Report
Investigation of Sources of Hazardous Substances in Lithuania, Latvia and Estonia

Completed within the project LIFE07 ENV/EE/000122
"Baltic Actions for Reduction of Pollution of the Baltic Sea from Priority Hazardous Substances"

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Funded by:

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Prepared by:

Zita Dudutytė, Baltic Environmental Forum Lithuania
Justė Buzelytė, Baltic Environmental Forum Lithuania
Laura Stančė, Baltic Environmental Forum Lithuania
Rita Poikāne, Latvian Institute of Aquatic Ecology
Solveiga Kadiķe, Latvian Institute of Aquatic Ecology
Heli Nõmmsalu, Baltic Environmental Forum Estonia
Kitty Kislenko, Baltic Environmental Forum Estonia
Ott Roots, Estonian Environmental Research Centre

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Liimi 1
10621 Tallinn, Estonia
http://www.bef.ee

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Introduction

One of the key issues within the project "Baltic Actions for the Reduction of Pollution of the Baltic Sea from Priority Hazardous Substances" (BaltActHaz) was to investigate on the occurrence of selected WFD, HELCOM priority substances and nationally important pollutants in the environment as well as track them down to the sources in order to work further on the reduction of discharges or phase out of hazardous substances from the sources.

The results of the screening of hazardous substances in the environment and WWTPs in Estonia and Latvia are laid down in the country specific reports and are available on the **project website** www.baltacthaz.bef.ee. The screening of hazardous substances in Lithuanian environment and WWTPs was performed in 2006 within another project "Screening of Hazardous Substances in the aquatic environment of Lithuania", funded by Finnish Ministry of Environment. Those results are available www.bef.lt or http://gamta.lt/cms/index?rubricId=3286b5eb-7ee8-413c-8f84-fc2d613de35a. These screening data were used as background information for further planning and investigation of sources of hazardous substances in the countries.

This report presents the results on the investigation of potential sources of hazardous substances. Investigation of the sources within the project was performed in different ways: identification of used hazardous substances in the pilot companies, sampling and analysis of industrial wastewater, sewage water, run-off water and other potential sources of hazardous substances as well as screening of the contracts at WWTPs.

This report focuses on the analytical results performed for the identification of sources of hazardous substances and documents the experiences and results of three countries: Estonia, Latvia and Lithuania. Furthermore, based on the findings, it contains recommendations and advice for the priority hazardous substances to be checked at first place by controlling authorities/WWTPs/industry itself in effluents of different industry branches or other sectors as well as recommendations for further tools for the identification of sources of hazardous substances.

The report is mainly targeted to the authorities that are responsible for the implementation and enforcement of policies for the control of hazardous substances, especially permitting authorities issuing permits to the commercial/industrial entities and monitoring the industrial effluents as well as those setting the reduction measures for the hazardous substances. It can also well function as a tool for WWTPs to identify the potential sources of hazardous substances discharged to the combined sewage system.

1. Country specific experiences

1.1. Lithuania

1.1.1. Selection of the hazardous substances and sampling sites

• Investigated hazardous substances

The substances for deeper investigation on their sources were chosen based on the results from screening of hazardous substances in Lithuanian environment and WWTPs in 2006. It was aimed to track the sources of the most widely spread or polluting substances (e.g. concentrations in the environment exceeded EQS or in treated wastewater from WWTPs exceeded ELV set by legislation or which were found in high concentrations in sediments of water bodies or sludge in WWTPs). Furthermore, survey covered also few additional substances where information is principally not available at all (perfluorochemicals) or that information that is present is very limited (paraffins).

Originally investigation of sources focused of 9 substances/groups of substances:

1. Nonylphenols and their ethoxylates (NP/NPE)
2. Octylphenols and their ethoxylates (OP/OPE)
3. Organotins (OT: tributyltin – TBT, triphenyltin – TPhT, dibutyltin – DBT)
4. Polybrominated diphenylethers (PBDE: pentaBDE & decaBDE)
5. Perfluorinated chemicals (PFC: perfluoroctane sulfonate – PFOS, perfluorooctanoic acid – PFOA)
6. Phtalates (di(2-ethylheksyl)phtalate – DEHP)
7. Hexabromcyclododecane (HBCDD)
8. Chloralkanes (short chain chlorinated parafins – SCCP, medium chain chlorinated parafins – MCCP)
9. Trichloromethane (chloroform – TCHM)

Analysis was carried out in ALS Scandinavia AB laboratory (Maskinvägen 2, Stockholm, Sweden). As this laboratory proposed to investigate larger range of substances within the selected substances group for the same price, the scope of the survey was extended. The whole list of analysed substances, analytical methods applied, LOQ and MU could be found in the Table 1.1.1.1.

Table 1.1.1.1. The list of hazardous substances analysed and the analytical methods applied (including LOQ and MU)

Parameter	Water & wastewater				Sludge & sediments			
	Method	LOQ	Unit	MU [%]	Method	LOQ	Unit	MU [%]
Organotin compounds								
Monobutyltin-cation	DIN EN ISO 17353 (F13)	0.001	µg/L	15	ISO 23161	1	µg/kg DW	23
Dibutyltin-cation		0.001	µg/L			1	µg/kg DW	
Tributyltin-cation		0.001	µg/L			1	µg/kg DW	
Tetrabutyltin-cation		0.001	µg/L			1	µg/kg DW	
Monooctyltin-cation		0.001	µg/L			1	µg/kg DW	
Dioctyltin-cation		0.001	µg/L			1	µg/kg DW	
Tricyclohexyltin-cation		0.001	µg/L			1	µg/kg DW	
Monophenyltin-cation		0.001	µg/L			1	µg/kg DW	
Diphenyltin-cation		0.001	µg/L			1	µg/kg DW	
Triphenyltin-cation		0.001	µg/L			1	µg/kg DW	

