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Monitoring of priority hazardous substances in Estonian water bodies and in the coastal Baltic Sea

Antti Roose[1)] and Ott Roots[2)]

[1)] *University of Tartu, Ülikooli 18, 50090 Tartu, Estonia*
[2)] *Estonian Environmental Research Centre, Marja 4D, 10617 Tallinn, Estonia*

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The water sub-programme of the Estonian National Environmental Monitoring Programme aims to monitor and to develop an information support system for the protection of inland surface waters, transitional waters, coastal waters and groundwater. Focusing on problem areas and reflecting intensive human impact, monitoring of hazardous substances is targeted at populated industrial metropolitan areas in Tallinn and in the oil-shale region of north-eastern Estonia. During the last decade the state of the environment regarding priority hazardous substances has continuously improved. According to monitoring results, the concentration of hazardous substances in sediments and in surface water remains low in the majority of Estonian rivers, and their quality by European standards is classified as good. Concentrations of hazardous substances found in Baltic fish in the Estonian coastal sea remain below standards established by the FAO/WHO for food. The key to the improvement of monitoring is the integration of source-oriented and load-oriented approaches, since both are lacking full-scale consistent data coverage.

Introduction

During the last ten years (1994–2003) the state of the environment regarding priority hazardous substances has continuously improved in Estonia (Roose *et al*. 2003). Although a lot of information is available, a comprehensive overview of priority hazardous substances is not available due to lack of data management, cross-national synthesis, and integrated framework projects in this field in Estonia. Reasons for the present trends: in majority, declining concentrations of hazardous substances, are not fully understood. Also, data and discussion in the context of the Baltic Sea Basin as a reference area is needed.

Efforts have been made to structure and manage national environmental monitoring activities since the early 1990s. As a result, the Estonian National Environmental Monitoring Programme (NEMP) was initiated in 1994 (Roots and Saare 1996). Presently there are altogether around 1800 monitoring stations in the monitoring set of 68 sub-programmes of 11 monitoring themes, the number of parameters reaching 250. Several NEMP projects are related to the European networks or regional projects in the Baltic Sea Basin and are founded on an international framework of standards, methodology and reporting. The following is the current list of important applied programmes in the field of hazardous substances:

— Cooperative Programme for Monitoring and Evaluation of the Long-range Transmission

of Air Pollutants (EMEP);
— Helsinki Commission COMBINE programme;
— UNEP Chemicals Persistent Organic Pollutants Global Monitoring Programme;
— International Cooperative Programmes (ICP) under Geneva Convention: ICP for Assessment and Monitoring of air Pollution Effects on Forest; ICP for Assessment and Monitoring of Acidification of rivers and Lakes; ICP on Integrated Monitoring of Air Pollution Effects on Ecosystems, etc. (UNEP 2002, HELCOM 2004b).

The political objective stated by the EU is to achieve concentrations in the water environment that are near background values for naturally occurring substances and close to zero for man-made synthetic substances (European Parliament 2002). Regarding environmental targets, the objective of the water sub-programme of NEMP is to establish a monitoring and information support system for the protection of inland surface waters, transitional waters, coastal waters and groundwater.

The aim of this paper is to summarise the results of the monitoring of priority hazardous substances, persistent organic pollutants and heavy metals in the Estonian water bodies and in the coastal Baltic Sea. This work is part of efforts to collect and evaluate all available monitoring data on priority hazardous substances in Estonia and in the coastal area. The article focuses on toxic priority substances that are listed in the Stockholm Convention and in UNEP Transboundary Air Pollution Convention protocols of persistent organic pollutants and heavy metals. The protocols require a ban or the minimisation of these priority substances (UNEP 2003). Persistent organic pollutants (POPs) and heavy metals (HM) are a group of toxic and persistent chemicals whose effect on human health and on the environment include dermal toxicity, immunotoxicity, reproductive effects and teratogenicity, endocrine disrupting effects and carcinogenicity (UNEP 2003). Import of chlororganic pesticides to Estonia was prohibited by a government regulation from 1967. Estonia itself has not been manufacturing chlorine organic pesticides.

In the first stage of drafting water management plans, the types of water bodies are determined, their status is assessed, and the water bodies are classified on the basis of existing monitoring data. As the concentration of POPs in rivers was below detection level, the focus of the survey shifted to the fish species of the coastal sea. It is essential for human health that all countries monitor potentially hazardous chemicals in food supplies. Many chemical contaminants are readily taken up by plankton, fish, birds, and mammals and become concentrated at the top of the food chain in marine mammals and fish (Wieder *et al*. 1998, Roots and Zitko 2004). In the human uptake of POPs in Finland, fish and fish products accounted for 82%, and Baltic herring *Clupea harengus* alone for 52% of the total intake (Kiviranta *et al*. 2001). The Estonian data is compared primarily with monitoring data from Finland and Sweden (Ukonmaanaho *et al*. 1998, Heikkilä 1999, Agrell *et al*. 2001, HELCOM 2004b, Voigt 2004). Due to the substantial differences in monitoring programmes the comparison of Estonian data with Latvian and Lithuanian data is in general unfeasible. Despite that surveys of heavy metals allow to draw some conclusions about the status of the Baltic states (Klavins *et al*. 2000, Klavins and Vircavs 2001).

Material and methods

Study area

In Estonia, the contents of toxic chlororganic compounds in the ecosystem of the Baltic Sea have been surveyed since 1974 (Roots 1996). The sampling time and location, i.e the population location, play an important role when different regions are compared. According to the objectives of the hazardous substances monitoring programme, the monitoring stations are predominantly located in the metropolitan area surrounding Tallinn and in the oil-shale region in north-eastern Estonia, reflecting intensive human impact. Monitoring stations of NEMP to survey priority substances are shown on the map in Fig. 1.

