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Water contamination issues in Estonia: a review

Ott Roots^{a*} and Tiit Lukki^b

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Abstract. This article deals with the analytical results of environmental monitoring and screening performed on the identification and sources of hazardous substances in the Estonian aquatic environment. The concentrations of hazardous substances have been studied at different sampling sites and matrices. A total of 130 hazardous substances from 12 groups of substances were investigated in the framework of the BaltActHaz project. The findings suggest that the status of the majority of Estonian surface water bodies is good: the concentrations of hazardous substances measured remained below the analytical detection limit in most of the samples analysed. The contents of only some phthalates, e.g. diisobutylphthalate, di-(2-ethylhexyl)-phthalate, and dimethylphtalate, exceeded the analytical detection limit. Mono- and dibutyltin and benzene were found from some water samples in rivers. However, the content of some heavy metals as well as mono- and dibasic phenols in the surface water/wastewater can still reach delicate levels, in particular in the Estonian oil shale region. The concentrations of organotin compounds are high in the areas of ports and shipyards. The assessment of the water contamination by hazardous substances indicates the relevance of the continuation of the monitoring due to its crucial role for an appropriate decision-making in the protection of the aquatic environment of Estonia. Continued monitoring is necessary to mitigate the exposure and to protect the living resources.

Key words: hazardous substances, metals, organics, priority pollutants, aquatic environment, Estonia.

INTRODUCTION

There is a need for general and simultaneous action by the Member States of the European Union (EU) to protect the aquatic environment from pollution, particularly that caused by certain persistent, toxic, and bio-accumulative substances. The Republic of Estonia is one of the smallest countries in the EU. Estonia joined the EU in 2004 [1]. With the Water Framework Directive (WFD; Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000) a framework for Community action in the field of water policy was established. Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 sets the environmental quality standards of priority

water and biota'.

The oil shale mining region in north-east Estonia continues to be of concern in terms of hazardous substances. In this region the largest industrial (Kunda Nordic Cement, Viru Keemia Grupp AS, Kiviõli Keemiakombinaat, etc.) and energy (Baltic and Estonian thermal

power plants) enterprises in Estonia are located [2].

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Estonian Ministry of Environment adapted the directive as Regulation No. 49 'The environmental quality standards for hazardous substances in surface water, including priority substances and priority hazardous substances and certain other pollutants, methods of application of environmental quality standards for priority substances and priority hazardous substances in surface water and biota'.

The oil shale mining region in north-east Estonia continues to be of concern in terms of hazardous substances and priority substances.

substances and certain other pollutants. The directive calls for the monitoring of the concentrations of these

compounds in surface water. On 9 September 2010 the

^a Estonian Environmental Research Institute, Maria 4D, 10617 Tallinn, Estonia

^b Tallinn University, Narva mnt 25, 10120 Tallinn, Estonia

^{*} Corresponding author, ottroots66@gmail.com

The environmental monitoring of hazardous substances originating in the Estonian environment was conducted as part of the Estonian National Environmental Monitoring Programme (NEMP) [3]. It was recommended that among the priority hazardous substances in Estonia, the substances that need more attention and periodic monitoring should include monobasic phenols (sum of p-, m-, o-cresols; 3,4-, 3,5-, 2,3-, 2,6-dimethyl phenols, and phenol), dibasic phenols (sum of resorcinol, 2,5-dimethyl resorcinol, and 5-methyl resorcinol), some heavy metals [4,5] and, for geological reasons, barium [6]. The NEMP includes inland, marine, and groundwater sub-programmes, but does not embrace all water environments and substances; impacts of pesticides in the intensive agricultural areas, effluent and sewage sludge are not surveyed in the framework of the NEMP.

In recent years the monitoring of hazardous substances has become more exhaustive as new substances have been included in the survey because of new requirements by the EU. Therefore, the Estonian priority substance list is not final. The objective of this article is to provide an overview of hazardous substances contaminating Estonia's aquatic environment. Upon receipt of new information, additional hazardous substances should be included in the list. Alternatively, if it can be shown that a listed substance poses no risk, the compound may be removed from the list [7–13]. Revised environmental quality standards (EQS) for existing

priority substances could be taken into account for the first time in river basin management plans covering the period 2015–2021. The newly identified priority substances and their EQS should be taken into account in the establishment of supplementary monitoring programmes and in preliminary programmes of measures to be submitted by the end of 2018 [14].

MATERIALS AND METHODS

Selection of hazardous substances and sampling matrices

The results were obtained during the course of international and national monitoring projects coordinated by the Estonian Ministry of the Environment. The concentrations of hazardous substances were studied at different Estonian sampling sites and matrices (Table 1).

The analytes, 130 hazardous substances from 12 groups (Table 1), were chosen from the list of LIFE07ENV/EE/ 000122 BaltActHaz (Baltic Actions for Reduction of Pollution of the Baltic Sea from Priority Hazardous Substances) Project. Many of these substances have not been investigated in Estonia previously. For the selection of sampling matrices, three main criteria were taken into account: solubility of substances in water, potential for bio-concentration, and persistence in the environment [7–10,15–18,20].

Table 1. Substances and groups of substances analysed in the water monitoring and screening projects in Estonian aquatic environment

	1	ı	
Substance group	National	International projects	
	projects	BaltActHaza	COHIBA ^b
	[11]	[15–18]	[19]
Heavy metals	+	+	+
Phenols, alkylphenols, and their ethoxylates	+	+	+
Polycyclic aromatic hydrocarbons	+	+	_
Volatile organic compounds	+	+	_
Chlorobenzenes	_	+	_
Organotin compounds	_	+	+
Phthalates	+	+	_
Polybrominated biphenyls,	_	+	+
diphenylethers, and other			
polybrominated organic compounds			
Short- and medium-chain chlorinated paraffins	_	+	+
Perfluoro compounds	_	+	+
Pesticides	+	+	_
Polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans	_	_	+

^a Baltic Actions for Reduction of Pollution of the Baltic Sea from Priority Hazardous Substances.

b Control of Hazardous Substances in the Baltic Sea Region.