Parameter	Water & wastewater				Sludge & sediments			
	Method	LOQ	Unit	MU [%]	Method	LOQ	Unit	MU [%]
Polobrominated diphenylethers (PBDE)								
PBDE 17	DIN EN ISO 22032 (GC-MSD)	0.0001	µg/L	15	DIN EN ISO 22032 (GC-MSD)	0.1	µg/kg DW	20
PBDE 28		0.0001	µg/L			0.1	µg/kg DW	
PBDE 47		0.0001	µg/L			0.1	µg/kg DW	
PBDE 66		0.0001	µg/L			0.1	µg/kg DW	
PBDE 71		0.0001	µg/L			0.1	µg/kg DW	
PBDE 85		0.0001	µg/L			0.1	µg/kg DW	
PBDE 99		0.0001	µg/L			0.1	µg/kg DW	
PBDE 100		0.0001	µg/L			0.1	µg/kg DW	
PBDE 138		0.0005	µg/L			0.1	µg/kg DW	
PBDE 153		0.0002	µg/L			0.1	µg/kg DW	
PBDE 154		0.0002	µg/L			0.1	µg/kg DW	
PBDE 183		0.001	µg/L			0.2	µg/kg DW	
PBDE 190		0.001	µg/L			0.2	µg/kg DW	
PBDE 196		0.001	µg/L			0.2	µg/kg DW	
PBDE 197		0.001	µg/L			0.2	µg/kg DW	
PBDE 203		0.001	µg/L			0.2	µg/kg DW	
NBDE		0.005	µg/L			1	µg/kg DW	
PBDE 209		0.005	µg/L			1	µg/kg DW	
HBCDD		0.01	µg/L			1	µg/kg DW	
Chlorinated paraffins								
Chlorinated paraffins (C10-C13)	SOP PI-MA M 3-80 (GC-MSD)	0,2	µg/L	40	SOP PI-MA M 3-80 (GC-MSD	100	µg/kg DW	40
Chlorinated paraffins (C14-C17)		0,2	µg/L			100	µg/kg DW	
Phtalates								
Dimethylphthalate	DIN EN ISO 18856 (GC-MSD)	1	µg/L	16	SOP PI-MA M 3-63 (GC-MSD)	50	µg/kg DW	17
Diethylphthalate		1	µg/L			50	µg/kg DW	
Di-n-Propylphthalate		1	µg/L			50	µg/kg DW	
Di-iso-Butylphthalate		1	µg/L			50	µg/kg DW	
Di-n-Butylphthalate		1	µg/L			50	µg/kg DW	
Di-Pentylphthalate		1	µg/L			50	µg/kg DW	
Butylbenzylphthalate		1	µg/L			50	µg/kg DW	
Di-(2-Ethylhexyl) phthalate		1	µg/L			50	µg/kg DW	
Di-Cyclohexylphthalate		1	µg/L			50	µg/kg DW	
Di-n-Octylphthalate		1	µg/L			50	µg/kg DW	
Octyl-/Nonylphenols + ethoxylates								
4-tert-Octylphenol	DIN EN ISO 18857 (GC-MSD)	0.01	µg/L	15	SOP PI-MA M 3-56 (GC-MSD)		µg/kg DW	20
4-n-Nonylphenol		0.01	µg/L				µg/kg DW	
iso-Nonylphenol (tech.)		0.1	µg/L				µg/kg DW	
OP1EO		0.01	µg/L				µg/kg DW	
OP2EO		0.01	µg/L				µg/kg DW	
OP3EO		0.01	µg/L				µg/kg DW	
NP1EO		0.1	µg/L				µg/kg DW	
NP2EO		0.1	µg/L				µg/kg DW	
NP3EO		0.1	µg/L				µg/kg DW	

Parameter	Water & wastewater				Sludge & sediments			
	Method	LOQ	Unit	MU [%]	Method	LOQ	Unit	MU [%]
Perfluorinated compounds								
PFUnDA	DIN 38407-42, draft (LC-MS/MS)	0,01	µg/L	3 - 14	SOP HM-MA M U 2-24 (LC-MS/MS)	10	µg/kg DW	2 - 20
PFHpA		0,01	µg/L			10	µg/kg DW	
PFOA		0,01	µg/L			10	µg/kg DW	
PFNA		0,01	µg/L			10	µg/kg DW	
PFDA		0,01	µg/L			10	µg/kg DW	
PFOSA		0,01	µg/L			10	µg/kg DW	
PFDoDA		0,01	µg/L			10	µg/kg DW	
PFBS		0,01	µg/L			10	µg/kg DW	
PFHxS		0,01	µg/L			10	µg/kg DW	
PFOS		0,01	µg/L			10	µg/kg DW	
PFDS		0,01	µg/L			10	µg/kg DW	
Trichloromethane								
Trichloromethane	DIN EN ISO 15680 (F19)	0.1	µg/L	15				

• Sampling sites

The survey in Lithuania has covered different types of sites, which could potentially emit the hazardous substances:

- wastewater from different industrial companies (discharged to combined sewage system or directly to the environment);
- wastewater from other commercial facilities (e.g. laundries, supermarkets);
- run-off from specific areas (e.g. recycling facilities, industrial areas, car repairing facilities);
- filtrate from landfills (not treated at site but discharged to combined sewage system);
- sewage water from household (residential areas).