The article uses data from four monitoring programmes of priority substances:

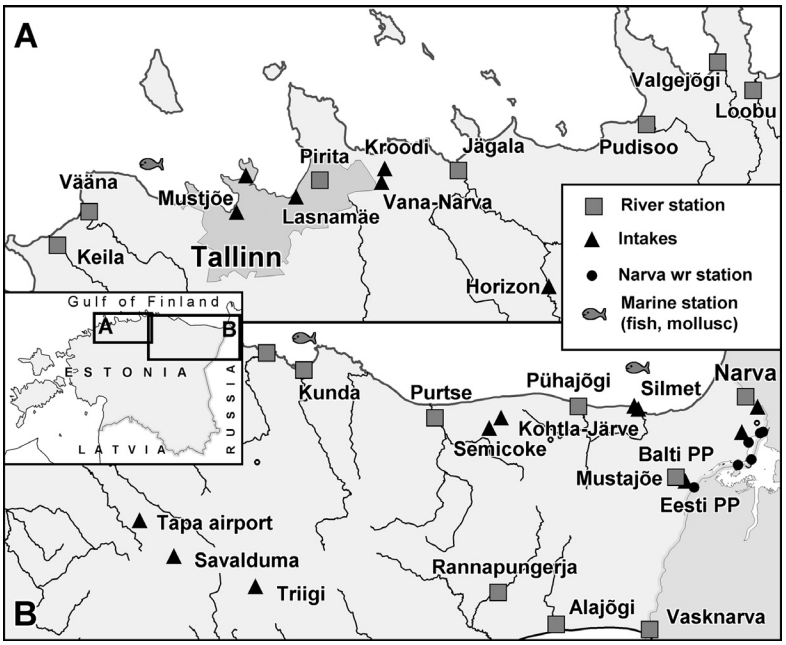

Fig. 1. Map of monitoring set of priority substances of the Estonian National Monitoring Programme (NEMP).

— rivers: sampling fisheries, in particular,
— intakes: sampling sediments as content in the water is extremely low,
— Narva reservoir: sampling water,
— coastal sea: sampling biota.

Overview and details of the monitoring programme of priority substances in the coastal sea, rivers and intakes, including the list of sampled toxic substances, is given by Roose *et al*. (2003). The extensive data set comprises water quality data from the national water registry and environmental monitoring programme. Although data on organic pollution is often incomplete, with some years missing, it is sufficient for identifying spatial and temporal trends in rivers and in marine water composition, and the impacts on living organism.

Chlororganic substances in fish and molluscs are sampled annually in three monitoring clusters (Pärnu Bay, Tallinn and Kunda Bay). Consistent with recommendations of the Helsinki Commission (HELCOM), the selected bio-indicator is the female Baltic herring of two–three years of age (HELCOM 2004b). In the case of zoobenthos, only the content of metals is analyzed in *Macoma baltica* and *Saduria entomon*. Monitoring samples are collected once a year from three to five points in the southern part of the Gulf of Finland. In Estonia, heavy metal content in the ecosystem of the Baltic Sea has been surveyed since 1974 (Jankovski *et al*. 1996), whereby comparable results are from the second half of the 1980s. In fish, the heavy metal content has been determined in their livers. Baltic herring have been caught in the autumn from the northeastern part of the Gulf of Riga as well as from Pärnu Bay and from the two areas (Tallinn and Kunda) in the Gulf of Finland.

Regarding the sampling in rivers, the concentrations of heavy metals are assessed in 15 Estonian rivers. The frequency of sampling of heavy metals is seasonal. Data series for water quality began in 1992 and have continued up to today. In 1999–2001, the inventory reports of hazardous substances in intakes (sediments and water) have been published separately for three Estonian counties: Lääne- and Ida-Virumaa (oil-shale region), and Harjumaa (Tallinn and its surroundings), and jointly for all other Estonian counties.

Taking into consideration the results of inventories, a new programme for monitoring hazardous substances of intakes has been launched in 2002. The design of the monitoring programme originates from the research methodologies and

location specifics of a certain natural phenomenon, taking into account also the spatial changeability of the phenomenon. The pilot sampling was split into three stages (Roose *et al.* 2003). Sampling in the first pilot year focused on northeastern Estonia (Fig. 1B), and in the second year, on the metropolitan area (Fig. 1A).

In general, the state of environment in Estonian water bodies depends directly on the efficiency of wastewater treatment and measures applied in industrial processes. The decrease in pollution load in the beginning of the 1990s was caused by a decline in industrial production. In the late 1990s up to the present, the improvement has been achieved with the construction and massive renovation of treatment plants (Kristensen and Hansen 1999, EEA 2003). Also, the amount of wastewater has decreased through the years, due to decreasing water consumption. In general, the water quality in Estonian water bodies, both rivers and lakes, is good or satisfactory (EEA 2003). By the content of organic matter the water quality is good. Main problems are related to phosphorus pollution in some northern rivers (Loigu and Leisk 2002). There are some rivers in the oil-shale region where concentrations of phenols and hydrocarbons are higher than European standards.