- 1. Solubility of substances in water (hydrophilic and hydrophobic chemicals) is described by the octanol—water partitioning coefficient ($K_{\rm OW}$). Generally, chemicals with $K_{\rm OW}$ < 1000 are considered hydrophilic and characterized by good solubility in water, low absorption to soil and sediments, and low propensity for bio-concentration. Chemicals with $K_{\rm OW}$ > 1000 are considered hydrophobic and characterized by low solubility in water, high absorption to soil and sediments, and high propensity for bio-concentration. As a rule, hydrophobic substances cannot be found dissolved in water, and for practical reasons there is no point in looking for them there.
- 2. The bio-concentration factor BCF of substances characterizes their ability to bio-accumulate. The BCF is the ratio of the concentration in an organism to the concentration in the environmental matrix (in this case water). It describes a chemical's propensity to transfer from the aquatic environment to tissues of a living organism. A substance is classified as bio-accumulative if its BCF value exceeds 2000. Generally, the propensity of a substance to bio-accumulate is considered low if it has a log $K_{OW} \leq 3$.
- 3. The persistence of compounds in the environment is accessed based on its half-life ($t_{1/2}$). A compound is considered persistent if $t_{1/2} > 2$ months in water or $t_{1/2} > 6$ months in soil or sediment. Alternatively, a compound is persistent if its BCF > 5000 and/or log $K_{OW} > 5$ [2,15–18].

The sampling matrices were chosen based on guidance documents on chemical monitoring of sediment and biota under the WFD [21,22]. The matrices are classified as preferred, optional, and not recommended.

- Preferred: monitoring should be performed in this matrix.
- Optional: monitoring can be performed in this matrix, but also in other compartments/matrices; the choice will also be made on the basis of the degree of contamination of a particular matrix.
- Not recommended: monitoring in this matrix is not recommended unless there is evidence of the possibility of accumulation of the compound in this matrix [21].

Based on the aforementioned criteria and considering the potential occurrence of various substances in certain parts of the environments, the analyses of hazardous substances were carried out in the following matrices:

- surface water
- effluent (treated wastewater)
- bottom sediment of surface waters
- sewage sludge.

Chemical analyses

The analyses of samples were performed using appropriate quality assurance and quality control

protocols. As the Estonian Environmental Research Centre (EERC) or any other national laboratory was not capable or certified to analyse all listed substances in Estonia, analyses were subcontracted to laboratories in Germany. The chemical analyses were carried out in two German laboratories: GALAB Laboratories GmbH and Gesellschaft für Bioanalytik Hamburg GmbH. The activity of German laboratories has been declared to be in conformity with the requirements of the standard EN ISO/IEC 17025.

The limits of detection (LOD), limits of quantification (LOQ), and measurement uncertainties (MU%) of the EERC and GALAB laboratories are presented in [15–18]. For more detailed specification of COHIBA project methods, LOQ, LOD, and MU% can be found in [19].

Sampling sites

Within the BaltActHaz project, samples were collected from Estonian inland surface waters (SW), from surface waters along coastal areas (SW), from the bottom sediment (BS), and from effluents (treated wastewater, E), and sewage sludge of wastewater treatment plants (wastewater sludge, WS). Sampling was performed all over Estonia in May and September 2010. Sampling points and the respective matrices where samples were taken are shown in Fig. 1 and Appendix 1.

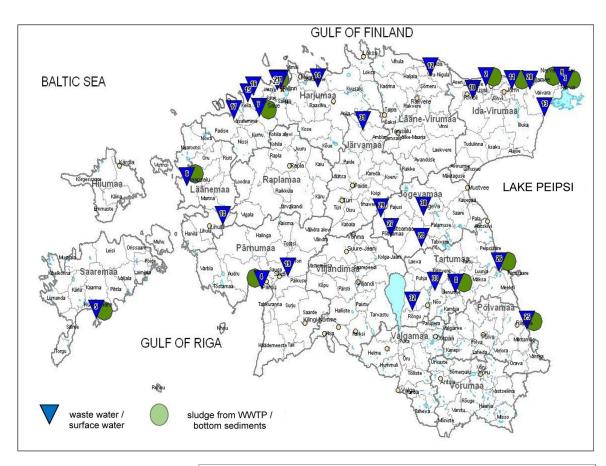
Hazardous substances were quantified at a total of 33 sampling locations, of which 8 were at wastewater treatment plants (WWTPs) (Nos 1–8), 11 were rivers (Nos 9–19), 5 were coastal regions (Nos 20–24), 2 were Lake Peipsi (Nos 25 and 26), and 7 were regions engaged in intensive agriculture (Nos 27–33) (Fig. 1).

Wastewater treatment plants:

- 1. Tallinn WWTP E, WS
- 2. Kohtla-Järve WWTP E, WS
- 3. Narva WWTP E, WS
- 4. Pärnu WWTP E, WS
- 5. Kuressaare WWTP E, WS
- 6. Haapsalu WWTP E, WS
- 7. Keila WWTP E, WS
- 8. Tartu WWTP E, WS.

Rivers:

- 9. Narva state monitoring station No. 32 SW, BS
- 10. Kohtla flowing into the Purtse River SW, BS
- 11. Pühajõgi state monitoring station No. 33 (the mouth of the river) SW, BS
- 12. Kunda state monitoring station No. 36 (the mouth of the river) SW, BS
- 13. Mustajõgi state monitoring station No. 60 SW, BS
- 14. Jägala state monitoring station No. 42 (the mouth of the river, Linnamäe) SW, BS
- 15. Keila state monitoring station No. 47 SW, BS
- 16. Vääna state monitoring station No. 45 (the mouth of the river) SW, BS



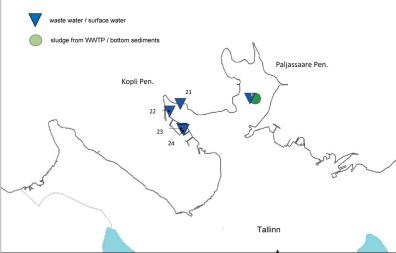


Fig. 1. Map showing sampling points all over Estonia (above) and in the area of Tallinn (below) ([15,16] with permission).

- 17. Vasalemma (the mouth of the river) SW, BS
- 18. Kasari state monitoring station No. 49 SW, BS
- 19. Pärnu state monitoring station No. 52 SW, BS.

