9.2	n.d.
Benzo(b)fluoranthenes	BbF	n.d.	n.d.	n.d.	n.d.	n.d.	7.2	6.1	41.7	2.9	79.9	1.5
Benzo(k)fluoranthenes	BkF	n.d.	n.d.	n.d.	n.d.	n.d.	6.4	5.3	19.9	1.2	15.6	0.8
Benzo(b+k)fluoranthenes	BF	437	377	1270	82.7	85.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Benzo(e)pyrene	BeP	234	230	762	53.3	45.7	15.3	19.4	n.d.	n.d.	31.3	n.d.
Benzo(a)pyrene	BaP	82.3	76.0	660	14.8	18.8	8.4	7.3	37.9	2.5	7.3	1.4
Perylene	PER	201	203	338	1190	479	15.6	13.2	348	10058	6880	9953
Indeno(1,2,3cd)pyrene	IND	94.8	114	117	23.3	18.8	4.1	3.2	n.d.	n.d.	7.8	n.d.
Dibenzo(a,h)anthracene	DBA	29.9	29.8	16.3	n.d.	n.d.	3.3	2.6	n.d.	n.d.	n.d.	n.d.
Benzo(g,h,i)perylene	BP	48.0	110	71.3	20.8	21.8	42.2	37.3	n.d.	n.d.	n.d.	n.d.
Total PAH	ΣΡΑΗ	2286	2387	13201	1815	1038	215	192	727	10259	7502	10096
Total PAH perylene excluded	ΣPAH-PER	2085	2184	12863	625	559	199	178	379	201	622	143
ANT/(ANT+PHE)	ANT/178	0.18	0.19	0.32	0.21	0.21	0.03	0.04	0.31	0.43	0.28	0.22
FLT/(FLT+PYR)	FLT/202	0.59	0.56	0.45	0.60	0.60	0.32	0.39	0.55	0.19	0.50	0.42
BAA/(BAA+CHR)	BAA/228	0.24	0.30	0.50	0.20	0.29	0.19	0.19	0.48	n.d.	0.50	n.d.
BAP/(BAP+BEP)	BAP/252	0.26	0.25	0.46	0.22	0.29	0.35	0.27	n.d.	n.d.	0.19	n.d.
IND/(IND+BP)	IND/276	0.66	0.51	0.62	0.53	0.46	0.09	0.08	n.d.	n.d.	n.d.	n.d.
TEQ for dioxin-like PAHs	TEQ _{PAH}	184	164	673	34.6	36.6	7.8	6.6	33.2	2.2	38.0	1.2

Table 3. Polycyclic aromatic hydrocarbons (PAHs, ng/g dry weight) in bottom sediments, PAH ratios and TCDD-equivalents for dioxin-like PAHs (TEQ_{PAH}) (pgTEQ/g dry weight) calculated using toxic equivalency factors (TEFs) proposed by Klimm et al. (1999).

n.d.=not detected; n..a.=not analysed

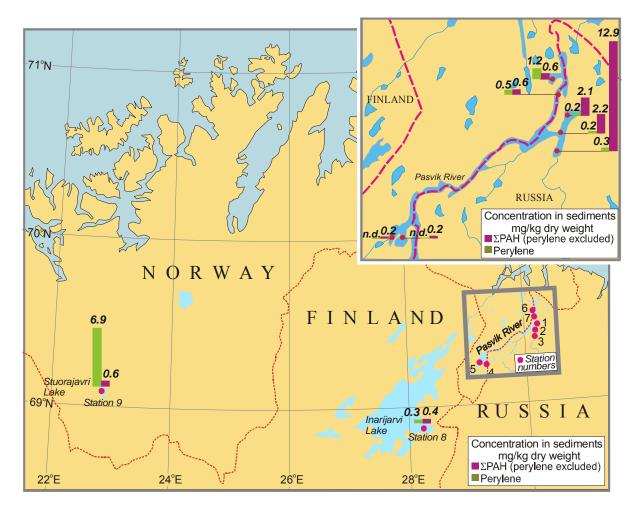


Figure 4. Polycyclic aromatic hydrocarbons (mg/kg dry weight) in surface (0-1 cm) bottom sediments. Number above bars are values of total PAH (perylene excluded) and perylene concentrations.

The highest Σ PAH-pervlene concentrations (2.1 – 12.9 mg/kg dry weight) were found in sediment samples collected in Lake Kuetsjarvi (stations 1-3) close to the Nikel's smelter (Figure 4). Pyrogenic PAHs (fluoranthene, pyrene and benzofluoranthenes) prevailed in PAH composition (*Figure 5*). North off the smelter area (stations 6 and 7) the Σ PAH-perylene concentration was lower than those found in samples from Kuetsjarvi Lake. Concentrations of total PAH-perylene (ΣPAH-perylene, Figure 4) found in surface sediment samples from stations 6 and 7 (0.62-0.56 mg/kg dw) did not differ from those found in sediments collected in Lake Stuorajavri (0.62 mg/kg dw). However, it should be noted that PAH-perylene concentrations in surface (modern) sediments (0-1 cm slice) from Stuorajavri Lake were 4 times higher than those found in deeper sediments (15-18 cm, pre industrialized time). Relatively low PAH concentrations were found both in Tjærebukta and Ruskebukta (stations 4 and 5) and in Lake Inari (station 8); Σ PAH-Pervlene concentrations measured in sediments from these sites varied from 0.18 to 0.38 mg/kg dw (Table 3). For both Lake Stuorajavri and Lake Inari, the PAHperylene concentration found in the deeper slice of the core sample was lower than those in modern (surface) bottom sediments (Table 3). The level of perylene in Lake Stuorajavri was high and it is probably due to peat and bogs in the catchment area.

Screening studies of POP levels in bottom sediments from selected lakes in the Paz watercourse

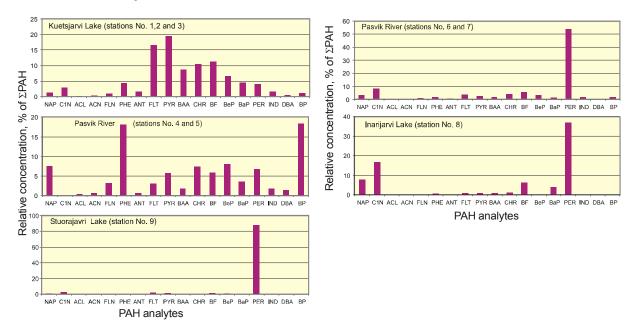


Figure 5. PAH profiles found in sediment samples from different sampling areas in 2003-2005.

Comparison of PAH ratios calculated for sediment samples from Lake Kuetsjarvi and Paz watercourse showed that in sample from station 3 values of three from five tested PAH ratios were higher compare with the other station investigated (*Table 3*). It can be confirmation of predominance of anthropogenic input into PAH level formation in sediments from station 3.

This is in agreement with the results from the Kola Ecogeochemistry project (Reimann *et al.*, 1995; 1997). During this study the highest concentrations of PAHs were found in the vicinity of Nikel. The results indicate that human sources are predominant. The PAH concentrations near Nikel were above the SFT threshold for areas for most sensitive use ((Vik *et al.*, 1999) of 2.0 ppm for Sum PAHs in soil (2.0 ppm)).

The Norwegian Pollution Control Authorities (SFT) has not developed an environmental classification system for pollutants in freshwater sediments other than for heavy metals. However, there is a classification system made for marine sediments (Molvær *et al.* 1997) that sometimes also are used for freshwater sediments (Rognerud *et al.* 1997). The conditions in the lake are classified in 5 different categories by using the concentrations of Σ PAH (minus perylene). Using this system the surface sediment from station 4 – 7, Lake Inari and Lake Stuorajavri are classified as "insignificantly contaminated (<300 ng/g dw)" or "moderately contaminated (300 – 2 000 ng/g dw)" of PAHs. However, sediments from station 1 and 2 in Lake Kuetsjarvi are classified as "markedly contaminated (2 000 – 6 000 ng/g dw)" and station 3 as "strongly contaminated (6 000 – 20 000 ng/g dw)". The results from our study are comparable to the results found by Skotvold *et al.* (1997) who studies sediments from 24 different lakes in Northern Norway in 1994 – 1996. In this study the levels of Σ PAH (minus perylene) in surface sediments from most lakes were less than 1 000 ng/g dw. The levels of Σ PAH-perylene in surface sediments from 5 lakes in Sør-Varanger municipality varied from <400 - 800 ng/g dw.

5.4. Persistent Organic Pollutants (POPs)

In science and daily language, POPs stands for persistent organic pollutants. In general, the term POPs does not have a clear definition and includes chemical compounds that are highly resistant to most forms of degradation and, therefore, have relatively long half-lives. POPs are often chlorinated and characterised by low water solubility and high lipid solubility. Due to their affinity for lipids they can easily be transported throughout the food chain and bioaccumulate in the fatty tissues of top-level predators, including humans. Most of the POPs are semi-volative compounds, and they are distributed to different degrees between gaseous, particulate and aqueous phases in the atmosphere, thereby facilitating their long- range transport.

Laboratory investigations and environmental impact studies have shown that POPs can cause birth defects, various cancers, immune system dysfunction, neurobehavioural effects and reproductive abnormalities in wildlife. Although the effects of POPs on human health are still quite unclear, there is a growing concern that even low-dose, long-term exposure may cause significant adverse health effects. For more information see de March *et al.* (1998) and AMAP (2004).

5.4.1. Chlorinated pesticides

Table 4 summarize the levels of organochlorine pesticides found in sediments from lakes within the study area. Geographic distributions of the selected OC concentrations are shown in *Figure 6*.

DDD

T was the dominating OC-pesticide in the sediment samples. The highest levels were measured close to the smelters (*Figure 6*). The levels of Σ DDT detected in this study are high compared to levels measured in sediments from the Arctic and from Norway (AMAP 1994, Muir *et al.*, 1995, Rognerud *et al.*, 1997, Skotvold *et al.*, 1997, Evenset *et al.*, 2006). Skotvold *et al.* (1997) found concentrations between 0.1 and 3.8 ng/g dw in surface sediments from 15 lakes in Finnmark County in 1995 - 1996. In 8 Arctic lakes in Canada the levels varied from 0.1 to 10 ng/g dw (Muir *et al.*, 1995). The levels of *p,p*'-DDE in Paz-watercourse is also high compared to levels measured by Skotvold *et al.* (1997). The reasons for the high levels of *p,p*'-DDT in both surface sediment and reference sediment from Stuorajavri Lake is not clear.