Additionally current survey in Lithuania has covered some WWTPs and 3 transboundary rivers (Neris near Belarusian border, Nemunas near Belarusian border and Nemunas below Sovetsk) to update information gathered in 2006 and to support further investigation of sources of hazardous substances.

The preliminary list of potential sources of hazardous substances was developed based on the information and experience from other countries or projects and considering relevance to the country, see Table 1.1.1.2. Due to the limited available financial resources it was decided to focus only on the most relevant substances, which can potentially occur in the effluents of specific industry branch, i.e. the less probable substances were excluded from the list of that industry branch.

Table 1.1.1.2. List of industry branches and other objects, which potentially emit selected hazardous substances

Industry branch/ Other objects	Hazardous substances that could be emitted from the object
Pharmaceutical industry (production of medicines)	NP, OP/OPE, chloroform
Household and industrial cleaning chemicals: production and use (especially meet, milk and fish industry)	NP/NPE, OP/OPE, PFOS (alkaline cleaners, waxes, polishing chemicals)
Wood pulp and paper production	NP/NPE, TBT, SCCP
Paint production	NP/NPE (water based paint), DEHP (paint, printing dyes)
Metal processing industry and galvanic	OP/OPE, NP/NPE, SCCP, MCCP, TBT, TPhT, PFOS
Electronic industry	NPE, chloroform, OP, PBDE
Photolaboratories	NPE, OP/OPE, PFOS
Printing houses (offset printing)	NPE, OP/OPE, PFOS,
Production of cement/ concrete/ asphalt	NPE, TBT (production of cement)
Textile industry having finishing processes (dyeing, printing, impregnation, other finishing)	NP/NPE, TBT (sunblind, tents, impregnated textile), TPhT (preservative), OP/OPE, PFOS (impregnation agent), decaBDE (flame retardant), HBCDD, SCCP, MCCP
Leather industry	NP/NPE, OP/OPE, PFOS (impregnation agent), SCCP, MCCP

Industry branch/ Other objects	Hazardous substances that could be emitted from the object
Production of panels/boards (plywood, laminated boards, wood fiber boards etc.)	NP/NPE
Plastic industry (PVC) and production of plastic products (floor, wallpapers, cables, wires, roofing materials, finishing panels, pipes etc.)	DBT, DEHP, PFOA (fluoropolymers), PBDE, SCCP, MCCP, NP, OP
Rubber industry	TPhT, DEHP, DBP, PBDE, SCCP, MCCP, OP
Shipyards	TBT (docks, rainwater), NP/NPE, SCCP/MCCP, OP/OPE
Production of building materials (sealants, foam...)	DEHP, pBDE/dBDE
Production of phenolic and formaldehyde resins	OP
Oil refinery industry	OP
Tyres production	OP
Production of semiconductors	PFOS, chloroform
Production of impregnated paper and packaging (fat resistant)	PFOS
PUR production	decaBDE,
Laundries	pBDE/dBDE, HBCDD
Paper recycling	MCCP
PVC/polystyrene/rubber production	MCCP, HBCDD
Car washing	DEHP, PBDE
Chemical industry	NP/NPE, OP/OPE, DEHP, DBP, chloroform, SCCP, MCCP
Leakage from landfills	NP/NPE, TBT, OP/OPE, PFOS, pBDE/dBDE, HBCDD
Surface run-off from waste recycling areas	NP/NPE, TBT, OP/OPE, PFOS, pBDE/dBDE, HBCDD
Surface run-off from industrial areas	NP/NPE, TBT, OP/OPE, PFOS, pBDE/dBDE, HBCDD
Surface run-off from car repairing yards	NP/NPE
Car shredding facilities – surface run-off	DEHP, pBDE/dBDE
Household effluents	NP/NPE, TBT, OP/OPE, PFOS, pBDE/dBDE, HBCDD
Surface run-off from electronics recycling areas	pBDE/dBDE, DEHP

The concrete sampling sites were selected in cooperation with Regional Environmental Protection Departments based on several criteria:

- considering the preliminary list on hazardous substances potentially occurring in specific industry branch or other effluent sources, see Table 1.1.1.2;
- if possible selecting several companies from specific branch/sector to get more representative results;
- including both large (IPPC) companies and SMEs;
- distributing sites all over the Lithuania;
- considering possibilities to take sample at site.

The sampling was performed in two rounds: one in March and second one in June after the winter is gone to be able to sample surface run-off (stormwater), surface waters and also some industrial facilities, which are operating seasonally (e.g. shipyard).