Coastal waters:

- 20. Coast of Sillamäe Bay (eastern part of the Gulf of Finland) SW, BS
- 21. BLRT Grupp AS (Baltic Ship Repair Company), Tallinn, effluents flow into Tallinn Bay E
- 22. BLRT Grupp AS Company Baltic Premator dock No. 2, effluents flow into Tallinn Bay E, WS
- 23. BLRT Grupp AS Company Baltic Premator dock No. 34, effluents flow into Tallinn Bay E
- 24. BLRT Grupp AS Company Baltic Premator dock No. 3, effluents flow into Tallinn Bay as dock No. 3 was not open during the time of planning sampling, it was not possible to take effluent samples from there.

Lakes:

- 25. Lake Peipsi State monitoring point Peipsi No. 17 SW, BS
- 26. Lake Peipsi State monitoring point Peipsi No. 38 SW, BS.

Agricultural regions:

- Alastvere. Main ditch of Alastvere (Võhma-Nõmme Village) – SW
- 28. Tõrve. Outlet to the Pedja River SW
- 29. Võisiku state monitoring station No. 61 (the main ditch of Võisiku) SW
- Pedja River state monitoring station No. 14 (Jõgeva Plant Breeding Station) – SW
- 31. Jänijõgi River state monitoring station No. 64 SW
- 32. Rannu. Main ditch of Konguta before flowing into Lake Liivaku (Tartu County) SW
- Rohu. Rohu Stream before the collection lake (Tartu County) SW.

The regulation prescribes the methods and installations for collecting sea water, surface water, effluent, bottom sediments, and sewage sludge in the process of trace level analyses described precisely in [15–20].

The samples were transported to the laboratory in thermo boxes with cold batteries and were placed in the refrigerator immediately after arrival. All samples were taken as two replicates, in case during transportation to Germany one of the sample bottles or jars should break. The samples were packed by the chemists of the EERC, who have previous experience in such activity.

RESULTS AND DISCUSSION

Levels of hazardous substances in surface waters

At the beginning of the 2000s the list of priority substances included first-rate heavy metals and phenols (monobasic and dibasic phenols) [5].

In 2008, within the framework of the international project 'EU Wide Monitoring Survey of Polar Persistent Pollutants in European River Waters', 122 water samples from 27 European Union Member States were studied [12,13]. Three rivers from Estonia were included in the project: the Narva, Purtse, and Emajõgi. The Narva River on the Estonian–Russian border has the largest catchment area - 56 225 km² - in the Estonian territory; its area is 17 145 km², and the mean flow rate at the river mouth is 380–400 m³/s. The Purtse River in the oil-shale region has a catchment area of 784 km² and the mean flow rate 6.7 m³/s. The catchment area of the Emajogi (together with the catchment area of Lake Võrtsjärv and the catchment in Latvian territory) is 9740 km², and its mean flow rate is 70 m³/s.

A first EU-wide data set has been created on the occurrence of polar persistent pollutants in river surface waters to be used for continental-scale risk assessment and related decisions. The level of contamination of a total of 100 European rivers and other similar bodies of flowing water were tested for 35 selected polar persistent organic compounds (POS). These included pharmaceuticals (e.g. carbamazepine, diclophenac), antibiotics (sulphamethoxazole), pesticides (e.g. 2,4-D, mecoprop, bentazone, terbutylazine), perfluorinated compounds (PFCs, e.g. perfluorooctane sulphonate (PFOS), perfluorooctanoic acid (PFOA)), benzotriazoles (corrosion inhibitors), hormones (estrone, estradiol), and alkylphenolics (bisphenol A, nonylphenol). Only dissolved (liquid) in the water phase, and not suspended, material was investigated. The content of the majority of substances in three Estonian rivers included in the international project remained below the LOD (Table 2).

The fact that hazardous substances are transported to the Baltic Sea from the whole catchment area was taken into account. Within the BaltActHaz project, the samples were collected from Estonian inland surface waters and from surface waters along coastal areas, from the bottom sediment, and from effluents and sewage sludge of WWTPs. In the first round (21 Apr.-3 May 2010) all chosen substances were analysed, and in the second (13-14 Sep. 2010) and third (May 2011) rounds only those substances were analysed that had very high values in the first round or for which the results were questionable for some reason. Special attention was paid to rivers with valuable food fishes (Fig. 2). The Vasalemma River (food fishes salmon and trout), which had previously not been a part of the national environmental monitoring programme, was added (Table 3).

In most cases, the concentrations of hazardous substances remained below the LOD [16] and did not exceed the environmental quality limit values [14]. The concentrations of the substances that exceeded the LOD but remained below the Estonian EQS are presented in Table 4. However, the oil shale mining region continues to be problematic in terms of the concentrations of hazardous substances.

The concentrations of hazardous substances in the rivers in most cases did not exceed the established environmental quality standards and were prevailingly below the LOQ. Only the contents of a few phthalates, e.g. diisobutylphthalate, di-(2-ethylhexyl)-phthalate, and dimethylphtalate, exceeded the LOQ but still remained below the environmental quality standard. However, high concentrations of monobasic phenols were found in the water samples taken from the Kohtla, Vasalemma, Narva, and Keila rivers. Mono- and dibutyltin were found in samples from the Narva, Keila, and Kasari rivers. A high content of benzene was measured in the water of the Kunda and Pühajõgi rivers. The concentrations

Table 2. Concentrations (ng/L) of priority substances and certain other pollutants in Estonia's rivers and comparison with other European Union rivers [12,13]

-		1		l	1	
Substance	LOD*	Emajõgi	Purtse	Narva	Concent	rations
		River	River	River	in EU 1	rivers
					Maximum	Average
Diuron	1	2	0	2	864	41
Simazine	1	0	0	0	169	10
Isoproturon	1	0	0	0	1 959	52
Atrazine	1	0	0	0	46	3
Nonylphenol	50	0	0	0	4 489	134
4- <i>tert</i> -Octylphenol	10	0	0	0	557	13
Perfluorooctanoic acid	1	1	1	0	174	12
Perfluorooctane sulphonate	1	1	0	1	1 374	39
Bisphenol A	5	0	0	0	323	25
Nitrophenol	n.a.	14	6	9	3 471	99
2,4-Dinitrophenol	1	14	0	7	174	18
Ibuprofen	1	6	0	3	31 323	395
Diclophenac	1	3	1	2	247	17
Bentazone	1	2	0	1	250	14
Benzotriazole	1	13	0	0	7 997	495
Caffeine	1	22	22	15	39 813	963
Carbamazepine	n.a.	15	0	3	11 561	248
Methylbenzotriazole	1	0	90	0	19 396	617
Nonylphenoxyacetic acid	2	74	16	30	7 491	553

^{*} LOD – limit of detection; n.a. – not applicable.