Also for Hexachlorobenzene (HCB) and Chlordanes were the highest levels were measured close to the smelters. However, the levels of these components were significantly lower than the DDT concentrations. HCH and endrin were only detected in samples from stations 4 and 5. Dieldrine and mirex were not detected in any of the samples. In sediment samples from station 4 and 5, pentachlorobenzene, octachlorostyrene, aldrin, dachtal, PCPME and photomirex were analysed in addition to the listed OCs. Aldrin and photomirex were not detected in any samples. Concentrations of the others above-listed OC compounds were low, ranging from 0.012 to 0.082 ng/g dw (*Table 4*).

OCs				St	ation nu	mber an	d sedime	ent slice			
	1	2	3	6	7	4	5	8a	8b	9a	9b
	Kuets-	Kuets-	Kuets-	Skrukke	Bjørn-	Ruske-	Tjære-	Lake	Lake	Lake	Lake
	jarvi	jarvi	jarvi	-bukta	vatn	bukta	bukta	Inari	Inari		Stuorajavri
	0-1 cm								15-18cm		22-23cm
α-НСН	n.d.	n.d.	n.d.		n.d.	0.010	n.d.	n.d.	n.d.		n.d.
β-НСН	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.		n.d.
ү-НСН	n.d.	n.d.	n.d.		n.d.	n.d.	n.d.	n.d.	n.d.		n.d.
¹ ΣHCH	n.d.	n.d.	n.d.		n.d.	0.014	0.027	n.d.	n.d.		n.d.
Heptachlor	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.	n.d.	n.d.		n.d.
Heptachlor epoxide	n.d.	n.d.	n.d.		n.d.	0.003	n.d.	n.d.	n.d.	n.d.	n.d.
Oxychlordane	n.d.	n.d.	n.d.		n.d.	0.008	0.016	n.d.	n.d.	n.d.	n.d.
trans-Chlordane	n.d.	n.d.	n.d.		n.d.	0.007	0.010	n.d.	n.d.	n.d.	n.d.
cis-Chlordane	n.d.	n.d.	n.d.		n.d.	0.005	0.014	n.d.	n.d.		n.d.
trans-Nonachlor	0.21	n.d.	0.54	n.d.	n.d.	0.013	0.048	n.d.	n.d.	0.7	n.d.
cis-Nonachlor	0.11	n.d.	0.22		n.d.	0.006	0.013	n.d.	n.d.		n.d.
$^{2}\Sigma CHL$	0.32	n.d.	0.76	n.d.	n.d.	0.041	0.101	n.d.	n.d.	0.7	n.d.
<i>o,p</i> `-DDE	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.	n.d.	n.d.	n.d.	n.d.
<i>p,p</i> `-DDE	10.9	8.7	12.0		1	9.8	8.7	0.47	0.11	0.5	n.d.
o,p`-DDD	0.34	n.d.	n.d.	1.4	n.d.	n.a.	n.a.	n.d.	n.d.	n.d.	n.d.
<i>p,p</i> `-DDD	8.56	7	11.8	3.7	1	0.014	n.d.	n.d.	n.d.	1.5	n.d.
o,p`-DDT	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.	n.d.	n.d.	n.d.	n.d.
<i>p,p</i> `-DDT	1.21	0.8	1.09	0.3	n.d.	0.021	n.d.	n.d.	n.d.	26	10.6
$^{3}\Sigma DDT$	21	16	24.9	9.2	2.0	9.8	8.7	0.47	0.11	27.7	10.6
Endrin	n.d.	n.d.	n.d.	n.d.	n.d.	0.030	n.d.	n.d.	n.d.	n.d.	n.d.
Dieldrin	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Mirex	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Hexachlorobenzene	0.92	0.7	1.05	0.3	0.3	0.014	0.027	n.d.	0.24	0.40	0.13
Pentachlorobenzene	n.a.	n.a.	n.a.	n.a.	n.a.	0.024	0.082	n.a.	n.a.	n.a.	n.a.
Octachlorostyrene	n.a.	n.a.	n.a.	n.a.	n.a.	n.d.	0.036	n.a.	n.a.	n.a.	n.a.
Aldrin	n.a.	n.a.	n.a.	n.a.	n.a.	n.d.	n.d.	n.a.	n.a.	n.a.	n.a.
Dachtal	n.a.	n.a.	n.a.	n.a.	n.a.	n.d.	0.012	n.a.	n.a.	n.a.	n.a.
PCPME	n.a.	n.a.	n.a.	n.a.	n.a.	n.d.	0.015	n.a.	n.a.	n.a.	n.a.
Photomirex	n.a.	n.a.	n.a.	<u>n.a.</u>	n.a.	<u>n.d.</u>	n.d.	n.a.	n.a.		n.a.

Table 4. Chlorinated pesticides (OCs) (ng/g dry weight) in bottom sediments, 2003-2005.

¹SHCH is sum of α -HCH, β -HCH, and γ -HCH, ²SCHL is sum of heptachlor, heptachlor epoxide, oxychlordane, *trans*-chlordane, *cis*-chlordane, *trans*-nonachlor and *cis*-nonachlor; ³SDDT is sum of *o*,*p*`-DDE, *p*,*p*`-DDE, *o*,*p*`-DDD, *p*,*p*`-DDT and *p*,*p*`-DDT; n.d.=not detected; n.a.=not analysed.

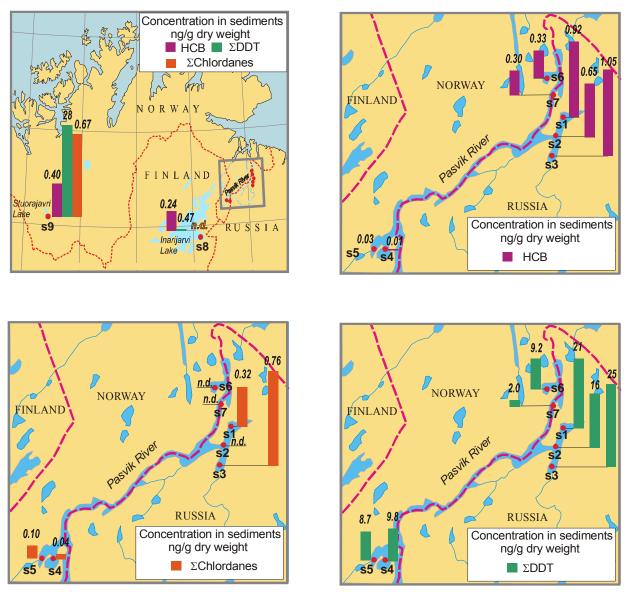


Figure 6. Chlorinated pesticide levels (ng/g dry weight) in surface (0-1 cm) bottom sediments, 2003-2005. Numbers above bars represent concentrations of the contaminants.

5.4.2. Polychlorinated biphenyls

Polychlorinated biphenyls (PCBs) are a family of 209 synthetic compounds made up of attached benzene rings with varying numbers and locations of chlorine atoms. PCBs are characterized by their low flammability, low electrical conductivity, high resistance to thermal breakdown and to other chemical agents, and high degree of chemical stability. These qualities make them effective coolants, lubricants, and insulators. However, the same properties that led to their extensive use in industry (mainly resistance to degradation and low volatility) also make them persistent environmental contaminants and a serious health threat to humans and wildlife. PCBs concentrate in the food web and bioaccumulate in the fatty tissues of animals and humans. Chronic low-level PCB exposures can cause liver damage, reproductive abnormalities, immune suppression, neurological and endocrine system disorders, retarded infant development, and stunted intellectual function. The International Agency for Research on Cancer ranks PCBs as a probable human carcinogen. Non-ortho and some mono-ortho CB congeners are the most toxic contaminants among all PCBs because they exert their toxic effect via the same mechanism as dioxins. Such PCBs are called dioxin-like PCBs.

Table 5 summarize the result of PCB analyses in bottom sediment samples. Geographical distribution of total PCBH concentrations is shown in *Figure 7*.

Table 5. Polychlorinated biphenyls (PCBs) (ng/g dry weight) in bottom sediments. TCDD-equivalents (TEQ_{PCB}) (pgTEQ/g dry weight) are calculated using toxic equivalency factors (TEFs) according to the WHO International Program on Chemical Safety (IPCS) model (Ahlborg et al., 1994). Non-ortho and mono-ortho substituted CB congeners are marked by bold font.