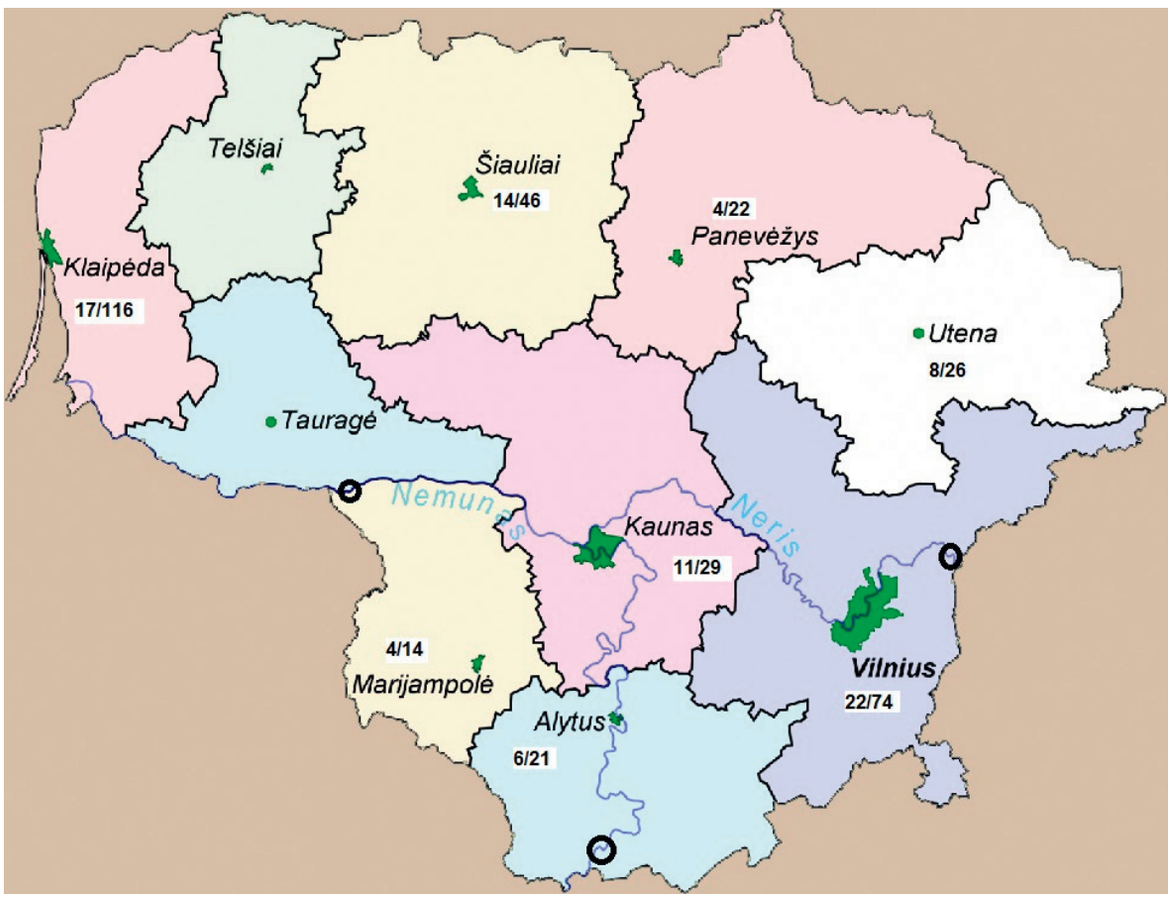
During first sampling round in total **77 sites were sampled** and for the second round **9 sites were sampled**. The list of the sites, including the matrix and substances investigated are given in the Table 1.1.1.3. The distribution of sites over the regions of Lithuania is presented in Picture 1.1.1.1.

The range of substances investigated in different sectors was dependant also on the laboratory's ability to analyse given substances in groups by the same method. Due to that reason for example PBDEs, Chloroalkanes and HBCDD were analysed in all samples where at least one of those substances were relevant.

Table 1.1.1.3. List of the sites and hazardous substances investigated in Lithuania

Industry branch/ Other objects	Hazardous substances investigated	Number of companies investigated	Matrix	Sampling time
Pharmaceutical industry (production of medicines)	OT, APEs, chloroform	4	WW	March
Household and industrial cleaning chemicals: production and use (especially meet, milk and fish industry)	APEs	4+9	WW	March
Wood pulp and paper production	APEs, OT, PBDE/SCCP/MCCP/HBCDD	3	WW	March
Paint production	APEs, Phthalates	1	WW	March
Metal processing industry and galvanics	APEs, PBDE/SCCP/MCCP/HBCDD, PFC, Phthalates, OT	4+4	WW	March
Electronic industry	Chloroform, PBDE/SCCP/MCCP/HBCDD, APEs	1	WW	March
Printing houses (offset printing)	APEs, PFC, PBDE/SCCP/MCCP/HBCDD	3	WW	March
Production of cement/ concrete/ asphalt	OT, APEs	2	WW	March
Textile industry having finishing processes (dyeing, printing, impregnation, other finishing)	OT, APEs, PFC, PBDE/SCCP/MCCP/HBCDD	5	WW	March
Leather industry	OT, APEs, PFC, PBDE/SCCP/MCCP/HBCDD	4	WW	March
Production of panels/boards (plywood, laminated boards, wood fiber boards etc.)	OT, APEs	2	WW	March
Plastic industry (PVC) and production of plastic products (floor, wallpapers, cables, wires, roofing materials, finishing panels, pipes etc.)	OT, APEs, PFC, Phthalates, PBDE/SCCP/MCCP/HBCDD	4	WW	March
Rubber industry	OT, APEs, Phthalates, PBDE/SCCP/MCCP/HBCDD	1	WW	March
Shipyards	OT, APEs, Phthalates, PBDE/SCCP/MCCP/HBCDD	1	WW	June
Production of building materials (sealants, foam...)	PBDE/SCCP/MCCP/HBCDD, Phthalates	1	WW	March
Oil refinery industry	OP	1	WW	March
Production of semiconductors	PFC, chloroform	1	WW	March
Laundries	PBDE/SCCP/MCCP/HBCDD, APEs, PFC	4	WW	March
Car washing	PBDE/SCCP/MCCP/HBCDD, Phthalates, APEs	2	WW	March
Chemical industry	PBDE/SCCP/MCCP/HBCDD, Phthalates, APEs	2	WW	March
Regeneration of used oils	PBDE/SCCP/MCCP/HBCDD, Phthalates, APEs	1	WW	March
Leakage from landfills	OT, PBDE/SCCP/MCCP/HBCDD, Phthalates, APEs, PFC	4	WW	March
Surface run-off from industrial areas	OT, PBDE/SCCP/MCCP/HBCDD, Phthalates, APEs, PFC	1	WW	June
Car shredding facilities – surface run-off	PBDE/SCCP/MCCP/HBCDD, Phthalates, PFC	1	WW	June
Supermarkets	OT, PBDE/SCCP/MCCP/HBCDD, Phthalates, APEs, PFC	2	WW	March
Household effluents	OT, PBDE/SCCP/MCCP/HBCDD, Phthalates, APEs, PFC	4	WW	March/June
WWTPs	OT, PBDE/SCCP/MCCP/HBCDD, Phthalates, APEs, PFC	7	WW + sludge	March/June
Transboundary rivers	OT, PBDE/SCCP/MCCP/HBCDD, Phthalates, APEs, PFC	3	SW	June