Sampling

The Estonian Environmental Research Centre, where all the samples of the coastal sea and intakes programmes were analysed, is acknowledged by the German accreditation bureau Deutshes Akkreditieruns-system Prüfwesen GmbH (DAP) DAP-PL-3131.00 (2008-11-22). Description of sampling techniques as well as the analytical procedures for persistent organic pollutants can be found in Roots (2001). For quantitative determination of polychlorinated biphenyls (PCB) congeners, the internal standard IUPAC 189 was added. PCBs were analysed on a 90 m capillary column (DB-5) using gas chromatography (Varian 3380) with an electron capture detector (ECD). PCB isomers with IUPAC numbers 28, 52, 101, 105, 118, 138, 153 and 180 were analysed. The detection limit for different PCBs was 1 μg kg^{-1} fresh weight.

The analysis of heavy metals follows ISO 8288-1986 (E) (ISO 1994). Analysis uses AAS VARIAN SpectrAA-250 Plus atom absorption spectrophotometer with graphite and flame furnaces. The analysis encompassed the evaluation of heavy metal levels in river and marine environments, to assess potential effects and to identify pollution sources. Detection limits are of great importance in the analysis of river water as concentrations of heavy metals are very low. Higher detection limit may affect much higher load estimates than the actual load. Detection limits of two Estonian laboratories which are involved in sampling are given in Table 1. Long-term metal pollution in the Gulf of Finland has also been documented in bioaccumulation studies of the widespread bottom species, which exhibited elevated concentrations of Hg, Pb, Zn, and Cd (Ukonmaanaho *et al.* 1998, Sipiä *et al.* 2002). Having determined the amounts of heavy metals in rivers, in the liquid phase, and in the sediment, one can calculate heavy metal mobility, bioavailability, and toxicity values (Leivuori 1998, Wieder *et al.* 1998, Toro *et al.* 2001). The methodology of ecological risk assessment is not applied in this article as the scope is purely to introduce monitoring results.

Results and discussion

Persistent organic pollutants in the Estonian coastal waters

The distribution of PCBs in the surface sediment reported in HELCOM (2002) suggests that 'hot

Table 1. Detection limits (µg l^{-1}) for river water in Estonian laboratories.

Laboratory	Cu	Cd	Pb	Zn	Hg
Estonian Environmental Research Centre	1.0	0.02	1.0	10	0.05
Tartu Environmental Research Ltd	0.1	0.02	0.2	2	0.1

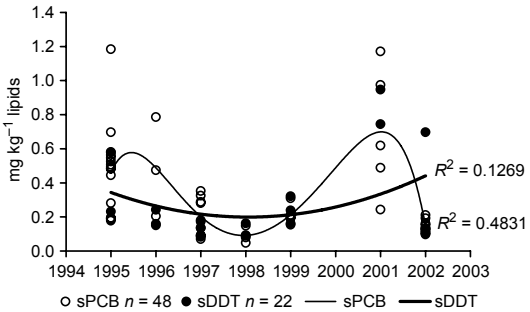

Fig. 2. Contents of sDDT and sPCB (mg kg^{-1} lipids) in the muscle tissue of Baltic herring from different parts of the Estonian coastal sea (Roots and Simm 2003).

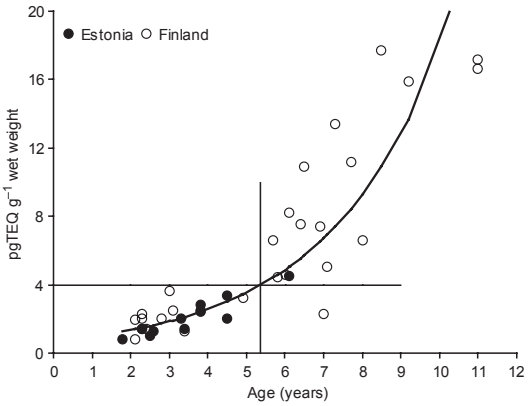

Fig. 3. Comparison of dioxin concentration in muscle tissue of the Baltic Sea herring in Estonia and in Finland (Roots *et al.* 2003).

spots' have been identified in several locations, but not in the Estonian coastal sea. The highest level of PCB contamination was observed in the eastern Gotland Basin and in Lübeck Bay. Higher concentrations were also found near Stockholm, Viipuri and Klaipeda. To summarise, PCBs had entered the environment in large quantities for more than 37 years and were bio-accumulating and depositing in sediments (Koppe and Keys 2001). The role of long-range transport dominates in Estonia and its coastal sea, though the interaction of (airborne) POPs with surface media is not sufficiently understood (Scheringer *et al*. 2004).

The concentrations of DDT and PCBs in the tissues of Baltic herring decreased in 1995–1998, but there was a certain rise after 1998 (Fig. 2). However, the reasons for the increase are unclear (Roots and Simm 2003). It is possible that DDT have recently been used and discharged from Latvian or closely adjoining territory (Olsson *et al*. 1999). In the area of the Baltic Sea during 1994–1998, the highest DDT and PCB concentrations in herring muscle tissue were found near the German coast. The lowest PCB concentrations were found along the Estonian coast, but also in the northern Bothnian Bay and in the Kattegat (Olsson *et al*. 2002b).

European Union (EU) Council Regulation 2375/2001 put the threshold limit value of PCDD/Fs in fish at 4 pgTEQ g^{-1} wet weight. The Baltic Sea fish have been separately highlighted because, in terms of PCDD/Fs content, they may presumably exceed the threshold, in particular for older Baltic Sea herring. The comparison of dioxin concentration in the muscle tissue of the Baltic herring in Estonia and in Finland shows statistically reliable correlation between concentration of dioxins and age of fish ($r > 0.8$) (Fig. 3). The highest dioxin contaminated herring were found in the Gulf of Bothnia (HELCOM 2003). According to the data from HELCOM (2004b) the highest dioxin concentrations for Baltic Sea herring were found in the central Baltic. No differences were found between the commercial landings of Baltic Sea herring in 1996 and 1999 (Karl and Ruoff 2004). The accumulation of organochlorines in salmon might have been increased by their feeding on relatively older specimens of herring and, more especially, on the whole age-range of the more slowly growing sprat (Vuorinen *et al*. 2002).