				S	tation nu	mber and	d sedime	ent slice			
PCBs	1	2	3	6	7	4	5	8a	8b	9a	9b
	Kuets- jarvi	Kuets- jarvi	Kuets- jarvi	Skrukke bukta	- Bjørn- vatn	Ruske- bukta	Tjære- bukta	Lake Ina	ri Lake Inari	Lake Stuora javri	Lake - Stuora- javri
		0-1cm	0-1 cm	0-1 cm	0-1 cm		0-1 cm	0-1 cm	15-18cm		22-23cm
#1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.		n.d.		n.d.
#4/#10	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.		n.d.		n.d.
#3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.		n.d.	n.d.	n.d.
#8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.		n.d.	n.d.	n.d.
#15	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.		n.d.	n.d.	n.d.
#17/#18	n.d.	n.d.	0.42	0.43	0.57	n.d.	n.d.		0.07		n.d.
#19	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.		n.d.	n.d.	n.d.
#22	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.		0.06		n.d.
#28/#31	0.10	0.12	0.44	0.25	0.33	n.d.	n.d.		0.29		0.09
#33	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.		n.d.	n.d.	n.d.
#37	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.18
#44	0.35	0.38	0.43	0.60	0.49	n.d.	n.d.	0.82	n.d.	0.13	n.d.
#49	n.d.	0.05	0.32	0.21	0.14	n.d.	n.d.	1.38	n.d.	0.17	0.23
#52	2.05	1.47	1.14	0.89	0.57	n.d.	n.d.	1.40	2.94	0.28	n.d.
#54	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
#70	1.42	1.13	1.14	0.26	1.00	0.03	0.02	1.22	0.52	0.66	0.92
#74	0.65	0.67	0.38	0.13	0.39	n.d.	n.d.	0.68	0.43	0.48	n.d.
#77	n.d.	0.09	n.d.	0.07	n.d.	n.d.	n.d.	0.11	n.d.	0.20	n.d.
#81	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.		n.d.		n.d.
#87	n.d.	1.85	0.79	0.82	0.69	n.d.	n.d.	0.95	n.d.	0.27	0.12
#95	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.		n.d.	0.32	n.d.
#99	1.64	2.15	1.94	0.85	0.51	n.d.	n.d.		0.23		1.60
#101	2.53	2.24	2.18	0.96	0.78	0.43	0.80		0.36		0.13
#104	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.		n.d.		n.d.
#105	1.14	1.21	3.83	0.47	0.31	0.95	1.19		0.63		0.31
#110	3.56	4.50	3.03	1.60	1.03	n.d.	n.d.		0.81	1.24	0.49
#114	n.d.	n.d.	0.55	n.d.	n.d.	1.02	1.23		0.55		n.d.
#118	2.98	3.08	6.67	1.34	0.97	0.66	0.75		0.92		0.27
#119	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.		n.d.		n.d.
#123	0.15	0.33	0.49	0.1	0.08	n.d.	n.d.		n.d.		0.11
# 126	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.		n.d.		n.d.
#128	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.		n.d.	0.21	n.d.
#138/#158 #149	2.11	2.20	3.02	0.84	0.67	0.87 1.19	1.10 1.23		0.06		0.17
#149 #151	n.d. n.d.	3.16 n.d.	1.05	0.81	0.71 n.d.	0.38	0.54		n.d. n.d.		n.d. n.d.
#153/#168	3.84	3.80	n.d. 5.22	n.d. 1.18	0.97	0.38	1.09		0.08		0.11
#155	5.84 n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.		n.d.		n.d.
#155 # 156	n.d.	n.d.	n.d.	n.d.	n.d.	n.d. n.d.	n.d. n.d.		n.d. n.d.		n.d.
#150 #157	n.d.	n.d.	n.u. n.d.	n.u. n.d.	n.d.	n.u. n.d.	n.u. n.d.		n.d.		n.d.
#157 #167	n.d.	n.d.	n.d.	0.35	n.d.	n.d.	n.d.		n.d.		n.d.
#107 #169	n.d.	n.d.	n.u. n.d.	0.33 n.d.	n.d.		n.d.		n.d.		n.d.
#170	n.d.	0.51	0.76	0.01	n.d.	0.32	0.36		n.d.		n.d.
#171	n.d.	n.d.	n.d.	n.d.	n.d.	0.32	0.27		n.d.		n.d.
#177	n.d.	n.d.	n.d.	n.d.	n.d.	0.54	0.69		n.d.		n.d.
#178	n.d.	n.d.	n.d.	n.d.	n.d.	0.45	0.54		n.d.		n.d.
#180	n.d.	0.64	2.57	n.d.	0.3	1.95	1.77		0.25		n.d.
			/			0.76	0.92		÷.=•		

Screening studies of POP levels in bottom sediments from selected lakes in the Paz watercourse

				St	ation nur	nber and	sedimen	t slice			
PCBs	1	2	3	6	7	4	5	8a	8b	9a	9b
#187	n.d.	n.d.	n.d.	n.d.	n.d.	0.23	0.41	n.d.	n.d.	n.d.	n.d.
#188	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
#189	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
#191	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
#194	n.d.	n.d.	n.d.	n.d.	n.d.	0.01	0.03	n.d.	n.d.	n.d.	n.d.
#199	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
#201	n.d.	n.d.	n.d.	n.d.	n.d.	1.38	1.62	n.d.	n.d.	n.d.	n.d.
#202	n.d.	n.d.	n.d.	n.d.	n.d.	0.27	0.41	n.d.	n.d.	n.d.	n.d.
#205	n.d.	n.d.	n.d.	n.d.	n.d.	0.02	0.03	n.d.	n.d.	n.d.	n.d.
#206	n.d.	n.d.	n.d.	n.d.	n.d.	0.01	0.02	n.d.	n.d.	n.d.	n.d.
#208	n.d.	n.d.	n.d.	n.d.	n.d.	0.12	0.15	n.d.	n.d.	n.d.	n.d.
#209	n.d.	n.d.	n.d.	n.d.	n.d.	0.02	0.02	n.d.	n.d.	n.d.	n.d.
$^{1}\Sigma(n,m-o)PCB$	4.27	4.71	11.5	2.33	1.36	2.63	3.17	8.11	2.10	2.40	0.69
$^{2}\Sigma PCB$	22.5	29.6	36.4	12.2	10.5	12.7	15.2	28.8	8.2	8.6	4.7
TEQ _{PCB}	0.427	0.507	1.374	0.230	0.136	0.670	0.809	0.855	0.430	0.352	0.069

n.d.=not detected. ¹ Σ (n,m-o)PCB is sum of non-*ortho* and mono-*ortho* CBs; ² Σ PCB is sum of 64 PCB congeners.

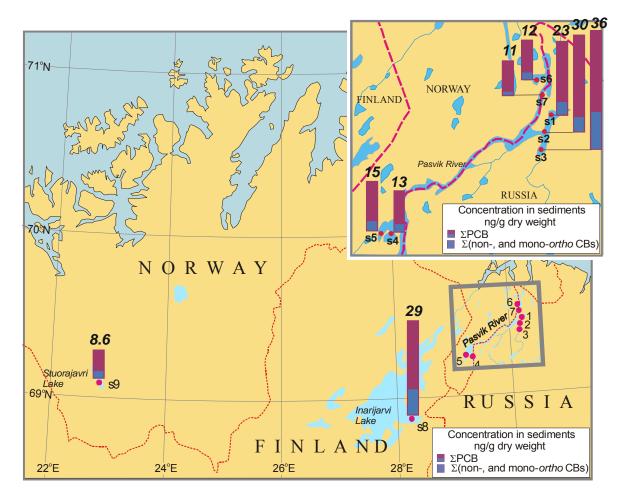


Figure 7. Polychlorinated biphenyls (ng/g dry weight) in surface (0-1 cm) bottom sediments. Numbers above bars represents total PCB concentrations (Σ PCB).

The levels of Σ_{64} PCB in the Paz watercourse varied from 10.5 to 36.4 ng/g dw. The highest PCB levels were detected in the bottom sediments from Lake Kuetsjarvi (36.4 ng/g dw, *Table 5*). There was a tendency of decreasing PCB levels (including non-ortho and mono-ortho substituted PCB congeners) with increasing distance from the smelter (*Figure 7*). However, a high PCB concentration (28.8 ng/g dw) was also found in the surface sediment sample from Lake Inari (3.9 times higher than in the deeper sediment core slice). The PCB-pattern in sediment from the two

areas was similar (*Figure 8*). For identification of PCB contamination source in the Lake Inari area more detailed studies are needed.

The levels of PCB in the Paz watercourse are high compared to levels found in surface sediments from other lakes in Northern Norway. Skotvold *et al.* (1997) investigated 24 different lakes and detected levels from <1.0 ng/g dw - 14 ng/g dw of Σ_7 PCB in surface sediments. The levels of PCB in sediments from 5 lakes in the municipality of Sør-Varanger were higher (>5 ng/g dw) compared to the levels from 10 other lakes in Finnmark County (<3 ng/g dw).

The Norwegian Pollution Authorities have not developed an environmental classification system for pollutants in freshwater sediments other than for heavy metals. However the classification system made for marine sediments (Molvær *et al.*, 1997) is sometimes used for freshwater sediments (Rognerud *et al.*, 1997). According to this system the PCB levels measured in the Paz watercourse and the reference lakes are classified as either "Moderately contaminated" (5-25 ng/g dw) or "Markedly contaminated" (25 – 100 ng/g dw).

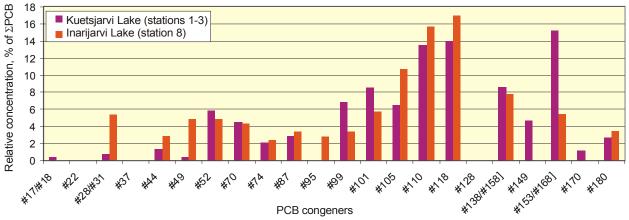


Figure 8. PCB patterns on sediment samples from Kuetsajarvi and Inarijarvi lakes. PCBs with valid concentrations are shown only.

Concentrations of sum of non-ortho and mono-ortho substituted PCBs (planar PCBs) ranged from 1.48 ng/g dw (station 3) to 0.14 ng/g dw (station 7). PCBs #118, 105 and 114 were the most abundant planar PCB. Their contributions to sum of planar PCBs were 42%, 24%, and 21% respectively.

5.4.3. Toxaphenes

The complex mixtures of polychlorobornanes and camphenes known as toxaphene were widely used in the USA on cotton crops. Similar products have been, and may continue to be used in Mexico, Central America, eastern Europe, and the former Soviet Union (de March *et al.*, 1998). Toxaphene is extremely persistent in soils following pest control application, with reported halv-lives ranging from one to 14 years (Howard, 1991). Data on toxaphene levels in sediments from the study area are presented in *Table 6*.

Table 6. Selected toxaphene congeners (Parlar et al., 1995) and sum of hexa-, hepta-, octa- and nona/deca-chlorobornane toxaphenes (ng/g dry weight)in bottom sediments.