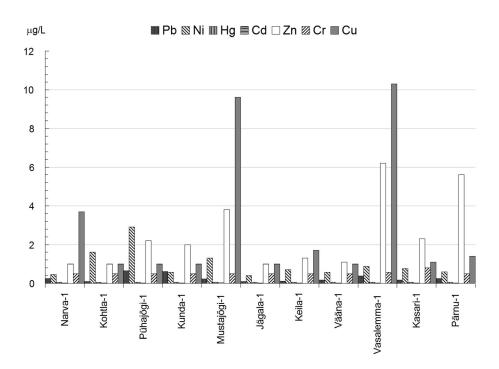


Fig. 2. Contents of heavy metals in river water in the first sampling round (based on [15,16]).

Table 3. The list and of sampling points/monitoring stations (site numbers correspond to Fig. 1) and valuable fishes of the rivers [15,16,23]

Site No. ^a	River	Catchment area ^a , km ²	Valuable fish
9	Narva	56 225 (17 145 in Estonian territory)	Salmon, carp
10	Kohtla	784 (Purtse River catchment area)	Salmon
11	Pühajõgi	196	Salmon
12	Kunda	530	Salmon
13	Mustajõgi	994	
14	Jägala	1573	Salmon
15	Keila	682	Salmon
16	Vääna	316	Salmon
17	Vasalemma	395.6	Salmon
18	Kasari	3210	Carp
19	Pärnu	6920	Salmon

a Keskkonnaregister – http://register.keskkonnainfo.ee/envreg/main?list=VEE&mount=view

of hazardous substances in the bottom sediment of rivers were in most cases below the LOQ. However, heavy metals, such as nickel, chromium, zinc, and copper, were found in sediment from the Narva River, and high concentrations of 2.5-dimethylresorcinol were found in the sediments of the Keila, Narva, and Pühajõgi rivers [15,16].

During 2008, as an assignment from the Helsinki Commission (HELCOM), a screening study was performed in the eastern Baltic Sea environment on the occurrence of eight substances/substance groups (organotin compounds (OT), polybrominated diphenyl ethers (PBDE), hexabromocyclododecane (HBCDD), perfluorinated substances (PFAS), chlorinated paraffins, endosulphan, and phenolic substances) identified as priority hazardous substances under the Baltic Sea Action Plan. The project was funded by the Nordic Council of Ministers. Estonian coastal waters were sampled at four places: eastern (Narva Bay near Sillamäe) and western (near Dirhami) parts of the Gulf of Finland, western coast of Saaremaa Island, and Pärnu Bay [24].

In all Estonian coastal water samples analysed, PFAS (PFOS, PFOA, etc.), phenolic substances (nonylphenols and nonylphenol ethoxylates, octylphenols and octylphenol ethoxylates), bisphenol A, and triclosan were below the LOQ. From phenolic substances only 4-NP was detected above the LOQ (<10 ng/L) in some Estonian coastal water samples (from <10 ng/L to 66 ng/L in the coastal area near Sillamäe). Based on the results, it can be concluded that the concentrations found for different substances in the coastal waters of

Table 4. List of the sampling points/monitoring stations (site numbers correspond to Fig. 1) of the rivers and Lake Peipsi where the concentrations of hazardous compounds are above the limit of detection but below the annual average value of the environmental quality standard of inland surface waters [15,16,23]

Site No.	Water body	Hazardous substances
9	Narva R.	Lead, nickel, copper, phenol, <i>p</i> -and m-cresol, monobutyltin
10	Kohtla R.	Nickel, phenol, bromoform, diisobutylphthalate, di-(2- ethylhexy) phthalate (DEHP)
11	Pühajõgi R.	Lead, nickel, zinc, benzene, trichloromethane (chloroform)
12	Kunda R.	Lead, nickel, zinc, benzene, trichloromethane, diisobutylphthalate, DEHP
13	Mustajõgi R.	Lead, nickel, cadmium, zinc, copper, naphthalene
14	Jägala R.	Nickel, trichloromethane, dimethylphtalate, DEHP
15	Keila R.	Lead, nickel, zinc, copper, phenol, <i>p</i> - and <i>m</i> -cresol, tetrachloromethane (carbon tetrachloride), monobutyltin, dibutyltin
16	Vääna R.	Lead, nickel, zinc, diisobutylphthalate, DEHP
17	Vasalemma R.	Lead, nickel, zinc, chromium, copper, phenol, diisobutylphtalate
18	Kasari R.	Lead, nickel, zinc, chromium, copper, trichloromethane, diisobutylphtalate
19	Pärnu R.	Lead, nickel, zinc, copper, trichloromethane, diisobutylphtalate
25	Lake Peipsi	Lead, nickel, phenol, p- and m-cresol, dichloromethane, trichloromethane, dibutylphthalate
26	Lake Peipsi	Nickel

Estonia were low. A single sampling and analysis of a single random sample at different sampling dates for coastal water does not enable to draw essential conclusions about the state of Estonian coastal waters [24].

In a previous study [11], the maximum concentrations of nickel and iso-nonylphenol in a water sample taken in September 2010 from coastal waters of Pärnu Bay were 0.66 μ g/L and 0.39 μ g/L, respectively. However, other analytes such as cadmium, lead, octylphenol, chloroform, (aminomethyl)phosphoric acid (AMPA), glyphosate, and pyrene were below the LOQs [11].

The concentrations of organotin compounds are high in the harbour areas (sampling point 20 – Sillamäe Bay) and shipyards (sampling points 21-24): EQS for tributyltin compounds is $0.0002 \,\mu\text{g/L}$, but its maximum measured concentration in water samples was $0.06 \,\mu\text{g/L}$. Water samples taken from Tallinn Bay in the coastal area adjacent to the Baltic Ship Repair Company contained very high concentrations of organotin compounds. Additional studies are required to check the occurrence of these substances in the Estonian aquatic environment.