Picture 1.1.1.1. Distribution of sites investigated and samples taken in different regions of Lithuania



17/116 – number of sites investigated/samples taken
o – sites from transboundary rivers, where the samples were taken

1.1.2. Quality assurance issues

• Sampling and handling of the samples

Sampling within the survey was carried out in four phases:

1) 3 sampling phases in March 2011, in total 77 sites sampled (253 wastewater samples, 5 wastewater sludge samples);

2) 4th sampling phase in June 2011, in total 9 sites sampled (68 wastewater samples, 15 surface water samples, 10 wastewater sludge samples).

Sampling was carried out by the trained specialists of the Regional environmental protection departments (REPD) and Environmental Protection Agency and WWTPs. Sampling was performed following ISO/EN standards as given in Table 1.1.2.1.

Table 1.1.2.1. Standards and requirements for sampling procedures

Matrix	Standard reference	General remarks
Waste water	ISO 5667-10	• Samples are taken where wastewater is well mixed • Bottle is rinsed with wastewater before • Bottles are filled up to top • Samples for phthalates cannot be sampled with plastic equipment • Chloroform is sampled according specific instruction (2 HS bottles: one filled up to the top, second – 50%)
Waste water sludge	LST EN ISO 5667-13	• Dewatered sludge has to be sampled • If sludge is still quite diluted, some jars to be taken from one site (min 50 g of dry weight is required for analysis) • Jars are filled up to the top
Surface water	LST EN ISO 5667-6	• Samples are taken against the current • Bottle is rinsed with water before • Samples for phthalates cannot be sampled with plastic equipment
Run-off water (stormwater)		• There should be at least one day of no greater than trace precipitation before sampling. However, it is recommended to sample after longer dry period. • If possible, a time-proportionate sample is recommendable (it is one sample made up of a number of small samples (subsamples) of equal volume collected at regular time intervals combined into a single large sample). Such samples have to be started within the first 30 minutes after discharge begins and be taken over a two-hour period. • A single sample "grabbed" by filling up a container, either by hand or with the container attached to a pole. It is recommended that samples are to be collected within the first hour after stormwater discharge begins. • The sampling should take place where the flow is highly/moderate turbulent. This ensures a complete mixing of the water. Sampling in still water should be avoided. • It is recommended that the storm have a rainfall intensity of at least 3 mm of rain in a 24-hour period. • It is desirable in addition to record the following information for each storm event sampled: - number of dry days before the day the sample was collected - duration of the storm in hours and mm of rain - time from the beginning of rain until sample is taken

All bottles for the samples were delivered prepared by the subcontracted laboratory and did not require further preparation. The bottles and jars were delivered in special transport boxes, functioning as thermo boxes and included also cooling elements. No special pre-treatment or preservation of samples was required by laboratory, except storing the samples in dark and cold.

Special care has been taken during sampling to avoid contamination of the samples for analysis of:

- phthalates: any contact with plastic materials;
- perfluorinated compounds: bottles without PTFE sealing/gaskets;
- chloroform: headspace vials used.

Also additional agreements were made with the specialists taken samples:

- priority was given to automatic 24-hours sampling whenever possible;
- as for automatic sampling usually plastic equipment is used, the sample of phthalates was taken separately manually;
- in case of momentary sample the working regime of entity had to be considered (at least main production processes had to take place, samples were not taken if production processes are stopped and only "household" effluents are discharged);
- unknown sites were discussed or sampled together with WWTPs specialists;
- specific circumstances that may affect sampling results have to be recorded.

- **Analysis of the samples**

All analytical methods used for the investigation are accredited according to ISO/IEC 17025. In some cases (sludge) accredited in-house methods were used. For more detailed description of methods applied, limits of quantifications (LOQ) and MU, see Table 1.1.1.1.

When evaluating proposals of the laboratories the level of LOQ was evaluated. The minimum required LOQ was based on the requirements of 2009/90/EC directive on EQS as well as ELV values set in the national Regulation on Waste Water Management (Order adopted by Ministry of Environment of the Republic of Lithuania on 17.05.2006, No. of Order 21-236) and its amendments for discharges of hazardous substances to the sewage system or the environment. According to regulation for evaluating the samples from the environment LOQ that is applied in laboratory must be at least 1/3 of EQS. The only parameter, which does not meet minimum requirements for the LOQ for evaluating surface water is TBT (see Table 1.1.2.2 for details). However none of the laboratory provided required minimum LOQ for this substance.