Toxaphenes				Sta	tion nu	mber and	d sedim	ent slice	;		
-	1	2	3	6	7	4	5	8a	8b	9a	9b
	Kuets- jarvi	Kuets- jarvi	Kuets- jarvi	Skrukke bukta	- Bjørn- vatn	Ruske- bukta	Tjære- bukta	Lake Inari	Lake Inari	Lake Stuora- javri	Lake Stuora- javri
	0-1 cm	0-1cm	0-1 cm	0-1 cm	0-1 cm	0-1 cm	0-1 cm	0-1 cm	15-18cm	n 0-1 cm	22-23cm
Parlar#26	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.	n.d.	n.d.	n.d.	n.d.
Parlar#50	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.	n.d.	n.d.	n.d.	n.d.
Parlar#62	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.	n.d.	n.d.	n.d.	n.d.
Hexa-toxaphene	n.a.	n.a.	n.a.	n.a.	n.a.	4.39	3.18	n.a.	n.a.	n.a.	n.a.
Hepta-toxaphene	n.a.	n.a.	n.a.	n.a.	n.a.	2.03	2.12	n.a.	n.a.	n.a.	n.a.
Octa-toxaphene	n.a.	n.a.	n.a.	n.a.	n.a.	1.02	0.06	n.a.	n.a.	n.a.	n.a.
Nona/deca-toxaphene	n.a.	n.a.	n.a.	n.a.	n.a.	0.02	0.01	n.a.	n.a.	n.a.	n.a.
ΣToxaphene	n.a.	n.a.	n.a.	n.a.	n.a.	7.46	5.37	n.a.	n.a.	n.a.	n.a.

n.d.=not detected; n.a.=not analysed.

Single congeners were not detected in any of the analysed samples. Analyses of hexa-, heptaocta- and nona/deca-toxaphanes were carried out on sediments from two sites only (stations 4 and 5). Total toxaphene concentrations (as a sum of hexa-, hepta- octa- and nona/decatoxaphanes) in sediment samples from these sites were 5.37 and 7.46 ng/g dw respectively (*Table 7*.)

5.4.4. Polybrominated diphenyl ethers (PBDEs)

Polybrominated diphenyl ethers (PBDEs) are commonly used as flame retardants in a variety of applications such as foams, textiles and computer materials. Most industrially manufactured PBDEs contain mixtures of brominated diphenyl ethers. There are 209 possible PBDE congeners and positions of the bromine atoms on the two phenyl rings. There is evidence that some PBDEs bioaccumulate and exert toxic effects at low levels. EPA has classified decabromodiphenyl ether as a possible human carcinogen. PBDEs are also endocrine disrupters. Some resemble the thyroid hormone thyroxin and others are estrogenic. More information on PBDEs can be found in Rahman *et al.* (2000), de Wit (2002), de Wit & Muir (2004) and in the special issue of a Journal of Environmental Science, Risk & Health ("The State of Science and Trends of BFRs in the Environment" v. 29, 2003).

Table 7 present the PBDE concentrations (Sum of 7 congeners) found in sediment samples. Geographical distribution of the sum of these contaminants is shown in *Figure 9*.

Tuble 7. Tolybr	ommuteu	i uipne.	nyi cine	/ S (I D.	DLS (I	<u>, g u </u>	y weigi			imenis	•
PBDEs				St	ation nu	mber an	d sedime	ent slice			
	1	2	3	6	7	4	5	8a	8b	9a	9b
	Kuets- jarvi	Kuets- jarvi	Kuets- jarvi	Skrukke- bukta	Bjørn- vatn	Ruske- bukta	Tjære- bukta	Lake Inari	Lake Inari	Lake Stuora- javri	Lake Stuora- javri
	0-1 cm	0-1cm	0-1 cm	0-1 cm	0-1 cm	0-1 cm	0-1 cm	0-1 cm	15-18cm	0-1 cm	22-23cm
PBDE # 28	1.98	0.98	n.d.	1.2	1.5	n.a.	n.a.	3.05	0.41	0.79	n.d.
PBDE # 47	52.0	28.9	9.47	33	31	8.03	6.00	56.1	5.52	3.05	10.1
PBDE # 99	42.3	35.6	31.2	27	29	1.14	0.70	45	3.05	7.23	1.99
PBDE # 100	8.17	6.2	1.65	5.8	6.1	1.04	2.00	12.3	0.67	1.88	0.37
PBDE # 153	n.d.	n.d.	9.18	n.d.	n.d.	1.33	2.00	7.79	0.8	1.65	0.58
PBDE # 154	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.	9.08	0.77	1.56	0.48
PBDE # 183	n.d.	n.d.	14.4	n.d.	n.d.	n.a.	n.a.	13.4	1.88	3.46	1.67
Sum of PBDE	104	71.7	65.9	67	68	11.5	10.7	147	13.1	19.6	15.2

Table 7. Polybrominated diphenyl ethers (PBDEs) (pg/g dry weight) in bottom sediments.

n.d.=not detected; n.a.=not analysed.

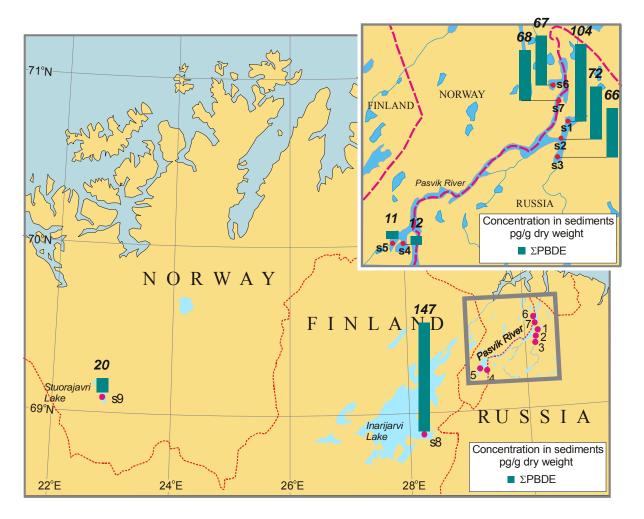


Figure 9. Polybrominated diphenyl ethers(pg/g dry weight) in bottom sediments. Numbers above bars are values of total PBDE concentrations ($\Sigma PBDE$).

The highest PBDE levels were found in sediment samples from Lake Inari (147 pg/g dw) (station 8) and from Lake Kuetsjarvi (104 pg/g dw) (station 1). However, the PBDE pattern varied between areas (*Figure 10*) indicating different sources for the PBDE contamination. In general, PBDEs #47 and 99 were the most abundant; their total contribution to Σ PBDE varied between 53% (station 9) and 90% (station 1).

There are not many studies on PBDE levels in surface sediments from lakes in Norway. However, there are some studies from Ellasjøen on Bjørnøya, Svalbard in the Norwegian Arctic and some studies in the Canadian Arctic. The levels detected in the Paz-watercourse are lower than the levels in sediments from Ellasjøen from Bjørnøya (740 pg/g dw) and from Great Lakes in the Canada (500 - 3100 pg/g dw) (Song *et al.*, 2004, 2005). In Ellasjøen a dated sediment core the levels are increasing rapidly the last years (Evenset *et al.*, 2006).

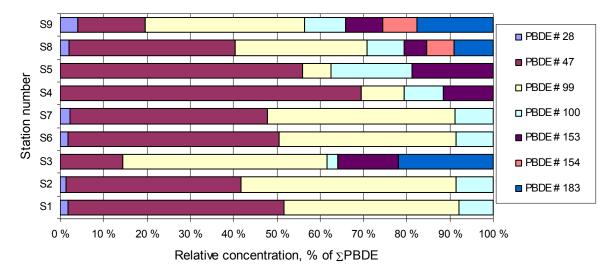


Figure 10. Contributions of PBDE congeners to total PBDE concentration in bottom sediments.

5.4.5. Polychlorinated dibenzo-para-dioxins and polychlorinated

dibenzofurans (PCDDs/PCDFs)

Neither dioxins nor furans are produced commercially because they have no known use. These are by-products resulting from the production of other chemicals. Dioxins may also be released into the environment through the production of pesticides and other chlorinated substances. Furans are a major contaminant formed during production of PCBs. Both dioxins and furans are produced in a variety of incineration reactions, and during the synthesis and use of a variety of chemical products. Dioxins and furans have been detected in emissions from the incineration of coal, peat and wood, as well as from the incineration of wastes and in emission from smelters. Dioxins and furans are two groups of planar tricyclic compounds that have very similar chemical structures and properties. They may contain between 1 and 8 chlorine atoms; dioxins have 75 possible positional isomers and furans have 135 positional isomers. They are generally very persistent and lipophilic. The most toxic compound is 2,3,7,8-tetrachlorodibenzo-p-dioxin or TCDD. The toxicity of other dioxins and chemicals like PCBs that act like dioxin are measured in relation to TCDD. Of the 210 dioxins and furans, 17 contribute most significantly to the toxicity of complex of mixtures. In order to facilitate a comparison of mixtures, International Toxicity Equivalency Factors (TEFs) have been assigned to individual dioxins and furans based on a comparison of toxicity to 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). The IARC has determined that 2,3,7,8-TCDD can cause human cancer. Table 8 summarise of the results of PCDD/F analyses. Geograpical distribution of total dioxin concentration found in sediment samples from the sites investigated is presented in Figure 10.

Table 8. Polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) (pg/g dry weight) in bottom sediments. TCDD-equivalents (TEQ) (pgTEQ/g dry weight) calculated using toxic equivalency factors (TEFs) of the international (I-TEF) model (NATO/CCMS, 1988) are also presented.