Concentrations of HCH-isomers (lindane) in water and biota have decreased considerably since the early 1980s. Concentrations of dioxin and PCBs in marine ecosystems declined in the 1980s, but this decrease levelled off in the 1990s. Dioxin levels in fish still exceed the new EU food safety limits in some areas, particularly further north in the Baltic Sea. Concentration levels of POPs are still so high that they have potential biological effects, at least in the Kattegat, the Belt Sea, and the Sound. The conditions differ substantially between the Baltic Proper and the Estonian coastal sea. The dioxin congener profiles in the Estonian coastal sea from herring in the western Gulf of Finland are similar to those from the central Baltic; those from the middle of the Gulf of Finland are similar to those from

the Gulf of Riga (Roots and Zitko 2004). Of the twelve Baltic herring samples taken from Estonian coastal waters and the central Baltic, the dioxin content of only one of them (a fish older than 6 years and more than 17 cm in length from the central Baltic) was above the internationally permitted threshold. For other endocrine disrupting substances and new contaminants like flame retardants, a full assessment of their levels or effects is not possible due to the lack of monitoring data.

The concentrations of chlororganic substances in the biota of the Estonian coastal sea do not exceed quality standards set by the EU (Council Regulation 2375/2001). The risk of toxicants is determined by acceptable daily intake (ADI), the exceeding of which could be dangerous to health. The dose is given by weight. In this case, the amount of fish eaten should be taken into consideration. The second risk indicator that is commonly applied is the highest concentration of the substance that does not affect test animals (NOEL, No-Observed-Effect-Level) (Wexler 1998). The latter is applicable for infants and the elderly.

Heavy metals in biota in coastal waters

Heavy metals can reach the marine environment via the atmosphere or through discharges and natural runoff. As a direct impact, annual emissions of heavy metals from the Baltic Sea countries decreased in 1996–2000, by 26% for cadmium, 15% for mercury and 10% for lead (HELCOM 2003). According to estimates, about 9 tonnes of cadmium was deposited in the Baltic Sea during the year 2000. Concentrations of cadmium, lead and zinc are on average higher in the south-western parts of the Baltic Sea, where atmospheric deposition of heavy metals is greater and waste containing high levels of heavy metals has been dumped. One fifth of the cadmium input to the Baltic Sea comes from atmospheric deposition, carried by the prevailing south-westerly winds (HELCOM 2004a). Atmospheric emissions of Estonian power plants have declined from 1 t to 0.7 t in 1997–2000.

In 1994–2000, discharges of heavy metals (mostly cadmium and lead) decreased in most of the sub-regions neighbouring Estonia. The riverine loads of cadmium and lead in 2000

Table 2. Concentrations of cadmium in the biota in the Estonian coastal areas (Simm and Roots 2003).

Organism	Marine area	Period	*n*	mg kg^{-1} dry weight	mg kg^{-1} wet weight
Saduria (whole organism)					
	Klooga	1990–1995	50	0.72 ± 0.04	0.18 ± 0.01
	Kakumäe	1988–2001	69	0.94 ± 0.04	0.23 ± 0.01
	Käsmu	1988–2001	125	1.00 ± 0.06	0.25 ± 0.01
	Kunda	1988–2001	78	0.86 ± 0.06	0.21 ± 0.01
	Narva	1990–2002	114	0.96 ± 0.06	0.23 ± 0.02
Macoma (soft web)					
	Klooga	1990–2002	40	1.03 ± 0.10	0.22 ± 0.03
	Kakumäe	1988–2002	130	1.49 ± 0.07	0.27 ± 0.01
	Käsmu	1988–2001	116	1.11 ± 0.06	0.22 ± 0.01
	Kunda	1988–2001	99	1.63 ± 0.10	0.28 ± 0.02
	Narva	1990–2002	65	1.65 ± 0.11	0.25 ± 0.02
Baltic herring (muscles)					
	Gulf of Riga	1994–1999	89	0.09 ± 0.03	0.02 ± 0.01
	Baltic Proper	1994–1999	87	0.02 ± 0.00	0.01 ± 0.00
	Tallinn	1994–1999	291	0.11 ± 0.02	0.02 ± 0.01
	Kunda	1994–1999	52	0.27 ± 0.16	0.06 ± 0.04
Baltic herring (liver)					
	Gulf of Riga	1994–2002	34	1.72 ± 0.20	0.44 ± 0.04
	Baltic Proper	2002	1	1.18	0.36
	Tallinn	1994–2002	172	2.47 ± 0.12	0.55 ± 0.03
	Kunda	1994–2002	34	1.50 ± 0.11	0.42 ± 0.03
Perch (liver)					
	Pärnu	2002	10	0.36 ± 0.03	0.09 ± 0.01

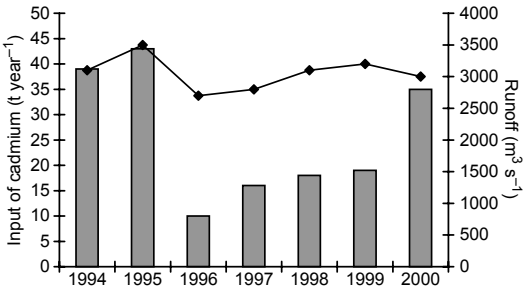

Fig. 4. Riverine input of cadmium (t year^{-1}) and annual average riverine runoff (m^3 s^{-1}) and into the Gulf of Finland, 1994–2000 (HELCOM 2003).