Organochlorine pesticides (OCPs) have never been produced in Estonia and their import was banned in Estonia beginning in October 1967 [2,25]. Under the BaltActHaz project, there were seven sampling points (Nos 27–33) in intensive agricultural regions at which pesticides were determined. Samples were taken in spring, from the end of April to the beginning of May 2010. All together 23 pesticides (among them endosulfan, chlorfenvinphos, alachlor, atrazine, isoproturon, chlorpyriphos, trifluralin, simazine, glyphosate, AMPA and MCPP and some chlorinated pesticides such as aldrin, dieldrin, endrin, isodrin, hexachlorocyclo-hexanes, etc.) were investigated. The concentrations of all these compounds were below the LOQs [15,16].

The highest concentrations of AMPA and glyphosate were found in the Räpu River in September 2010: 0.93 μ g/L and 0.29 μ g/L, respectively [11]. However, in most cases the concentrations of pesticides were below the LOQs. These findings suggest that the status of the majority of Estonian surface water bodies is good with respect to pesticides.

Levels of hazardous substances in the effluents of wastewater treatment plants

The NEMP does not include effluents from WWTPs and sewage sludge. The results of industrial and domestic wastewater analysis were compared to the limit values for the content of hazardous substances in the effluents discharged into the public sewerage system, laid down with the 16 October 2003 Regulation No. 75 of the Minister of the Environment 'Establishing of requirements for the discharge of hazardous substances into a public sewerage system'. In regard to the content of heavy metals, the effluents of all WWTPs (Fig. 1, sampling points 1–8) were in compliance with the requirements (Table 5). However, the contents of some heavy metals were still high (Fig. 3).

In the first sampling round, in May 2010, the contents of arsenic (0.9 μ g/L), lead (6.2 μ g/L), nickel (9.6 μ g/L), and zinc (35 μ g/L) were the highest in the effluent of the Tallinn WWTP. The contents of copper (58 μ g/L) and chromium (12.5 μ g/L) were high in the effluent of the Keila WWTP) (Fig. 3a).

In the second sampling round, in September 2010, the contents of arsenic (5.3 μ g/L), lead (1.2 μ g/L), nickel (6.7 μ g/L), zinc (33.9 μ g/L), and copper (59.4 μ g/L)

Table 5. Limits for the discharge of heavy metals into the public sewage system

Heavy metal	Limits, mg/L
Lead and its compounds	0.5
Nickel and its compounds	1.0
Mercury and its compounds	0.05
Cadmium and its compounds	0.2
Zinc and its compounds	2.0
Chromium (total)	0.5
Chromium (VI)	0.1
Copper and its compounds	2.0
Arsenic and its compounds	0.2

were the highest in the effluent of the Kohtla-Järve WWTP and the content of chromium (16.3 $\mu g/L$) in the effluent of the Keila WWTP. The content of mercury remained below the LOQ (0.05 $\mu g/L$) in all effluent samples and that of cadmium below the LOQ (0.02 $\mu g/L$) in the majority of the effluent samples (Fig. 3b).

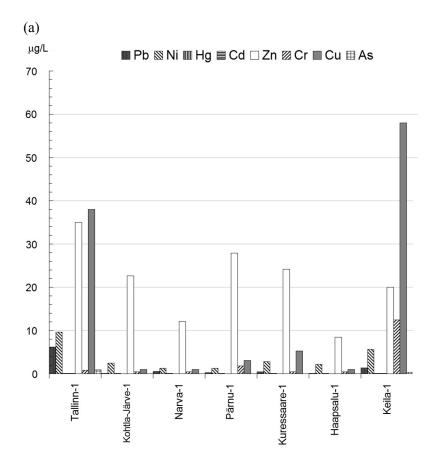
In the third sampling round, in May 2011, heavy metals were analysed in the effluent of the Kohtla-Järve WWTP. The content of arsenic was 3.4 µg/L (parallel sample 3.4 µg/L), lead 0.17 µg/L (1.5 µg/L), nickel 4.4 µg/L (5.0 µg/L), zinc 23 µg/L (24 µg/L), cadmium 0.06 µg/L (0.19 µg/L), chromium 0.94 µg/L (0.98 µg/L), and copper 5.2 µg/L (13 µg/L). The content of mercury in the effluent samples remained below the LOQ (0.05 µg/L) [16,17].

In the COHIBA project only mercury and cadmium were measured in the effluent samples from the WWTPs. The mercury concentrations in the effluents were equal to or lower than the LOQ (0.05 μ g/L). For cadmium, the highest detected concentration from effluents was 0.15 μ g/L [19]. The effluent samples collected in September 2010 from WWTP No. 1 (Kohtla-Järve WWTP) contained 0.63–21 μ g/L of nickel and <0.5–2 μ g/L of lead. Cadmium remained below the LOQ [19].

Levels of hazardous substances in the mining and oil shale region

The north-east Estonian environmental problems are directly related to the mining and processing of oil shale in the region. The concentrations of hazardous substances still cause problems in that region. The largest industrial and energy enterprises are located there (Baltic and Estonian thermal power plants, Kunda Nordic Cement, Viru Keemia Grupp AS, Kiviõli Chemical Plant, etc.) [20,25–31].

Ida-Viru county in NE Estonia was chosen as the place for carrying out the monitoring of sources of hazardous substances in May 2011 [17,18]. Ida-



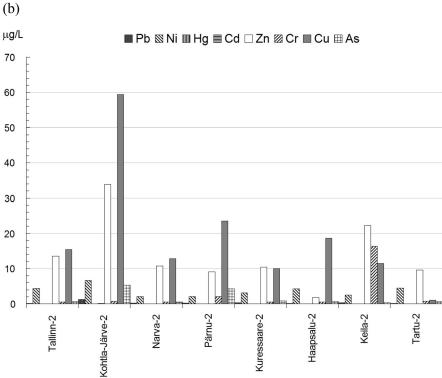


Fig. 3. Contents of heavy metals in the effluents of wastewater treatment plants (a) in the first sampling round and (b) in the second sampling round (based on [15,16]).

Viru county is characterized by long-term industrial traditions and an array of manufacturing enterprises. The Kohtla-Järve WWTP (Järve Biopuhastus OÜ) participated in the monitoring as most of the enterprises in the area send their wastewater for treatment to this plant. The type of treatment on Kohtla-Järve WWTP was mechanical + biological + biological nitrogen and phosphorus + chemical phosphorus separation. In addition to effluent from industrial enterprises, the Kohtla-Järve WWTP also treats household effluents (domestic wastewater) from the towns of Jõhvi, Kiviõli, Kohtla-Järve, and Püssi, the municipality of Kohtla-Nõmme, and the village of Kukruse.