Table 1.1.2.2. ELV, EQS limits and LOQ proposed by laboratory

Substances	CAS number	EQS (µg/l)	ELV for wastewater discharged into environment based on Lithuanian wastewater regulation (µg/l)	ELV for wastewater discharged into sewage system based on Lithuanian wastewater regulation (µg/l)	LOQ proposed by laboratory (µg/l)
4-nonylphenol	104-40-5	0.3	20	400	0.01
4-tert-octylphenol	140-66-9	0.01	20	400	0.01
TBT	36643-28-4	0.0002	0.02	0,4	0.001
DEHP	117-81-7	1.3	2	40	1
Polybrominated dipheny-lethers (pentaBDE)	32534-81-9	0.0002	-	-	0.0001
SCCP	85535-84-8	0.4	2	40	0.2
MCCP	85535-85-9	-	-	-	0.2
Perfluorooctanoic Acid (PFOA)	335-67-1	-	-	-	0.01
Perfluorooctane sulpho-nate (PFOS)	1763-23-1	-	-	-	0.01
Trichloromethane (chloroform)	67-66-3	2.5	200	1000	0.1

1.1.3. Results of analysis

- **Basis for the evaluation of results**

While making tests in laboratory 1/3 of answers did not correspond to the LOQ that was proposed by laboratory, this happened because of matrix interference. Anyway these results are showing the main tendencies.

The results of waste water were compared with ELV discharge limit into the environment if the wastewater after treatment is released into surface waters and with ELV discharge limit into sewage system if the wastewater is not treated at site and is being released into municipal sewage.

The results of surface water were compared to EQS.

The results of sludge were for indicating if there is any of tested substance and in what amount as there are no set official limits for these hazardous substances in sludge.

WASTEWATER

Chlorinated paraffins

MCCP (C14-C17) found in range of 0,32 – 170 µg/L in samples from metal processing industry and galvanic, wood and pulp industry, printing houses, leather industry, rubber industry, shipyards, laundries, car washing effluents. It was also detected in many samples from supermarkets and household effluents.

SCCP (C10-C13) found not so often as MCCP (C14-C17). But ELV limits were exceeded in laundries (53 µg/L) and in metal processing industry and galvanic (3,1 µg/L). SCCP (C10-C13) found widely in samples of metal processing industry and galvanic, wood and pulp industry, laundries and supermarkets.

Octyl-/nonylphenols + ethoxylates

4-tert-Octylphenol is widely found in all industry branches, range is 0,011 – 14,5 µg/L. Also found in 70% of WWTP samples after treatment, but ELV limits are not exceeded. Nonylphenol is found in 45% of WWTP samples after treatment.

4-tert-Octylphenol, nonylphenols and their ethoxylates are found in surface run-off from industrial areas.

4-Nonylphenol in one case detected concentration was 1100 µg/L, in other cases range is 0,14 – 40 µg/L.

Octyl-, nonylphenols are found in samples of pharmaceutical industry, household and industrial cleaning chemicals industry, wood pulp and paper production industry, paint production industry, metal processing industry and galvanic, printing houses, production of cement/concrete/asphalt, textile industry, leather industry, plastic industry, rubber industry, laundries, car washing, regeneration of used oil, leakage of landfills, surface run-off from industrial areas, not so widely detected in samples of household effluents.

Mainly detected octylphenol-1-ethoxylate (range 0,1-130 µg/L) and nonylphenol-1-ethoxylate (0,1- 230 µg/L) in household and industrial cleaning chemicals industry, wood pulp and paper production industry, paint production industry, metal processing industry and galvanic, printing houses, textile industry, leather industry, plastic industry, rubber industry, laundries, car washing, regeneration of used oil, leakage of landfills, small quantities in household effluents.

Octylphenol-2-ethoxylate (0,02 – 44 µg/L), octylphenol-3-ethoxylate (0,13 – 120 µg/L), nonylphenol-2-ethoxylate (0,142 – 18,8 µg/L), nonylphenol-3-ethoxylate (0,65 – 94 µg/L) were less often found, usually in same samples as octylphenol-1-ethoxylate and nonylphenol-1-ethoxylate.

Organotin compounds

In samples from all industry branches is found monobutyltin and dibutyltin. In samples from WWTP was found monobutyltin. ELV limits of tributyltin was exceeded in one site, in concentration of 14 µg/L.

Mono- and dibutyltin are found in range 0,0013 – 0,78 µg/L (0,0013 – 4,5 µg/L) in samples of pharmaceutical industry, wood pulp and paper production industry, metal processing industry and galvanic, textile industry, leather industry, rubber industry, shipyards, leakage of landfills, supermarkets, household effluents, surface run-off from industrial areas, car shredding facilities.

Only monobutyltin was found in samples of production of cement/concrete/asphalt, production of panels, plastic industry.

Mono- an dioctyltin was found in range 0,0014 – 0,32 µg/L (0,0014 – 0,13 µg/L) in samples of metal processing industry and galvanic, textile industry, leather industry, production of panels, shipyards, leackage of landfills, supermarkets, household effluents.

Tributyltin (except values in one site exceeding ELV limits) was found very rarely in range 0,0022 – 0,0037 µg/L in samples of leather industry, production of panels, shipyards and leakage from landfills.

Perfluorinated compounds

Perfluorinated compounds were found in some samples and in small amounts (0,012 – 0,42 µg/L) in leather, plastic industry, production of semiconductors and laundries, car shredding facilities surface run off. In most samples from leakage from surface run off were found PFOS, PFHpA, PFOA, PFNA, PFDA, PFBS, PFHxS.

Phthalates

Di(2-ethylhexyl)phthalate (DEHP) in 30% of samples exceeds ELV limits in range 8-71 µg/L. Big concentrations of this substance was found in leakages from landfills, paint production industry, metal processing industry and galvanic, car washing effluents, oil regeneration industry and in supermarkets and household effluents.

This substance in smaller amounts was found in some samples from shipyards, production of building materials.

Dietylphthalate (DEP) was found in amounts 1,3 – 26 µg/L in some samples from car washing facilities, leakage from landfills, supermarkets and household effluents.