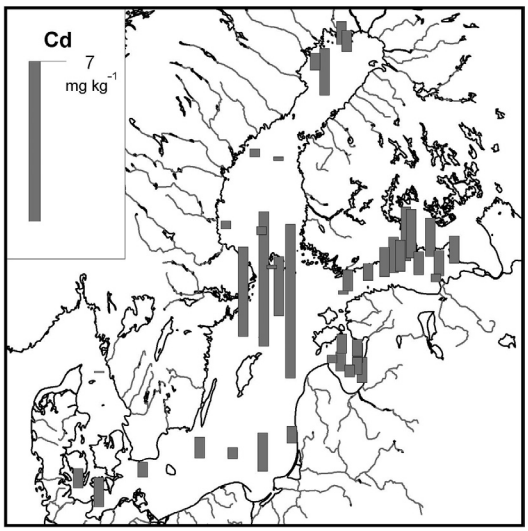

Fig. 5. Distribution of Cd levels in surface sediment in the Baltic Sea (data from HELCOM 2002).

amounted to about 36 t and 298 t for the Gulf of Finland (Fig. 4 for Cd), and 1.5 t and 12 t for the Gulf of Riga. Among other coastal countries, the Estonian input of cadmium and lead in 2000 was proportionally very low, accordingly 0.5 t and 1.9 t for the Gulf of Finland, and 0.04 t and 0.3 t for the Gulf of Riga (HELCOM 2004a). Information about unmonitored rivers, which theoretically may increase the load of cadmium and lead entering the Baltic Sea from Estonia, is not available.

Monitoring in 1994–2001 does not indicate any differences between the contents of heavy metals in the fish from the Gulf of Riga and those from the Gulf of Finland, nor detects any temporal changes, or trends (Table 2). Even though the concentrations of some heavy metals have decreased in many parts of the Baltic Sea, like in the Estonian coastal waters, high concentrations can still be found in certain marine organisms, notably in the Baltic herring. For example, mercury concentrations in herring have remained at roughly the same level since the 1980s, but cadmium concentrations in Baltic herring have increased significantly (HELCOM 2003). The behaviour of cadmium in water is complex and there is a high level of uncertainty in the prediction of cadmium loads entering the marine environment. The lowest Cd concentration in herring liver was found in the Kattegat and the highest concentration in the central part of the Bothnian Sea (Olsson *et al*. 2002a).

The distribution of cadmium in surface sediments was very uneven, ranging from very low levels (0.22 mg kg^{-1} dw) in the Gulf of Bothnia to the top levels in the Gotland Basin (7.16 mg kg^{-1} dw), the Farö Deep (6.20 mg kg^{-1} dw), and the western Gotland Deep (4.12 mg kg^{-1} dw). Slightly elevated levels were observed in the eastern Gulf of Finland although the levels in the sediments stay no higher than 1.6 mg kg^{-1} dw in the Estonian coastal sea (Fig. 5). The mapping illustrates the transportation of cadmium and its entrapment in the areas where the bottom waters are anoxic (HELCOM 2002).

Persistent organic pollutants in rivers

The survey in the target areas near Tallinn and in the oil-shale region indicated (Tables 3 and 4) that concentrations of all tested pesticides of sewage water was below target levels. Also, concentrations of aldine, dieldrine, endrine, DDT, hexachlorocyclohexane and hexachlorobenzene in the sediment samples were below permitted target levels. The concentration of POP was below detection level. In total, the use of agricultural chemicals decreased dramatically in Estonia in the 1990s. On the other hand, monitoring set has been extended gradually by governmental institutions.

Using the total water discharge into the Baltic Sea via rivers (475 km^3 y^{-1}) and using the median concentrations of 0.7 ng l^{-1} PCBs, 0.06 ng l^{-1} of

DDTs and 0.1 ng l^{-1} of HCHs, river transport results in an annual quantity of 332 kg of PCBs, 2.8 kg of DDTs, and 47.5 kg of HCHs to the Baltic Sea. At the beginning of the 1990s, the rivers and the atmosphere contributed about equally to the PCB load in the Baltic Sea, while for pesticides, atmospheric deposition was about 5–7 times more important (Fig. 6) (Agrell *et al*. 2001).

The PCBs hot spot in river water, nearest to the Estonian coast in the Gulf of Finland is situated in the mouth of the Neva river (Russian Federation) and its tributatory. According to the data by Shushkin (1997), the highest concentration of PCBs was in the mouth of Okhta river (1.5 μg l^{-1}). High PCB levels were also registered in the Chernaya river, near the Bely island, and the Sestroretsk coast. Another site of elevated PCB concentrations close to the Estonian coast in the Gulf of Riga is in the mouth of the Daugava river (Nordic Env. Research Programme 1999). Since the water exchange rate at this location is high, it is possible that the discharge may affect the Gulf of Riga and even the Baltic Proper (Olsson 1999, Olsson *et al*. 1999).

Heavy metals in rivers

Long-term (1994–2003) annual average variations of heavy metals in relation to discharge, measured at the main monitoring stations, show that maximum metal levels occur in autumn–winter, whereas lower concentrations occur during the months of low flow. Similarly to Latvia, the metal concentrations in Estonian rivers were around natural background values. This may be explained by geochemical factors and the abundance of sedimentary deposits in the drainage basins of rivers in Latvia, as well as by minimal anthropogenic loads (Klavins *et al*. 2000, Klavins and Vircavs 2001).