During the survey, wastewaters from four participating industrial plants (three chemical industries and one timber industry), leachate from semi-coke and ash deposits, and domestic wastewaters from the towns of Jöhvi, Kiviöli, Kohtla-Järve, and Püssi, Kohtla-Nõmme municipality, and Kukruse village were analysed (Table 6). In NE Estonia, mining and processing of oil shale are considered to be the major sources of hazardous substance contamination to surface water. Additional studies are required to verify the occurrence of the substances identified by the survey in the Estonian aquatic environment.

CONCLUSIONS AND RECOMMENDATIONS

Recent environmental monitoring and screening of the Estonian aquatic environment shows that the concentrations of hazardous substances in surface water are, in most cases, below the LOD and rarely exceed the EQS. However, the concentrations of some heavy metals and monobasic phenols (especially phenols and *p*- and *m*-cresols) and dibasic phenols in some surface waters and effluents may be of concern. Further, concentrations of organotin compounds are high in ports and shipyards. The concentrations of only some phthalates, e.g. diisobutylphthalate, di-(2-ethylhexyl)-phthalate, and dimethylphtalate, exceeded the LOQ, but were below the EQS. Mono- and dibutyltin and benzene were found in some rivers.

Contamination with hazardous substances from the oil shale industry continues to be a concern in NE Estonia. In this area, surface waters are contaminated with mono- and dibasic phenols, pentachlorophenol, polycyclic aromatic hydrocarbons, organotin compounds, and phthalates. Considering the relatively high quantities of hazardous substances in the wastewater, the Kohtla-Järve WWTP copes relatively well. Even though the

Table 6. Hazardous substances in wastewaters from north-east Estonia [17,18]

Source	Hazardous substances
Chemical industry	Mono- and dibasic phenols, pentachlorophenol, polycyclic aromatic hydrocarbons (naphthalene, anthracene, fluoranthene), phthalates (di-(2- ethylhexyl)-phthalate, diisobutylphthalate, dibutylphthalate)
Timber industry	Organotin compounds (dioctyltin, monobutyltin), volatile organic compounds (dichloromethane, 1,2-dichloroethane), alkylphenols (isononylphenol, 4- <i>tert</i> -butylphenol), phthalates (di(2-ethylhexyl)phthalate, diisobutylphthalate)
Semi-coke and ash deposit	Mono- and dibasic phenols, arsenic, pentachlorophenol, polycyclic aromatic hydrocarbons (naphthalene, fluoranthene, anthracene), volatile organic compounds (benzene), organotin compounds (monooctyltin, monobutyltin)
Domestic wastewater (household effluents)	Phthalates (di(2-ethylhexyl)phthalate, diisononylphthalate, diethylphthalate, diisobutylphthalate), alkylphenols and their ethoxylates (isononylphenol, 4-t-octylphenol-monoethoxylate), organotin compounds (monobutyltin, monooctyltin)

influent contains industrial and domestic wastewater as well as leachate from semi-coke and ash deposits, the effluent meets the environmental quality requirements of Estonian legislation.

Additional studies are required to verify the occurrence of hazardous substances in the Estonian aquatic environment. The priority substances list is not final. Upon receipt of new information, hazardous substances should be added to the list. Compounds may also be removed from the list if environmental monitoring and risk assessment shows that the risk is limited. When monitoring hazardous substances in water bodies, consideration should be given to future emissions, and attention should be paid to improved conditions to minimize unwanted production and transport of hazardous substances. Care must also be taken for proper incineration of disposal of hazardous wastes. Sustainable environmental strategies for the aquatic environment should be developed as well to mitigate exposure to hazardous substances to protect living

In recent years, the monitoring of hazardous substances has become more exhaustive as new substances have been included in the surveys based on requirements by the European Union. The EU Commission has conducted a review of the list of priority substances and has come to the conclusion that it is appropriate to amend the list of priority substances by identifying new substances for priority action at Union level, setting Environmental Quality Standards (EQS) for those newly identified substances, revising the EQS for some existing substances in line with scientific progress and setting biota EQS for some existing and newly identified priority substances. The revised EQS for existing priority substances should be taken into account for the first time in river basin management plans covering the period 2015 to 2021 (Directive 2013/39/EU).

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APPENDIX 1

Table 1A. List of sampling points/monitoring stations

Sampling	Description	Description Coordinates		
point	,	N	Е	
numbera		1,		
-	Wastewater	treatment plan	ts	
1	Tallinn WWTP	59°28′6.64″	24°42′13.57″	
2	Kohtla-Järve WWTP	59°24′16.61″	27°14′57.89″	
3	Narva WWTP	59°23′50.47″	28°10′28.41″	
4	Pärnu WWTP	58°23′10.48″	24°27′6.96″	
5	Kuressaare WWTP	58°13′12.67″	22°29'49.25"	
6	Haapsalu WWTP	58°56′38.48″	23°33′21.65″	
7	Keila WWTP	59°18′52.3″	24°26′3.93″	
8	Tartu WWTP	58°20′28.64″	26°44′53.83″	
		ivers ^b		
9	Narva station No. 32	59°25′13.01″	28°8′6.98″	
10	Kohtla	59°22'44.35"	28 8 0.98 27°2′37.72″	
10	Pühajõgi station No. 33	59°25′12″	27°31′40.01″	
12	Kunda station No. 36	59°30′35″	26°32′18″	
13	Mustajõgi station No. 60	59°15′42.35″	20°54′19.67″	
14	Jägala station No. 42	59°28′25.31″	25°9'4.87"	
15	Keila station No. 47	59°23'42.99"	24°17′47.03″	
16	Vääna station No. 45	59°25′53″	24°17'47.03"	
17	Vasalemma	59°18′18.75″	24°21'31.03 24°7'38.99"	
18	Kasari station No. 49	58°44′1.01″	23°59′22.02″	
19	Pärnu station No. 52	58°27′18.99″	24°45′48.98″	
1)		tal waters	21 13 10.70	
20			27944/52 01//	
20 21	Sillamäe Bay BLRT flow into Tallinn	59°24′39.09″ 59°28′0.92″	27°44′52.01″ 24°39′26.2″	
21	Bay	39 20 0.92	24 39 20.2	
22	BLRT flow into Tallinn	59°27′52.35″	24°39′0.44″	
	Bay			
23	BLRT flow into Tallinn	59°27′30.94″	24°39′29.94″	
24	Bay BLRT flow into Tallinn	59°27′29.37″	24°39′34.1″	
24	Bay	39 21 29.31	24 39 34.1	
Lakes ^b				
25	Peipsi station No. 17	58°7′10.99″	27°34′31.98″	
26	Peipsi station No. 38	58°26′36″	27°16′35.97″	
20	•		27 10 33.77	
27		ural regions ^b	260016.25#	
27	Main ditch of Alastvere	58°39′17.73″	26°0′6.35″	
28	Tõrve. Outlet to the Pedja River	58°35′42.21″	26°21′44.46″	
29	Võisiku station No. 61	58°45′35″	25°53′21.98″	
30	Jõgeva Plant Breeding	58°45′48″	26°24′0.98″	
21	Station	50012/50 00"	05041440.00"	
31	Jänijõgi station No. 64	59°13′59.99″	25°41′48.02″	
32	Rannu	58°15′13.06″	26°14′0.27″	
33	Rõhu	58°21′14.32″	26°30′32.5″	