Di-iso-butylphthalate and Di-n-butylphthalate found in smaller amounts and in less number of samples in range of 4-68 µg/L (1,8-4 µg/L) in samples from car washing facilities, leakage from landfills, regeneration of used oil and supermarkets.

Polybrominated diphenylethers

Mainly found brominated diphenylethers were PBDE47 (range 0,00057 – 0,0086 µg/L), PBDE99 (range 0,00012 – 0,054 µg/L) in samples of wood pulp and paper industry, shipyards, leakages from landfills, leather industry, household effluents

In plastic industry found nearly all tested polybrominated substances.

PBDE99 found in samples of printing houses.

In samples of production of building materials and supermarkets found HBCDD (range 0,14 – 0,76 µg/L).

In car shredding facilities found PBDE47, PBDE99, PBDE197, in surface run off from industrial areas PBDE47, PBDE99, PBDE100, PBDE209.

Trichloromethane

Trichloromethane exceeded ELV limits in production of semiconductors, also was detected in one sample from pharmaceutical industry.

SLUDGE

Hazardous substances in sludge were tested in 5 sites in waste water treatment plants and in shipyards. Huge amounts of organotin substances were found. Monobutyltin 49-260 µg/kg, dibutyltin 35-1600 µg/kg, tributyltin 2,9 – 5100 µg/kg, monooctyltin 9,7 – 53 µg/kg, dioctyltin 7,2 – 34 µg/kg.

Phenols are also detected nearly in all samples of sludge – 4-tert-octylphenol 29-1300 µg/kg, 4-nonylphenol 410-3200 µg/kg, octylphenol ethoxylates detected in WWTP samples in range 200-300 µg/kg, nonylphenol ethoxylates also found in WWTP but in higher amount 1300 – 4500 µg/kg.

From polybrominated diphenylethers were found PBDE47 (5,2-13 µg/kg), PBDE99 (7,3-15 µg/kg), PBDE209 (77-2900 µg/kg).

MCCP are detected in all samples in range of 2100 – 69000 µg/kg.

Di-n-butylphthalate was detected in range of 510 – 3300 µg/kg, Di-(2-ethylhexyl)-phthalate in range of 4100 -44000 µg/kg found in all samples.

In samples of shipyards also Di-cyclohexylphthalate was detected.

SURFACE WATERS

During this screening round for analysis only few points of surface waters were selected. In Neris river near the border of Belarus, in Nemunas river near the border of Belarus and in Nemunas river below Sovets there were not detected any tested chemical substances above LOQ concentration. As in earlier screening exercises that were made during other projects such substances were found very widely it might be that sites for sampling were selected too far from industrial areas.

1.1.4. Summary of results and recommendations

Table 1.1.4.1. Occurrence and significance of HS for country

Industry branch	Hazardous substances
Metal processing industry and galvanic	MCCP (C14-C17), SCCP (C10-C13), Octylphenol, Nonylphenol and their ethoxylates, Monobutyltin, Dibutyltin, Monooctyltin, Dioctyltin, DEHP
Wood and pulp industry	MCCP (C14-C17), SCCP (C10-C13), Octylphenol, Nonylphenol and their ethoxylates, Monobutyltin, Dibutyltin
Printing houses	MCCP (C14-C17), Octylphenol, Nonylphenol and their ethoxylates,
Leather industry	MCCP (C14-C17), Octylphenol, Nonylphenol and their ethoxylates, Monobutyltin, Dibutyltin, Monooctyltin, Dioctyltin, Tributyltin, Perfluorinated compounds
Rubber industry	MCCP (C14-C17), Octylphenol, Nonylphenol and their ethoxylates, Monobutyltin, Dibutyltin
Shipyards	MCCP (C14-C17), Monobutyltin, Dibutyltin, Monooctyltin, Dioctyltin, Tributyltin, DEHP
Laundries	MCCP (C14-C17), SCCP (C10-C13), Octylphenol, Nonylphenol and their ethoxylates, Perfluorinated compounds
Household effluents	MCCP (C14-C17), Octylphenol, Nonylphenol and their ethoxylates, Monobutyltin, Dibutyltin, Monooctyltin, Dioctyltin, DEHP
Car washing effluents	MCCP (C14-C17), Octylphenol, Nonylphenol and their ethoxylates, DEHP, DEP, Di-iso-butylphthalate, Di-n-butylphthalate
Supermarkets	MCCP (C14-C17), SCCP (C10-C13), DEHP, DEP, Di-iso-butylphthalate, Di-n-butylphthalate
WWTP	Octylphenol, Nonylphenol, Monobutyltin
Surface run-off from industrial areas	Octylphenol, Nonylphenol and their ethoxylates, Monobutyltin, Dibutyltin
Pharmaceutical industry	Octylphenol, Nonylphenol, Monobutyltin, Dibutyltin
Household and industrial cleaning chemicals	Octylphenol, Nonylphenol and their ethoxylates,
Production of cement/concrete/asphalt	Octylphenol, Nonylphenol, Monobutyltin,
Textile industry	Octylphenol, Nonylphenol and their ethoxylates, Monobutyltin, Dibutyltin, Monooctyltin, Dioctyltin
Plastic industry	Octylphenol, Nonylphenol and their ethoxylates, Monobutyltin, Perfluorinated compounds
Regeneration of used oil	Octylphenol, Nonylphenol and their ethoxylates, DEHP, Di-n-butylphthalate
Leakage from landfills	Octylphenol, Nonylphenol and their ethoxylates, Monobutyltin, Dibutyltin, Monooctyltin, Dioctyltin, Tributyltin, PFOS, PFHpA, PFOA, PFNA, PFDA, PFBS, PFHxS, DEHP, Di-iso-butylphthalate, Di-n-butylphthalate
Production of panels	Monobutyltin, Tributyltin, Monooctyltin, Dioctyltin
Car shredding facilities	Monobutyltin, Dibutyltin, Perfluorinated compounds
Production of semiconductors	Perfluorinated compounds, Trichloromethane
Paint industry	DEHP
Production of building materials	DEHP

Recommendation which HS must be considered by controlling/permitting authorities/WWTPs for specific industry branches/other sectors:

Octylphenol, Nonylphenol and their ethoxylates; MCCP (C14-C17), SCCP (C10-C13); Monobutyltin, Dibutyltin, Tributyltin, Monooctyltin, Dioctyltin; DEHP, DEP.