The range of concentrations of five metals (Pb, Cu, Ni, Cr and Zn) for eight stations is given for 2002 (Table 5). The concentration of Cu was between 1.0–36.0 μg l^{-1} in the rivers in 2002. In a comparison in recent years, an increasing concentration was found in the northern part of Estonia: Keila river 8–19 μg l^{-1} (140 μg l^{-1} in June 2002), Kunda river 10–33 μg l^{-1} (92 μg l^{-1} in December 2002), Purtse, Pühajõgi and Narva

Table 3. Hazardous substances in the river sediments in north-eastern Estonia, 2002.

Substances	Unit	National target value	Kohtla river: impact of VKG	Purtse river: impact of VKG	Eesti power plant	Narva Vesi: treatment plant	Balti power plant	Pljussa river: mouth
Aldrin	ng g^{-1}		< 5	< 5	< 5	< 5	< 1	< 1
Dieldrin	ng g^{-1}		< 5	< 5	< 5	< 5	< 1	< 1
Endrin	ng g^{-1}		< 5	< 5	< 5	< 5	< 1	< 1
DDT	ng g^{-1}		< 5	< 5	< 5	< 5	< 1	< 1
Lindane	ng g^{-1}		< 5	< 5	< 5	< 5	< 1	< 1
HCB	ng g^{-1}		< 5	< 5	< 5	< 5	< 1	< 1
PCB	ng g^{-1}							< 5
Hg	mg kg^{-1}	0.5	0.03–0.04	0.05–0.43	0.02–0.04	< 0.02	0.045–0.047	0.131–0.132
Cd	mg kg^{-1}	1	0.196–0.331	0.250–0.484	< 0.25	< 0.25	0.119–0.123	0.329–0.331
PAH	mg kg^{-1}	5						0.15
Petroleum hydrocarbons	mg kg^{-1}	100				36.9		
Sn	mg kg^{-1}	10	0.283–0.724	0.255–1.026		< 0.25		
Ni	mg kg^{-1}	50	3.54–3.84	5.14–15.50		1.44		
Cu	mg kg^{-1}	100	6.11–11.70	5.10–17.50		2.8		
Pb	mg kg^{-1}	50	2.5–4.01	10.0–15.8		< 2.5		
Zn	mg kg^{-1}	200	14.1–25.2	19.0–61.4		9.06		
Cr	mg kg^{-1}	100	10.3–11.6	5.56–6.96		< 1.25		
Mono-basic phenols	mg kg^{-1}	1					0.14	
Di-basic phenols	mg kg^{-1}	1					2.0	

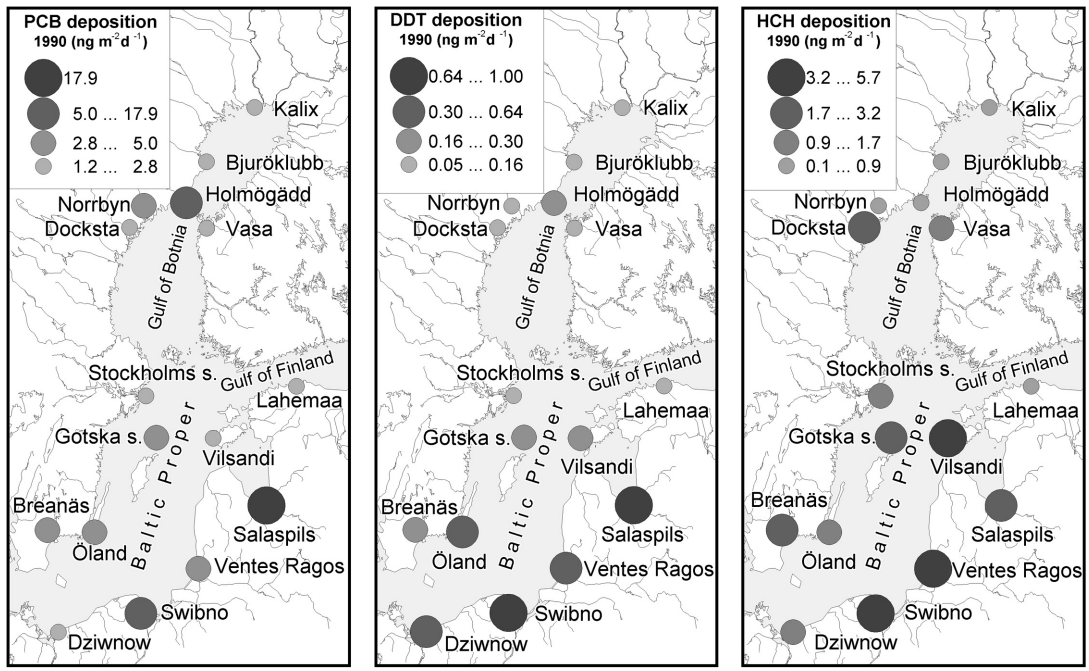

Fig. 6. PCB, DDT and HCH calculated depositions at the stations in the Baltic Sea Basin (data from Agrell *et al.* 2001).

Table 4. Hazardous substances in the water in north-eastern Estonia, 2002.