PCDD/PCDF			S	tation nu	mber and	l sedimer	nt slice		
	1	2	3	6	7	8a	8b	9a	9b
		uets- Kuet rvi jarvi		ke- Bjørn- vatn	Ruske- bukta	Tjære- bukta	Lake Lal Inari Ina	Sfuora	Lake - Stuora- javri
	0-1 cm	0-1cm	0-1 cm	0-1 cm	0-1 cm	0-1 cm	15-18cm	0-1 cm 2	22-23cm
2,3,7,8-TCDD	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1,2,3,7,8-PeCDD	n.d.	n.d.	0.42	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1,2,3,4,7,8-HxCDD	n.d.	n.d.	0.18	n.d.	n.d.	n.d.	n.d.	0.51	n.d.
1,2,3,6,7,8- HxCDD	n.d.	n.d.	0.63	n.d.	n.d.	n.d.	n.d.	0.97	n.d.
1,2,3,7,8,9- HxCDD	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.69	n.d.
1,2,3,4,6,7,8-HpCDD	4.65	5.88	4.18	9.30	4.34	8.40	0.42	6.44	0.56
OCDD	49.8	48.3	28.2	38.4	35.8	37.3	4.93	37.2	10.3
ΣPCDD	54.5	54.2	33.6	47.7	40.1	45.7	5.35	45.8	10.9
TEQ _{PCDD}	0.096	0.11	0.36	0.13	0.079	0.12	0.009	0.32	0.016
2,3,7,8-TCDF	5.22	3.30	2.53	1.24	1.18	n.d.	n.d.	0.27	n.d.
1,2,3,7,8-PeCDF	3.84	3.66	1.15	3.74	1.33	1.13	n.d.	0.56	n.d.
2,3,4,7,8-PeCDF	3.91	4.38	2.94	3.11	1.34	1.82	n.d.	0.81	n.d.
1,2,3,4,7,8-HxCDF	2.85	3.56	1.95	5.12	1.17	2.30	n.d.	1.44	n.d.
1,2,3,6,7,8- HxCDF	2.24	1.71	1.18	3.58	0.86	1.83	n.d.	0.90	n.d.
2,3,4,6,7,8-HxCDF	2.65	2.19	4.53	2.42	1.03	1.08	n.d.	0.79	n.d.
1,2,3,7,8,9-HxCDF	n.d.	n.d.	0.91	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1,2,3,4,6,7,8-HpCDF	28.4	18.7	9.18	5.34	6.18	6.80	0.18	5.22	0.24
1,2,3,4,7,8,9-HpCDF	1.88	1.16	0.89	2.40	n.d.	2.72	n.d.	0.46	n.d.
OCDF	20.1	10.6	22.9	19.4	4.55	12.8	0.43	8.56	n.d.
ΣPCDF	71.1	49.3	48.2	46.4	17.6	30.5	0.61	19.0	0.24
TEQ _{PCDF}	3.77	3.66	2.76	3.07	1.23	1.60	0.002	0.84	0.002
ΣPCDD/F	126	104	81.8	94.1	57.7	76.2	5.96	64.8	11.1
TEQ _{PCDD/F}	3.86	3.77	3.12	3.21	1.31	1.72	0.01	1.16	0.02

n.d. = no detected.

The highest total PCDD/F concentrations (126 pg/g dw) were found in bottom sediment from Lake Kuetsjarvi (Station 1). However there were not significant differences between the levels measured in "unpolluted" sites (stations 8 and 9) and the sites downstream the smelters. On the other hand concentrations of PCDD/F found in modern (surface) sediments from the reference lakes were much higher than those in deeper sediment core slices (*Table 8*).

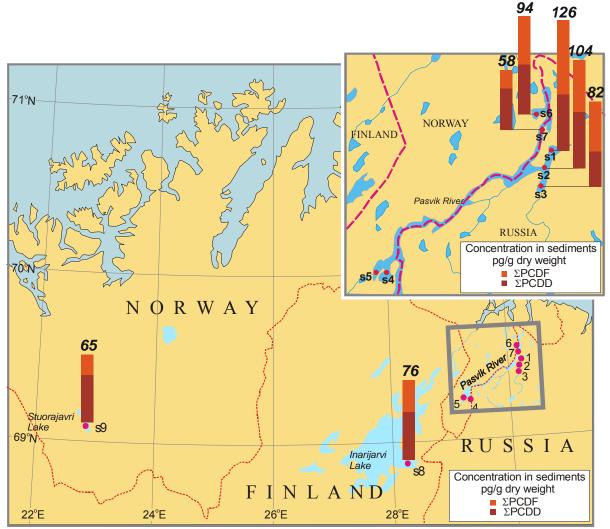


Figure 10. Polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) (pg/g dry weight) in surface (0-1 cm) bottom sediments. Numbers above bars are sum of PCDDs and PCDFs (Σ PCDD/F).

Applying of toxic equivalency factors (TEFs) (NATO/CCMS, 1988) allowed calculation of 2378-TCDD toxic equivalents (TEQ_{PCDD/F}) for sediment from the studied lake. The highest TEQ_{PCCD/F} values were found in Lake Kuetsjarvi (*Table 8*). PCDFs were the major contributors to the TEQ_{PCDD/F}.

Only limited information exists on dioxin levels in freshwater sediments from the study area. In the end of 1990s, studies on PCDD/PCDF levels in lacustrine bottom sediments were carried out on Varanger and Kola Penisulas (Schlabach and Skotvold, 1996; Skotvold and Schlabach, 1997; Skotvold and Savinov, 2003). High PCDD/PCDF levels were found in both areas. There is not recent available information for comparison.

Figure 11 shows geographical distribution of the $TEQ_{TCDD/F}$ calculated for bottom sediments from the Arctic lakes in 1996 (Skotvold *et al.*, 1997) and for reported data.

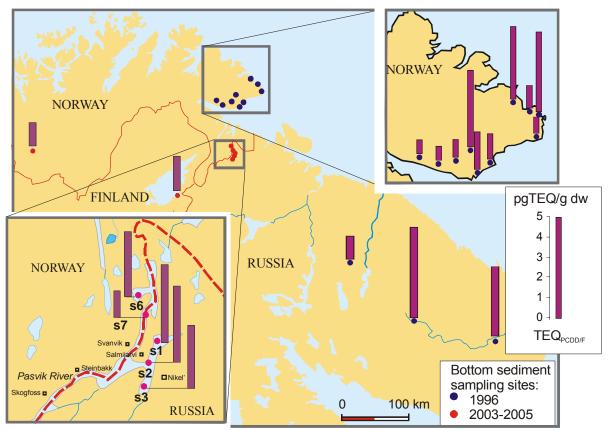


Figure 11. TCDD toxic equivalent ($TEQ_{PCDD/F}$) (pgTEQ/g dry weight) calculated for PCDDs and PCDFs in bottom sediments from the Arctic lakes in 1996 (Skotvold et al. 1997) and 2003-2005 (reported data).

6. Toxicity of contaminant mixture

In mixture together with others contaminants, some OCs can cause additive effects, others antagonize, and others synergistic responses (de March et al., 1998). Non-*ortho* (IUPAC nos. 77, 81, 126 and 169) and some mono-*ortho* CBs (IUPAC nos. 105, 114, 118, 123, 156, 157, 167 and 189) are stereochemically similar to 2,3,7,8 tetrachlorodibenzo-*p*-dioxin (2378-TCDD) and exert their toxic effect via the same mechanism as 2378-TCDD. Such PCBs are known as dioxin-like PCBs. Effect of a mixture of dioxin-like PCBs, and TCDD/F seems to be additive (de March et al., 1978). Individual toxicity of both PCDD/Fs and dioxin-like PCB congeners in relation to the most toxic 2378-TCDD can be calculated using toxic equivalency factors TEFs (NATO/CCMS, 1988; Ahlborg et al., 1994). Recent studies have shown that some polycyclic aromatic hydrocarbons (PAHs) exert dioxin-like activity, being aryl hydrocarbon receptor (AhR) agonist and potent inducers of EROD activity. This has facilitated the development of 2378-TCDD-related TEFs for these PAHs (TEF_{PAH}) (Willet et al., 1997; Clemons et al., 1998; Klimm et al., 1999).

Applying of the TEF values and the individual congener concentrations allowed calculation of total TCDD-equivalent toxicity (Total TEQ) for a mixture of PCDD/Fs, PCBs, and PAHs and evaluation of contributions of each of them to Total TEQ.

The developed absolute TEF_{PAH} values are differerent (*Table 9*).

PAHs	$\mathrm{TEF}_{\mathrm{PAH}}$							
	Willet et al., 1997	Clemons et al.,1998	Klimm et al., 1999					
Anthracene		0.00010						
Benzo[a]pyrene	0.000354	0.00001	0.000300					
Dibenzo[a,h]anthracene	0.002030	0.05000	0.000078					
Benzo[a]anthracene	0.000025	0.00001	0.000027					
Benzo[k]fluoranthene	0.004780	0.05000	0.000290					
Benzo[b]fluoranthene	0.002530		0.000380					
Chrysene	0.000200	0.01000						
Indeno[1,2,3-cd]pyrene	0.001100		0.000086					

Table 9. Toxicity equivalency factors proposed for selected PAHs showed dioxin-like activity

The results of the TEQ_{PAH} calculated for PAHs found in Northwest Mediterranean sediment samples using different TEFs proposed considerably differed (Eljarrat et al., 2001). The lowest TEQ_{PAH} values were obtained, applying TEFs proposed by Klimm et al. (1997), followed by those using TEFs assigned by Willet et al. (1997), and finally, the highest values were obtained, employing TEFs proposed by Clemons et al. (1998).

Multiplying the concentrations of PCDD/F and dioxin-like PCB congeners by the corresponing TEFs (NATO/CCMS, 1988; Ahlborg et al., 1994) and further also the concentrations of selected PAH analytes by TEF_{PAH} proposed by Klimm et al. (1999) allowed calculations of total TEQ for mixture of these contaminants in sediment (*Tables 2* and *3*). Table 10 shows that contributions of PAHs in total TEQ (TEQ_{PAH}) in all sediment samples make 83-99% and greatly exceed sum of TEQ_{PCDD/F} and TEQ_{PCB}, even though the lowest values of TEF_{PAH} were used for calculation.

Table 10. Total 2,3,7,8-TCDD-equivalents (total TEQ) (pgTEQ/g dry weight) calculated for a mixture of PCDD/F, PCBs and PAHs found in bottom sediment samples.

TEQs	Station number and sediment slice										
	1	2	3	6	7	4	5	8a	8b	9a	9b
		Kuets- jarvi	Kuets- jarvi	Skrukke- bukta	Bjørn- vatn	Ruske- bukta	Tjære- bukta	Lake Inari	Lake Inari	Lake Stuora- javri	Lake Stuora- javri
	0-1 cm	0-1cm	0-1 cm	0-1 cm	0-1 cm	0-1 cm	0-1 cm	0-1 cm	15-18cm	0-1 cm	22-23cm
TEQ _{PCDD/F}	3.9	3.8	3.1	3.2	1.3	n.a.	n.a.	1.7	0.01	1.2	0.02
TEQ _{PCB}	0.43	0.51	1.4	4 0.23	0.14	0.67	0.81	0.86	0.43	0.35	0.07
TEQ _{pah}	183.9	164.2	672.6	5 34.6	36.6	7.8	6.6	33.2	2.2	38.0	1.2
Total TEQ	188.3	168.5	677.1	l 38.0	38.0	8.5	7.4	35.8	2.6	39.6	1.3

n.a.=not analysed.