^a The numbers correspond to Fig. 1.

b Monitoring station numbers of the Estonian National Environmental Monitoring Programme (NEMP).



Ott Roots was born in 1946. He graduated from Tallinn Technological University as a chemist-technologist in 1969. In 1983 he received his PhD degree (Candidate of Chemical Sciences, speciality: Organic Chemistry and Hydrobiology). Dr Roots's research interests include the distribution

of toxic persistent organic pollutants in the ecosystems, food safety, working out and improvement of Estonian Environmental Monitoring Programme, materials corrosion, etc. He has participated in various international scientific programmes such as 1993-2015 UN/ECE International Co-operation Programme on Effects on Materials, including Historic and Cultural Monuments (Estonian Task Force), 2002-2003 UNEP Regionally Based Assessment of Persistent Toxic Substances (European regional team member/expert), 2002–2006 EC FP6 (FOOD-CT-2004-513988) SAFEFOODNET, 2006–2015 Monitoring of persistent organic compounds in the air using the passive air sampling technique (MONET EU), 2010-2012 Baltic Action for Reduction of Pollution of the Baltic Sea from Priority Substances (LIFE+07ENV/EE/000122) BaltActHaz project, 2002–2015 Dioxins and other priority hazardous substances in Estonian food, etc. He has been awarded Estonian and international (Soros Foundation, McArthur Foundation) scientific grants. He was a nominee of the Estonian Science Award in 1997 and 2000. From time to time he has delivered special lectures at different universities and EUROACADMY. He has published more than 260 scientific publications (more information: www.etis.ee or Ott Otto Roots Researchgate).



Tiit Lukki was born in 1948. He graduated from the Faculty of Chemistry and Physics, University of Tartu, in 1972 and received his MSc degree from Tallinn Pedagogical University, Estonia, in 1993. His current scientific research projects involve statistical methods and data analysis in science. His study area is Natural Sciences and Sustainability. At

present he is Lecturer of Statistical Methods in Environmental Sciences at Tallinn University School of Natural Sciences and Health.

REFERENCES

- Roots, O. Book Chapter: Part III: Chronologies of world countries and regions. Europe. Estonian Republic. In A General World Environmental Chronology (GWEC Editorial Working Committee and Takahashi, M., eds). Suirensha, Hosei, Japan, 2014, 689–692.
- Roots, O., Zitko, V., Kumar, K. S., Sajwan, K., and Loganathan, B. G. Contamination profiles and possible trends of organohalogen compounds in the Estonian environment and biota. In *Global Contamination Trends of Persistent Organic Chemicals* (Loganathan, B. G. and Lam, P. K. S., eds). CRC Press, 2011, 307– 225
- Roots, O. and Saare, L. Structure and objectives of the Estonian Environmental Monitoring Program. *Environ. Monit. Assess.*, 1996, 40, 289–301.
- Roots, O. and Roose, A. Hazardous substances in the aquatic environment of Estonia. *Chemosphere*, 2013, 93, 196–200.
- Roots, O. Proposal for selection of national priority hazardous substances for Estonian surface water bodies. *Ékologicheskaya khimiya*, 2008, 17, 22–34.
- Marandi, A., Karro, E., and Puura, E. Barium anomaly in the Cambrian–Vendian aquifer system in North Estonia. *Environ. Geol.*, 2004, 47, 132–139.
- Roots, O. PCDDs, PCDFs and DL-PCBs in some selected Estonian and imported food samples. *Fresen. Environ. Bull.*, 2007, 16, 1662–1666.
- Roots, O. Nutrition recommendations for Estonian fishermen (dioxins and dioxin-like polychlorinated biphenyls). *Latvian Journal of Chemistry*, 2012, 51, 316–323.
- Roots, O., Simm, M., Kiviranta, H., and Rantakokko, P.
 Persistent organic pollutants (POPs): food safety
 control in Estonia. In *The Fate of Persistent Organic Pollutants in the Environment* (Mehmetli, E. and
 Koumanova, B., eds). NATO Science for Peace and
 Security Series. Springer, 2008, 173–185.
- Roots, O., Roose, A., Kull, A., Holoubek, I., Cupr, P., and Klanova, J. Distribution pattern of PCBs, HCB and PeCB using passive air and soil sampling in Estonia. *Environ. Sci. Pollut. Res.*, 2010, 17, 740–749.
- 11. Tamm, I. Euroopa Parlamendi ja Nõukogu 6. detsembri 2008 direktiivi 2008/105/EÜ nõuete täitmiseks prioriteetsete ainete inventuur ning seirekorralduse analüüs. Report, 2010 (in Estonian). http://www.envir.ee/ et/ veevaldkonna-uuringud-ja-aruanded (accessed 2015-01-23).
- 12. Loos, R., Gawlik, B. M., Locoro, G., Rimaviciute, E., Contini, S., and Bidoglio, G. EU Wide Monitoring Survey of Polar Persistent Pollutants in European River Waters. Publications Office of the European Union, Luxembourg, LU, 2008. http://publications.jrc.ec.europa.eu/repository/handle/JRC48459 (accessed 2015-02-17).
- Loos, R., Gawlik, B. M., Locoro, G., Rimaviciute, E., Contini, S., and Bidoglio, G. EU-wide survey of polar organic persistent pollutants in European river waters. *Environ. Pollut.*, 2009, 157, 561–568.
- 14. Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013 amending Directives