Substances	Unit	Kohtla river after VKG discharge	Kohtla river in Lüganuse	Purtse river after Kohtla	Purtse river: mouth	Narva Vesi: treatment plant	Pljussa river: mouth
Aldrin	ng l^{-1}	< 10	< 10	< 10	< 5	< 10	< 10
Dieldrin	ng l^{-1}	< 10	< 10	< 10	< 5	< 10	< 10
Endrin	ng l^{-1}	< 10	< 10	< 10	< 5	< 10	< 10
DDT	ng l^{-1}	< 10	< 10	< 10	< 5	< 10	< 10
Lindane	ng l^{-1}	1	< 10	< 10	< 5	< 10	< 10
HCB	ng l^{-1}	< 10	< 10	< 10	< 5	< 10	< 10
1,2-dichloro-ethane	µg l^{-1}	< 1	< 1	< 1	< 1	< 1	< 1
Chloroform	µg l^{-1}	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Trichloro-ethylene	µg l^{-1}	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Tetrachloro-ethylene	µg l^{-1}	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Carbon tetrachloride	µg l^{-1}	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Hg	µg l^{-1}	0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
Cd	µg l^{-1}	0.1	< 0.1	< 0.1	< 0.1	0.1	< 0.02
PAH	µg l^{-1}						0.011
Petroleum hydrocarbons	µg l^{-1}					87.6	
Sulphide	mg l^{-1}					< 0.02	
Sn	µg l^{-1}					< 0.005	
Ni	mg l^{-1}					< 0.001	
Cu	mg l^{-1}					0.018	
Pb	µg l^{-1}					0.002	
Zn	µg l^{-1}					< 0.01	
Cr	mg l^{-1}					< 0.001	

rivers accordingly 18, 12 ja 36 μg l^{-1}. Regarding the standards for heavy metals, the listed rivers belong to the poor quality class. In 2003, elevated concentrations were found in Kunda and Mustajõe rivers although the status improved in major rivers of northern Estonia. The rise of the cadmium concentration was examined in all rivers. Higher concentrations, between 0.23 and 0.85 μg l^{-1}, were detected in Keila, Pirita, Loobu and Jägala rivers (moderate class). Concentration of Cd in the majority of rivers was in the range 0.02–0.1 μg l^{-1} (good class). The concentration of Cd decreased in several rivers in 2003 as compared with that in 2002. The concentrations of Pb fluctuated between 0.2 and 1.0 μg l^{-1}, showing that Pb stayed at the natural level, and rivers belong to the good-quality class. Higher content of Pb was analysed in north-eastern Estonia (Selja river 1.0 μg l^{-1}, Kunda river 1.0–4.0 μg l^{-1}, Purtse river 5.0 μg l^{-1}, Pühajõgi 4.0 μg l^{-1}: moderate class). In an annual comparison, the concentration of Pb has increased. The concentrations of Zn were very low and quite stable in the last years, averaging 2–8 μg l^{-1} up to 15–22 μg l^{-1} in the samples taken from Keila, Pirita, Jägala and Kunda rivers. In 2002, the concentration of mercury was below analytical detection (0.1 μg l^{-1}). In 2003, higher levels of mercury were detected in Kunda river, in Selja river and in Mustajõgi, 1.60, 1.23 and 1.73 μg l^{-1}, respectively.

To summarise, concentrations of heavy metals were predominantly low in Estonian rivers. In north-eastern Estonia, concentrations of Zn, Pb, Cd, Ni, and Cr have tended to increase during the recent years. This is because of a large quantity of sewage and industrial wastewater flowing into the rivers. According to EU freshwater standards on water quality classes (Council Directive 76/464/EEC, Council Directive 78/659/EEC), the Estonian rivers are classified regarding their content of heavy metals as good and moderate. Critically important are standards of analysis and detection levels in the assessment, since concentrations vary. In future, the enrichment factor can serve as an indicator of the degree of heavy metal pollution from anthropogenic source into a river.

In general, in regions with poor equipment, waste water overflows can be of high importance for heavy metal emissions to surface waters. Measures for source control have to be evaluated in every single case. For lead and cadmium, there is no prevailing source. The major part of the zinc emissions into the sewer system originates from surface runoff (roofs, streets). The input of heavy metals (especially chromium and nickel) via coagulants into the treatment plant and sewage sludge has to be considered (Baltic Environmental Forum 2000). Further analyses are required to specify whether metals exist in their carcinogenic form, in order to assess their toxicity and impact on biota.

In order to assess pollution sources in the oil-shale region a comprehensive survey has been carried out in the north-eastern part of Estonia (Tables 3 and 4). The concentrations of cadmium in the river sediments were not exceeded in the surveyed area in the north-eastern part of Estonia. The highest Cd concentration (0.48 mg kg^{-1} dw) was detected in sediments of the Purtse river near the mouth of the Kohtla river (Fig. 7 and Table 3). The concentration of cadmium reached one third of the target value (0.33 mg kg^{-1} dw, target value 1 mg kg^{-1} dw) near the mouth of the Pljussa river

Table 5. Concentrations of heavy metals (µg l^{-1}) in Estonian rivers in 2002 (Hannus *et al.* 2003).

River	Cu	Cd	Pb	Zn	Hg
Kasari in Kasari	1.5	0.03	0.2	4	0.10
Keila in mouth	8.0–19.0	0.05–0.54	< 0.2–0.8	3–22	< 0.10
Pirita, Lükati bridge	2.6	0.29	0.2	19	< 0.10
Pärnu, Oreküla	3.0	< 0.10	< 1.0	< 10	< 0.05
Selja, mouth	2.0	0.06	1.0	10	0.15
Kunda, mouth	10.0–33.0	0.06–0.08	1.0–4.0	< 10–21	0.10–0.65
Narva , Narva	36.0	0.09	< 1.0	< 10	0.13
Emajõgi, Tartu	< 1.0–2.5	< 0.02–0.04	0.4–1.0	3–9	< 0.10