7. Conclusions/Recommendations

This screening study of POPs in bottom sediments carried out in the Paz watercourse reveals higher levels of all environmental contaminants studied in the bottom sediments from Lake Kuetsjarvi. There was a clear trend that the contamination levels decreased with increasing distance from the smelters.

Trace elements

All trace element levels decreased with increasing distance from the smelters. According to SFT environmental classification (Andersen *et al.*, 1997) of freshwater sediments, Lake Kuetsjarvi sediments can be considered as "strongly contaminated" with Cu and Ni, "markedly contaminated" with Hg, and "moderately contaminated" with Cd.

The sediments from the stations downstream Lake Kuetsjarvi can be classified as "markedly contaminated" with Ni and Cu, "moderately contaminated" with Cd, and Hg levels were as low as "background" levels (Andersen *et al.*, 1997).

PAHs

High levels of PAHs were measured in sediments from the Paz watercourse compared to other studies in Northern Norway. PAH levels in the sediments decreased with increasing distance from the smelters. Sediments from Lake Kuetsjarvi are classified as "markedly contaminated".

POPs

Among the chlorinated pesticides analysed, the highest levels were found for DDT with a tendency of decreasing levels with increasing distance from the smelter. The levels of Σ DDT detected in this study are high compared to other studies from the Arctic and from Norway.

The highest PCB levels were detected in the bottom sediments from Lake Kuetsjarvi, and there was a tendency of decreasing PCB levels (including planar and mono-ortho substituted PCB congeners) with increasing distance from the smelter. The levels of PCB in Paz watercourse were high compared to levels measured in surface sediments from other lakes in Northern Norway.

The highest PBDE levels were found in sediment samples from Lake Inari and from Lake Kuetsjarvi. However, differences in PBDE compositions found in the compared areas suggesting different source of PBDE contamination. The levels in Lake Stuorajavri and Paz watercourse are lower compared to studies from the Great lakes in Canada and from Ellasjøen on Bjørnøya, Svalbard.

The highest levels of PCDD/PCDFs were found in the bottom sediments from Lake Kuetsjarvi. There was no significant difference in levels of PCDD/PCDFs between the lakes and no correlation between distance from the smelter and levels of PCDD/PCDFs.

The PAHs contribute 83-99% to the total toxic equivalent (TEQ_{PAH}) in all sediment samples and greatly exceed sum of TEQ_{PCD/F} and TEQ_{PCB},

Thus, the results from this screening study indicate that smelter can be considered as a potential source of POPs for the freshwater environment. However, more detailed survey is needed.

8. Acknowledgement

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Appendix 1

Methods for determination of POPs and selected trace elements in sediment and fish tissue samples from Pasvik area

The following persistent pollutants have been determined in the bottom sediment and fish samples:

- chlorinated pestcides and industrial organochlorines: DDT-group (o,p) and p,p'-DDE, o,p) and p,p'-DDD, o,p) and p,p'-DDT), HCH (α -, β and γ isomers of HCH), Hexachlorobenzene (HCB), chlordanes (Heptachlor, Heptachlor epoxide, Oxychlordane, *trans* and *cis*-Nonachlors, *trans* and *cis*-Chlordanes), mirex, endrin and dieldrin;
- ortho-substituted congeners of polychlorinated biphenyls;
- planar and *non-ortho*-substituted congeners of PCBs (IUPAC): # 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, 189, as well as PCB congeners # 170 and 180;
- toxaphene compounds Parlar-26, Parlar-50, Parlar-62;
- brominated flame-retardants 2,4,4`-TrBDE (#28); 2,2`,4,4`-TeBDE (#47); 2,2`,4,4`,5-PBDE (#99); 2,2`,4,4`,6-PBDE (#100); 2,2',4,4',5,5'- HeBDE (#153); 2,2',4,4',5,6-HeBDE (#154); 2,2',3,4,4',5,6-HpBDE (#183);
- polychlorinated dibenzo-*p*-dioxines and dibenzofurans (PCDD/PCDF);
- -40 individual polycyclic aromatic hydrocarbons (PAHs), included alkyl-homologues and 16 PAHs recommended by EPA

Samples have been analyzed in the analytical batches, which included laboratory procedural blanks, spiked blank samples and samples of standard reference material of mussel tissue SRM 2977 of NIST, US and dogfish muscle certified reference material for trace metals DORM-2, National Research Council Canada. To control recovery of analytes surrogate isotope-labelled substances have been used, which were introduced into samples before extraction. Extracts have been analyzed using GC/MS.

Sub-samples were analysed for quality control purpose at analytical laboratory of University of Michigan (Environmental Health Sciences).

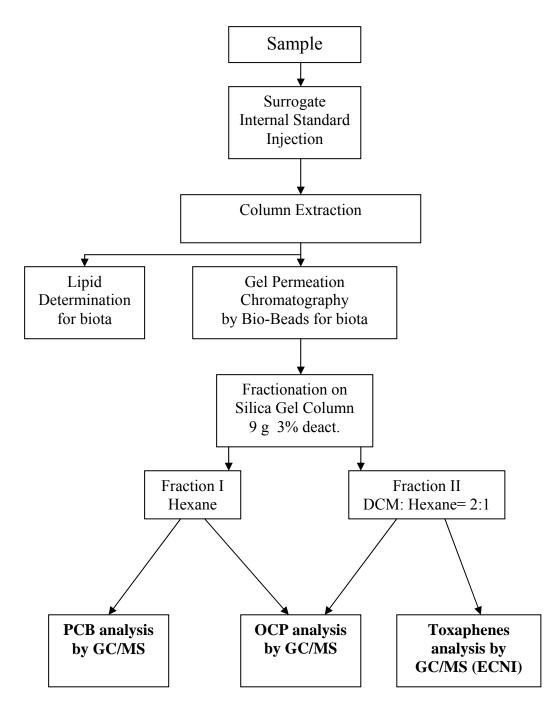
Sample preparation for analysis of POPs

Before analysis samples were refrozen and homogenized. The samples of bottom sediments were dried. Extraction of bottom sediments was carried out in Soxhlet apparatus using solvent mixture benzene-ethanol during 16 hours. Determinations of PCBs, chlorinated pesticides and toxaphenes, PCDD/PCDFs, PBDEs and planar congeners of PCBs were carried out from the same extract. Base digestion and ultrasonic extraction procedures were used to determine PAHs. Schemes of clean-up for all types of extracts are presented in *Figures 1.1, 1.2, 1.3* and *1.4*.

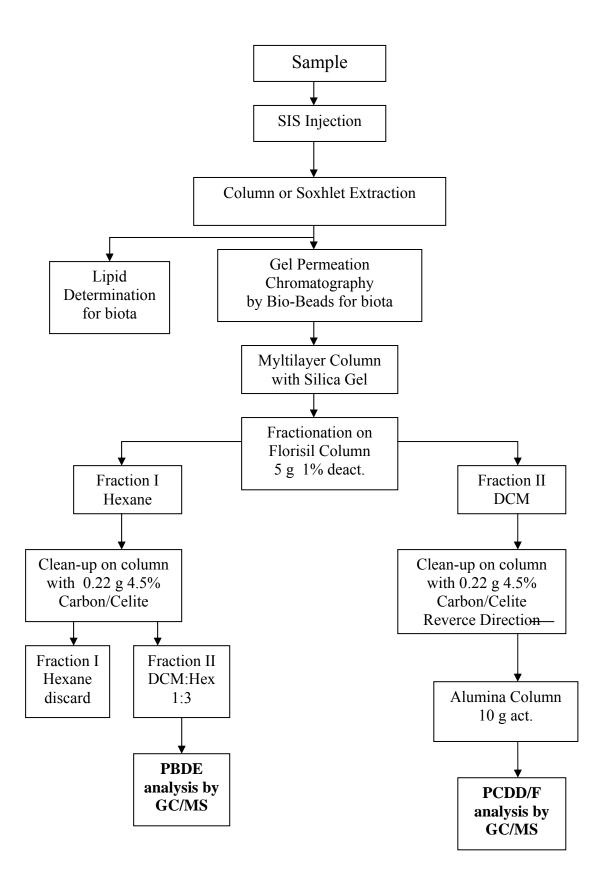
Extraction of fish tissues samples Extraction of PCBs, PBDEs, PCDD/Fs, OCPs and toxaphenes

POPs from fish tissue samples were extracted by column extraction method. As extragent the mixture of solvents – hexane : dichlormethane = 1:1 (v/v) was used. Lipid content was determined by gravimetric method from 10% of extract volume. The 50 % of extract volume was used for clean up for PCDD/Fs and PBDEs analysis. The 15 % of extract volume was used for clean up for planar congeners of PCB analysis. The 25 % of extract volume was used for clean up for another POPs analysis.

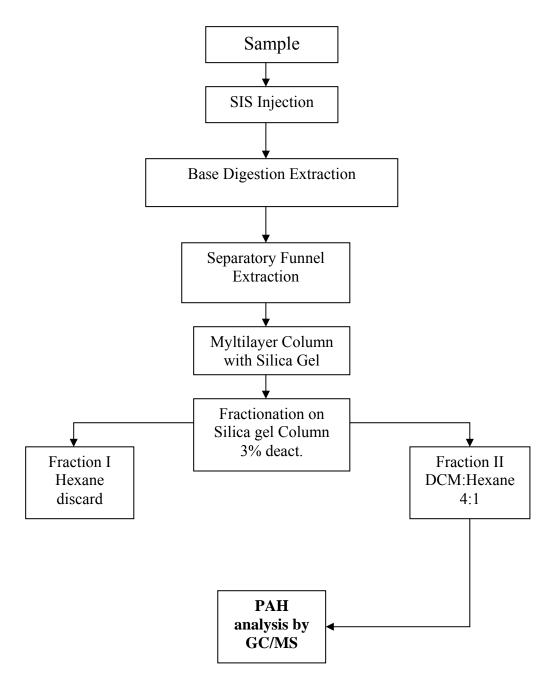
Extraction of PAHExtraction of PAH from the samples of the tissues of fish was carried out using base digestion with methanol and 50% KOH solution. The analytes from base solution were extracted with two portions of hexane in separatory funnel.