- 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy. *Official Journal of the European Union*. 24.08.2013, L226/1-L2226/17. http://eur-lex.europa.eu/legal-content/EN/ALL/?uri=CELEX:32013L0039 (accessed 2015-01-02).
- Roots, O. and Nõmmsalu, H. Aruanne veekeskkonnale ohtlike ainete sõeluuringu tulemustest Eestis (Viisimaa, M., ed.). BEF Estonia, Tallinn, 2011 (in Estonian). www.klab.ee/ wp-content/2011/10/soeluuringu_aruanne.pdf (accessed 2016-05-25).
- Roots, O. and Nõmmsalu, H. Report on Hazardous Substances Screening in the Aquatic Environment in Estonia (Viisimaa, M., ed.). BEF, Tallinn, 2011. www.baltacthaz.bef.ee/publications (accessed 2016-05-25).
- Roots, O., Nõmmsalu, H., and Kislenko, K. Veekeskkonnale ohtlike ainete allikate analüüs. Report. BEF, Tallinn, 2011 (in Estonian). www.baltacthaz.bef.ee/ publications (accessed 2016-05-25).
- Dydutyte, Z., Buselyte, J., Stanče, L., Poikane, R., Kadike, S., Nõmmsalu, H., et al. *Investigation of Sources of Hazardous Substances in Lithuania, Latvia and Estonia*. Report. BEF, Tallinn, 2011. http://www.baltacthaz.bef.ee (accessed 2016-05-25).
- Kõrgmaa, V., Laht, M., Paasrand, K., Parts, L., Põllumäe, A., Volkov, E., et al. WP3 Innovative Approaches to Chemical Controls of Hazardous Substances. National Report of Estonia. Estonian Environmental Research Centre, 2011. www.cohiba_project.net/publications (accessed 2015-01-14).
- Erm, A., Voll, M., Buschmann, F., and Roots, O. Profiles of Hg, Cd, Cu, Pb and Zn, PCDDs, PCDFs and dl-PCBs in the bottom boundary layer of some north Estonian coastal areas. Baltic International Symposium (Baltic). IEEE, Tallinn, 2014, 1–12 (978-1-4799-5707-1).
- Guidance Document No. 25, 2010. On Chemical Monitoring of Sediments and Biota under the Water Framework Directive. European Union, 2010 (accessed 2015-03-26).

- Guidance Document No. 32, 2014. Guidance on Biota
 Monitoring (the Implementation of EQS BIOTA) under
 the Water Framework Directive. European Union,
 2014 (accessed 2015-05-26).
- 23. EE 11, 2002 (http://entsyklopeedia.ee/artikkel/eesti j%C3%B5ed) (accessed 2015-02-19).
- 24. Lilja, K., Nordström, K., Remberger, M., Kaj, L., Egelrud, L., Junedahl, E., et al. Screening of Selected Hazardous Substances in the Eastern Baltic Marine Environment. IVL Report B187. Nordic Council of Ministers, 2009.
- Müür, J. Taimekaitsevahendite kasutamine Eestis [Use of pesticides in Estonia]. In *Keskkond 1995* (Meikas, E., ed.). Tallinna Raamatutrükikoda, Tallinn, 1996, 66–68.
- 26. Roots, O. Polychlorinated biphenyls (PCB), polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) in oil shale and fly ash from oil shale-fired power plant in Estonia. *Oil Shale*, 2004, 21, 333–339.
- 27. Schleicher, O., Jensen, A. A., Roots, O., Herrmann, T., and Tordik, A. Dioxin and emissions from a shale oil processing plant in Estonia. *Organohalogen Compounds*, 2004, **66**, 1665–1671.
- Schleicher, O., Roots, O., Jensen, A. A., Herrmann, T., and Tordik, A. Dioxin emission from two oil shale fired power plants in Estonia. *Oil Shale*, 2005, 22, 563–570.
- Roots, O., Aps, R., Kuningas, K., and Talvari, A. Monitoring of oil products and hazardous substances in Estonian surface water bodies. *Proc. Estonian Acad. Sci. Chem.*, 2007, 56, 75–86.
- 30. Suursaar, Ü., Aps, R., Kotta, I., and Roots, O. North-East Estonian coastal sea: recovery from the past anthropogenic pressure and new stressors on the background of natural variability. In *Ecosystems and Sustainable Development VII* (Brebbia, C. A. and Tiezzi, E., eds). WIT Transactions and the Environment, 122. WIT Press, 2009, 331–342.
- Kumar, K., Priya, M., Sajwan, K., Kölli, R., and Roots, O. Residues of persistent organic pollutants in Estonian soils (1964–2006). *Estonian J. Earth Sci.*, 2009, 58, 109–123.

Vee saastumise probleemid Eestis (ülevaade)

Ott Roots ja Tiit Lukki

Ülevaateartiklis on keskendutud Eestis läbiviidud veekeskkonnale ohtlike ainete alasele ja Keskkonnaministeeriumi tellitud ning rahvusvaheliste uuringute tulemusel saadud analüüsile. On antud ülevaade, milliseid veekeskkonnale ohtlikke aineid või ainerühmi on eelmainitud uuringute raames analüüsitud ja millistest proovivõtukohtadest ning -maatriksitest proove võeti. Artiklis on ka soovitusi proovimaatriksite valikul, lähtudes kolmest valiku põhikriteeriumist: ainete või ainerühmade lahustuvusest vees, nende võimest bioakumuleeruda ja püsivusest meid ümbritsevas keskkonnas. Edaspidise ohtlike ainete seire käigus tuleks rohkem tähelepanu suunata Kirde-Eesti põlevkivi kaevandamise ja ümbertöötlemise ning sadamate ja laevaremonditehaste aladele. Seiratavate ohtlike ainete nimekiri pole kunagi lõplik, kuna probleemide tekkel tuleb uusi ohtlikke aineid või ainerühmi seireprogrammi lisada, probleemide puudumisel aga sellest kõrvaldada. Kogutud teave võimaldab arendada seireprogramme, tõhustada ohtlike ainete heitealast kontrolli ja olla Eesti aruannete koostamisel ohtlike ainete kohta abiks Euroopa Komisjonile ning Helsinki Komisjonile.