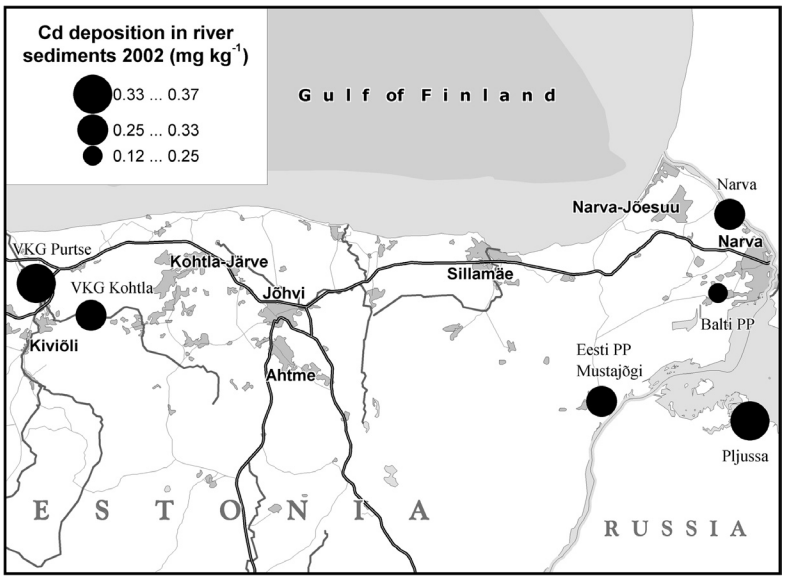

Fig. 7. Cd deposition in river sediments in the north-eastern part of Estonia.

in Russia and in the Kohtla river near the intake of Viru Keemia Group. Also, the concentration of mercury in the river sediments was below target values (0.5 mg kg^{-1} dw) at all sampling sites. The highest mercury concentration (0.43 mg kg^{-1} dw) was found in sediments of the Purtse river near the mouth of the Kohtla river. The sediment sampling proves that the rivers have been affected by discharges of oil-shale industries for decades.

The concentrations of Cd and Hg were lower than target values for intake quality. Pb, Cu, Ni, Cr, Zn were sampled in the Narva river after the outlet of the water treatment plant of the Narva City. The concentration of mercury in the Narva water reservoir was 0.13 mg kg^{-1} dw. The concentrations were above the permissible limits. As heavy metals are present in sediments, aquatic organisms can be exposed to these elements. As expected, the concentrations of heavy metals were much higher in sediment samples than in water samples. The presence of metals in sediments is related to runoff or deposits of water discharge.

Conclusions

During the last ten years the condition of the Estonian environment improved in respect to hazardous impacts. The major pollution sources at the regional level are related to north-eastern Estonia, since the Estonian energy and chemical industries are based on the oil shale mined there. Internationally, elevated levels of hazardous substances are associated with the islands of western and southern Estonia, where the concentrations of hazardous substances are elevated due to long-range transportation of air pollution from central and western Europe. Long-range transport of chlororganic compounds (PCB, etc.) from southern sources outside Estonia dominates in pollution loads.

As the objective of this article was to determine the relative significance of different hazardous substances in the Estonian rivers and in the coastal sea we can conclude that the freshwater quality criteria are not exceeded in river stations for all metals studied. Metals enrichment may occur during the low flow periods, as well as during autumn–winter. Sediment sample values reflect the proximity of heavy-metal sources, in particular in the eastern Tallinn industrial zone.

It is not possible to draw any general conclusions from the limited changes observed in heavy metal concentrations in seawater or marine organisms. Concentrations of some metals, such as cadmium, are declining in organisms in the Gulf of Finland but increasing in the western

Baltic Proper. The clear decline in lead concentrations in herring is observed in most areas. The concentrations of the analysed toxic chlororganic compounds and heavy metals in the Baltic herring of the Estonian coastal sea remain below the standards established by FAO/WHO for fish (FAO 2001). The coastal waters and sediments do not appear to pose any threat to human health and aquatic life. The same is true for riverine and atmospheric inputs of organic contaminants, though not enough accurate data are available to allow detailed analysis.

According to the Helsinki Commission data and based on Estonian national monitoring data, our assessment indicates that the loads of some hazardous substances fell considerably over the past 20–30 years, mostly as a result of tighter controls on point source inputs such as industrial discharges. On the other hand, critical sources should be further monitored and remedial actions taken. There is still too little comprehensive knowledge about the impact of the most widely used chemicals and their cocktail-like combinations on human health and the environment (HELCOM 2003).

In order to get an overview of the levels of air and water pollution in Estonia, a monitoring system should be developed across the country, simultaneously with monitoring of local air and water pollution point sources as well as transportation, which would give a constant overview of the effect of air and water pollution impacts on living nature and of critical loads. The national monitoring programme should deliver data from pollution sources, end-of-pipe data, downstream to the coastal sea. In the long term, the quality of surveys could be raised by combining conventional analytical methods and surveys of bioaccumulation in polluted water-bodies and in the coastal sea.

The implemented Estonian national environmental monitoring programme of hazardous substances, which follows EU and HELCOM recommendations, covers all major problem areas, sites, and aspects on a national scale. Operational monitoring by companies, required by the environmental permit system, complements the national network and gives the opportunity for detailed assessment of trends in waterbodies. Nevertheless, the statistical power of the present sampling is weak; in particular, the temporal frequency should be increased. Databases and inventories of industrial chemicals and hazardous substances should be developed next years in addition to the extensive site surveys where sources are found. Further, as proposed by HELCOM, it could be fruitful to integrate source-oriented and load-oriented approaches, since both are lacking full-scale consistent data coverage (HELCOM 2004a). In the future, in the course of developments in environmental management and the implementation of integrated pollution prevention and control (IPPC), monitoring obligations will be shifted towards industrial companies. The public authorities remain in charge of national surveys, assessments, reporting, and inspection.

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