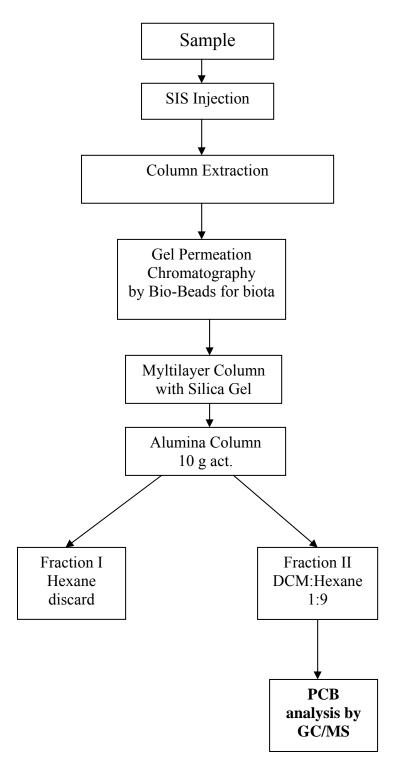
Appendix Figure 1.1 Analysis scheme for OCP and toxaphenes



Appendix Figure 1.2. Analysis scheme for PCDD/PCDF and PBDE



Appendix Figure 1.3. Analysis scheme for PAH



Appendix Figure 1.4 Analysis scheme for PCB.

Instrumental analysis (HRGC/LRMS)

Polychlorinated biphenyls and OCPs

The analysis was performed with *GC/MS Varian Saturn 2200 T*. Calibration of the instrument was carried out using a standard mixture of biphenyls BP-MS, Wellington Laboratories and SRM-1492, NIST. Results of analyses were processed with software package Varian 5.2.

Toxaphenes, Polychlorinated dibenzo-p-dioxins/dibenzofurans and Polybrominated diphenyl ethers

The analysis was performed with GC/MS Varian Saturn 1200 using chemical ionization with detection of negative ions (NCI) in the selective ion monitoring (SIM) mode. The reagent gas was methane.

Calibration of the instrument was carried out using standard solutions of Toxaphenes TOX 482, PROMOCHEM, standard solutions of PCDD/PCDF prepared on the base of the mixture EDF 7999 Cambridge Isotope Lab.and standard solutions of PBDE prepared on the base of the mixture EO-4980, Cambridge Isotope Lab.

Analysis of trace elements

The trace element analyses were carried out by AAS method after decomposition of the bottom sediment samples with nitric acid.

Cd, Ni and Pb were measured by a furnace technique on Perkin Elmer Z-3030 with Zeeman correction of background.

Zn and Cu were measured by AAS method by flame procedure on Perkin Elmer B-3030.

Hg was measured in bottom sediment and fish samples by method of "cold vapor" on MHS 15 after a decomposition of a sample by mixture of sulphuric and nitric acids.

QA/QC results

The internal QA/QC program in samples analysis for organic pollutants involved control for possible contamination of samples during sample preparation and measurements.

The analysis was performed in batches. Each batch included a procedural blank, spiked blank sample with the known content of added analytes.

Recovery of analytes was controlled using isotope-labelled analogues of determined analytes. QA/QC results are presented in the Tables 1.1 - 1.14.

Quality assurance and quality control for heavy metals included analyses of blanks, analyses of duplicates, use of reference materials and matrix spike recoveries. Results on QA/QC analysis for biota samples are presented in table 1.15-1.16.

QA/QC DATA REPORT for congeners of PCB in sediment

Compound	Procedural Blank PBS 02,	Method Detection Limit,		erence Materials of EC-5, ng/g
Compound	ng	ng/g	Detected	Reference Value
#1 [CL1]	n.d.	0.02	_	_
#3 [CL1]	n.d.	0.02	_	_
#4/#10 [CL2]	n.d.	0.02	_	_
#8 [CL2]	n.d.	0.02	—	-
#19 [CL3]	n.d.	0.02	—	-
#17/#18 [CL3]	n.d.	0.02	4.1	3.0 ± 1.1
#15 [CL2]	n.d.	0.02	_	_
#28/#31 [CL3]	0.24	0.04	6.2	5.3 ± 1.3
#54 [CL4]	n.d.	0.05	_	_
#33 [CL3]	n.d.	0.05	_	_
#22 [CL3]	n.d.	0.05	_	-
#52 [CL4]	n.d.	0.02	10.9	13.3 ± 4.1
#49 [CL4]	n.d.	0.02	_	_
#104 [CL5]	n.d.	0.02	_	_
#44 [CL4]	n.d.	0.02	5.9	7.3 ± 2.4
#37 [CL3]	n.d.	0.02	_	_
#74 [CL4]	n.d.	0.02	_	_
#70 [CL4]	n.d.	0.02	_	_
#95 [CL5]	n.d.	0.02	_	_
#155 [CL6]	n.d.	0.02	_	_
#101 [CL5]	n.d.	0.05	27.3	24.6 ± 6.0
#99 [CL5]	n.d.	0.02	_	_
#119 [CL5]	n.d.	0.02	_	_
#87 [CL5]	n.d.	0.02	10.1	9.6 ± 1.4
#110 [CL5]	n.d.	0.10	26.4	33.3 ± 11.9
#151 [CL6]	n.d.	0.02	8.3	8.4 ± 2.8
#149 [CL6]	n.d.	0.02	_	_
#123 [CL5]	n.d.	0.02	_	_
#118 [CL5]	n.d.	0.07	10.9	17.0 ± 7.4
#188 [CL7]	n.d.	0.02	_	_
#153/#168 [CL6]	n.d.	0.02	25.3	27.2 ± 5.5
#105 [CL5]	n.d.	0.05	9.0	7.6 ± 2.7
#138/#158 [CL6]	n.d.	0.05	27.6	28.6 ± 9.1
#178 [CL7]	n.d.	0.05	_	_
#155 [CL6]	n.d.	0.05	_	_
#187 [CL7]	n.d.	0.05	_	-
#183 [CL7]	n.d.	0.05	6.8	7.2 ± 2.8
#128 [CL6]	n.d.	0.05	5.0	5.5 ± 2.3
#167 [CL7]	n.d.	0.05	_	_
#177 [CL7]	n.d.	0.05	_	_
#202 [CL8]	n.d.	0.05	_	-
#171 [CL7]	n.d.	0.05	_	_

Cont. table 1.1

Compound	Procedural Blank	Blank Detection Limit,		l Reference M EC-5, ng/g	Aaterials
-	PBS 02, ng	ng/g	Detected	Reference Value	
#156 [CL6]	n.d.	0.05	_	_	
#201 [CL8]	n.d.	0.05	3.5	5.7 =	= 2.7
#157 [CL5]	n.d.	0.05	_	-	_
#180 [CL7]	n.d.	0.05	26.4	22.3	± 7.6
#191 [CL7]	n.d.	0.02	_	-	_
#170 [CL7]	n.d.	0.02	10.0	10.1	± 1.6
#199 [CL8]	n.d.	0.05	_	_	
#189 [CL7]	n.d.	0.02	_	_	
#208 [CL9]	n.d.	0.05	_	_	
#194 [CL8]	n.d.	0.02	9.6	8.1 ±	10.1
#205 [CL9]	n.d.	0.05	—	-	_
#206 [CL9]	n.d.	0.05	2.1	2.2 =	= 0.9
#209 [CL10]	n.d.	0.10	1.6	1.20	± 0.9
Surrogate Internal Standa	urds, % Recovery		Detected, ng	Added, ng	% Recovery
#28 [CL3] C^{13}	88	0.02	12.0	15.6	77
#52 [CL4] C^{13}	82	0.02	12.2	15.6 78	
#101 [CL5] C ¹³	83	0.02	14.7	15.6 94	
#153 [CL6] C ¹³	104	0.02	17.0	15.6 109	
#138 [CL6] C ¹³	93	0.02	16.8	15.6	108
#180 [CL7] C^{13}	88	0.02	16.4	15.6	105

QA/QC DATA REPORT for planar and mono-orthosubstituted congeners of PCB in sediment

	Procedural Blank	Method Detection	Spiked B	Blank Sample SMS 02		
5.1.1.1.1.1.1 Compound	PBS 02, ng/g	Limit, ng/g	Detected, ng	Added, ng	% Recovery	
#CL4 81	n.d.	0.010	3.32	4.00	83	
#CL4 77	n.d.	0.010	3.36	4.00	84	
#CL5 123	n.d.	0.010	3.84	4.00	96	
#CL5 118	0.19	0.10	3.48	4.00	87	
#CL5 114	n.d.	0.010	3.52	4.00	88	
#CL5 105	n.d.	0.030	3.08	4.00	77	
#CL5 126	n.d.	0.010	3.84	4.00	96	
#CL6 167	n.d.	0.020	3.36	4.00	84	
#CL6 156	n.d.	0.011	3.48	4.00	87	
#CL6 157	n.d.	0.015	3.96	4.00	99	
#CL6 169	n.d.	0.010	3.8	4.00	95	
#CL7 180	n.d.	0.010	4.08	4.00	102	
#CL7 170	n.d.	0.010	3.84	4.00	96	
#CL7 189	n.d.	0.010	3.72	4.00	93	
Surrogate Internal Standar	rds, % Recovery					
$\#CL4 \ 81 \ C^{13}$	44	0.005	3.20	5.00	64	
$\#CL4 77 C^{13}$	43	0.005	4.25	5.00	85	
$\#CL5 \ 123 \ C^{13}$	66	0.005	4.35	5.00	87	
$\#CL5\ 118\ C^{13}$	82	0.005	3.90	5.00	78	
$\#CL5\ 114\ C^{13}$	77	0.005	4.45	5.00	89	
$\#CL5 \ 105 \ C^{13}$	87	0.005	4.20	5.00	84	
$\#CL5 \ 126 \ C^{13}$	66	0.005	4.75	5.00	95	
$\#CL6\ 167\ C^{13}$	106	0.005	4.80	5.00	96	
$\#CL6\ 156\ C^{13}$	117	0.010	3.95	5.00	79	
$\#CL6\ 157\ C^{13}$	108	0.005	3.85	5.00	77	
$\#CL6\ 169\ C^{13}$	99	0.010	4.50	5.00	90	
$\#CL7\ 180\ C^{13}$	95	0.015	5.25	5.00	105	
$\#CL7\ 170\ C^{13}$	99	0.005	4.65	5.00	93	
$\#CL7\ 189\ C^{13}$	114	0.005	4.95	5.00	99	

	Procedural	Method	QOR076MS (Quasimeme)			
Compound	Blank PBS 02, ng/g	Detection Limit, ng/g	Detected, ng/g	Assigned Value, ng/g	Assigned Error, %	
НСВ	0.05	0.03	0.61	0.74	16	
α-НСН	n.d.	0.05	0.09	0.13	31	
β-НСН	n.d.	0.05	0.15	0.11	—	
γ-ΗCΗ	n.d.	0.05	0.38	0.34	20	
Heptachlor	n.d.	0.05		—	—	
Heptachlor epoxide	n.d.	0.10	_	—	_	
Oxychlordane	n.d.	0.08		—	_	
trans-Chlordane	n.d.	0.03		—	_	
cis-Chlordane	n.d.	0.03	_	—	—	
trans-Nonachlor	n.d.	0.01	8.90	8.36	—	
cis-Nonachlor	n.d.	0.01		—	—	
2,4`-DDE	n.d.	0.03	_	—	_	
4,4`-DDE	n.d.	0.03	17.4	17.02	13	
2,4`-DDD	n.d.	0.03	_	—	—	
4,4`-DDD	n.d.	0.03	14.2	9.47	13	
2,4`-DDT	n.d.	0.08	0.10	0.14	—	
4,4`-DDT	n.d.	0.08	9.80	11.53	13	
Endrin	n.d.	0.10		—	_	
Dieldrin	n.d.	0.05	1.70	1.86	14	
Mirex	n.d.	0.03	_	—	_	
Surrogate Internal Standards, % Recovery						
HCB C^{l3}	69	0.005	8.52	12.0	71	
γ -HCH C^{13}	100	0.005	9.20	12.1	76	
$4,4$ `-DDE C^{13}	77	0.005	8.28	11.5	72	
$4,4 \text{`-}DDT C^{13}$	72	0.010	9.61	11.3	85	

QA/QC DATA REPORT for Chlorinated Pesticides in sediment

QA/QC DATA REPORT for Polycyclic Aromatic Hydrocarbons in sediment

Compound	Procedural Blank	Blank Detection		Certified Reference Materials of NWRI EC-5, ng/g			
Compound	ng/g	Limit, ng/g	%D	Detec	ted	Reference Value	
Naphthalene	0.15	10.0	20	19.0	6	26 ± 6	
1 -Methylnaphthalene	1.13	5.0	23	_		—	
2 -Methylnaphthalene	0.06	5.0	24	_		—	
Acenaphthylene	n.d.	0.3	—	32.4	4	41 ± 9	
Acenaphthene	n.d.	0.3	_	28.:	5	29 ± 9	
Fluorene	n.d.	0.3	—	62.9	9	84 ± 26	
Phenanthrene	n.d.	0.3	22	585.		612 ± 57	
Anthracene	n.d.	0.3	25	93.′	7	113 ± 17	
Fluoranthene	n.d.	0.3	8	799.0		823 ± 74	
Pyrene	n.d.	0.3	13	742.0		987 ± 134	
Benzo(a)anthracene	n.d.	0.3	_	460.0		503 ± 47	
Chrysene	n.d.	0.3	—	549.	0	619 ± 60	
Benzofluoranthenes	n.d.	0.5	24	764.	0	899 ± 137	
Benzo(e)pyrene	n.d.	0.5	—	414.	0	440 ± 76	
Benzo(a)pyrene	n.d.	0.5	25	469.	0	449 ± 61	
Perylene	n.d.	1.5	10	198.	0	187 ± 28	
Indeno(1,2,3cd)pyrene	n.d.	1.5	—	368.	0	386 ± 66	
Dibenz(a,h)anthracene	n.d.	1.5	—	161.	0	195 ± 44	
Benzo(g,h,i)perylene	n.d.	1.5	—	352.	0	333 ± 53	
Surrogate Internal Sta	ndards, %			Detected,	Added		
Recovery	r			ng	ng	Recovery	
Naphthalene d ₈	77	0.05	_	0.16	0.20	81	
Acenaphthene d_{10}	84	0.05	—	0.20	0.20	98	
<i>Phenanthrene</i> d ₁₀	59	0.05	—	0.18	0.20	92	
<i>Chrysene d</i> ₁₂	60	0.05	—	0.16	0.20	78	
<i>Perylene d</i> ₁₂	65	0.10	_	0.10	0.20	52	

Appendix 1: Screening studies of POPs in bottom sediments from the Paz watercourse

Table 1.5

QA/QC DATA REPORT for toxaphenes in sediment

Compound	Procedural Blank	Method Detection	Spiked Blank Sample SMS 02			
Compound	PBS 02, ng	Limit, µg/kg	Detected, ng	Added, ng	% Recovery	
Parl 26	n.d.	0.0001	6.83	8.43	81	
Parl 50	n.d.	0.0002	6.83	8.43	81	
Parl 62	n.d.	0.0020	7.00	8.43	83	

Table 1.6

QA/QC DATA REPORT for Polybrominated diphenyl ethers in sediment

	Procedural Blank	Method Detection	Spiked Blank Sample SMS 02			
Compound	PBS 02, ng	Limit, ng/kg	Detected, ng	Added, ng	% Recovery	
PBDE # 28	n.d.	0.10	2.00	2.20	91	
PBDE # 47	n.d.	2.00	1.53	1.96	78	
PBDE # 99	n.d.	1.50	1.62	2.00	81	
PBDE # 100	n.d.	0.30	—	—	—	
PBDE # 153	n.d.	0.30	1.57	1.92	82	
PBDE # 154	n.d.	0.20	—	—	_	
PBDE # 183	n.d.	0.80	_	_	_	

QA/QC DATA REPORT for Polychlorinated dibenzo-p-dioxins and	
polychlorinated dibenzofurans in sediment	

	Proce-dural	Method	Spiked Blank Sample SMS 02			
Compound	Blank PBS 02, ng	Detection Limit, ng/kg	Detected, ng	Added, ng	% Recovery	
2,3,7,8-TCDD	n.d.	2.00	0.04	0.04	89	
1,2,3,7,8-PeCDD	n.d.	0.20	0.17	0.20	87	
1,2,3,4,7,8-HxCDD	n.d.	0.05	0.17	0.20	84	
1,2,3,6,7,8- HxCDD	n.d.	0.05	0.17	0.20	85	
1,2,3,7,8,9- HxCDD	n.d.	0.05	0.15	0.20	76	
1,2,3,4,6,7,8-HpCDD	n.d.	0.05	0.14	0.20	72	
OCDD	n.d.	0.05	0.34	0.40	84	
2,3,7,8-TCDF	n.d.	0.10	0.04	0.04	96	
1,2,3,7,8-PeCDF	n.d.	0.10	0.16	0.20	78	
2,3,4,7,8-PeCDF	n.d.	0.10	0.20	0.20	99	
1,2,3,4,7,8-HxCDF	n.d.	0.05	0.15	0.20	77	
1,2,3,6,7,8- HxCDF	n.d.	0.05	0.17	0.20	85	
2,3,4,6,7,8-HxCDF	n.d.	0.05	0.16	0.20	80	
1,2,3,7,8,9-HxCDF	n.d.	0.05	0.17	0.20	86	
1,2,3,4,6,7,8-HpCDF	n.d.	0.05	0.19	0.20	96	
1,2,3,4,7,8,9-HpCDF	n.d.	0.05	0.19	0.20	93	
OCDF	n.d.	0.05	0.32	0.40	79	
Surrogate Internal Standard	ls, % Recovery					
$({}^{13}C_{12})2,3,7,8$ -TCDD	93	2.00	0.95	1.25	76	
$({}^{l3}C_{12})2,3,7,8$ -TCDF	100	0.10	1.05	1.25	84	
$({}^{l3}C_{12})1,2,3,7,8$ -PeCDD	99	0.20	1.19	1.25	95	
$({}^{l3}C_{12})1,2,3,7,8$ -PeCDF	90	0.10	0.94	1.25	75	
$({}^{l3}C_{12})1,2,3,6,7,8$ - HxCDD	89	0.05	1.04	1.25	83	
$({}^{l3}C_{12})1,2,3,6,7,8$ - HxCDF	103	0.05	1.00	1.25	80	
(¹³ C ₁₂)1,2,3,4,6,7,8-HpCDD	100	0.05	1.18	1.25	94	
(¹³ C ₁₂)1,2,3,4,6,7,8-HpCDF	95	0.05	1.24	1.25	99	
$(^{l3}C_{12})OCDD$	90	0.05	2.23	2.50	89	

Analytical methods in determination of metals

		Sediment			Biota	
Metals	Technique	Method of analysis	Detection Limit, mg/kg	Technique	Method of analysis	Detection Limit, mg/kg
Cd	GFAA	SW-846 #7131A	0.005	GFAA	SW-846 #7131A	0.001
Cu	FLAA	SW-846 # 7210	1.5	FLAA	SW-846 # 7210	0.20
Ni	FLAA	SW-846 #7520	5.0	GFAA	SW-846 #7521	0.01
Pb	FLAA	SW-846 #7421	8.0	GFAA	SW-846 #7420	0.01
Hg	CVAA	SW-846 #7471A	0.005	CVAA	Russian	0.005
Li	FLAA	SW-846 #7430	4.0	-	-	-
Zn	FLAA	SW-846 #7950	0.8	FLAA	SW-846 #7950	0.10



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