CONCLUSIONS

- There were found exceeding of ELV limits into environment of tributyltin.
- There were found exceeding of ELV limits into sewage system of short chain chlorinated paraffins and di(2-ethylhexylphtalathe).
- There were about 30% of samples that cannot be evaluated properly because of matrix interference of the sample.
- Higher concentrations of hazardous substances were found in industrial wastewater despite that household effluents contain quite a lot of hazardous substances (especially MCCP (C14-C17), Octylphenol, Nonylphenol and their ethoxylates, Monobutyltin, Dibutyltin, Monooctyltin, Dioctyltin, DEHP) of concern and should be considered as a equivalent source of pollution.
- Most widely Octylphenol, Nonylphenol and their ethoxylates in wastewater from industries, household and WWTPs are found.
- Organotin compounds in high concentrations found in all samples.
- Phenols, PBDE47, PBDE99 and MCCP were found in all samples but not in high concentrations.

1.2. Latvia

According to the findings of screening within first two rounds in June 2010 and February 2011 the stakeholder group together with the representatives of WWTP decided to observe the potential sources of previously selected substances entering WWTP with waste water.

1.2.1. Selection of the hazardous substances and sampling sites

- **Investigated hazardous substances**

The source tracking focused on the substances selected in previous screening rounds in June 2010 and February 2011 from the list of WFD from Annex X and Annex III. The subcontracted laboratory proposed to investigate larger range of substances within the selected substances group for the same price. The total list of pollutants measured within the source tracking included analyses of 43 substances from five groups of substances:

- Alkylphenols – nonylphenols and their ethoxylates as well octylphenols and their ethoxylates.
- Polybrominated diphenylethers (PBDE: PentaBDE, OctaBDE and DecaBDE).
- Chlorinated paraffins (short chain chlorinated paraffins – SCCP, medium chain chlorinated paraffins – MCCP)
- Chloroorganic pesticides.
- Perfluoroctane sulfonate – PFOS.

The whole list of analyzed substances, analytical methods applied, LOQ and MU could be found in the Table 1.2.1.1.

Table 1.2.1.1. The list of hazardous substances analysed and the analytical methods applied (including LOQ and MU)

No.	CAS Nr.	Name of substance/ substance group	Method applied	Units	Water/ waste water		MU (%)
					LOD	LOQ/LOR	
Chloroorganic pesticides							
	634-66-2	1.2.3.4-Tetrachlorobenzene	CZ_SOP_ D06_03_169 CSN EN ISO 6468; US EPA 8081; DIN 38407-2	ug/L		0.010	40
	634-90-2 and 95-94-3	1.2.3.5- & 1.2.4.5-Tetrachlorobenzene		ug/L		0.020	40
	---	Sum of 3 tetrachlorobenzenes		ug/L		0.030	40
	72-55-9	4,4`-DDE		ug/L		0.010	40
	72-54-8	4,4`-DDD		ug/L		0.010	40
	789-02-6	2,4-DDT		ug/L		0.010	40
	50-29-3	4,4`-DDT		ug/L		0.010	40
		Sum of 4 isomers DDT		ug/L		0.040	40
	53-19-0	2,4-DDD		ug/L		0.010	40
	3424-82-6	2,4-DDE		ug/L		0.010	40
		Sum of 6 isomers DDT		ug/L		0.060	40
	15972-60-8	Alachlor		ug/L		0.010	40
	309-00-2	Aldrin		ug/L		0.010	40
	60-57-1	Dieldrin		ug/L		0.010	40
	72-20-8	Endrin		ug/L		0.010	40
	465-73-6	Isodrin		ug/L		0.010	40
	76-44-8	Heptachlor		ug/L		0.010	40
	28044-83-9	Heptachloroepoxide-cis		ug/L		0.010	40
	1024-57-3	Heptachloroepoxide-trans		ug/L		0.010	40

No.	CAS Nr.	Name of substance/ substance group	Method applied	Units	Water/ waste water		MU (%)
					LOD	LOQ/LOR	
	118-74-1	Hexachlorobenzene (HCB)	Z_SOP_D06_03_169 CSN EN ISO 6468; US EPA 8081; DIN 38407-2	ug/L		0.0050	40
	87-68-3	Hexachlorobutadiene		ug/L		0.010	40
	319-84-6	Hexachlorocyclohexane Alpha		ug/L		0.010	40
	319-85-7	Hexachlorocyclohexane Beta		ug/L		0.010	40
	319-86-8	Hexachlorocyclohexane Delta		ug/L		0.010	40
	58-89-9	Hexachlorocyclohexane Gamma		ug/L		0.010	40
	608-73-1	Sum of 4 hexachlorcyclohexanes		ug/L		0.040	40
	67-72-1	Hexachloroethane		ug/L		0.010	40
	72-43-5	Methoxychlor		ug/L		0.010	40
	608-93-5	Pentachlorobenzene		ug/L		0.010	40
	297-78-9	Telodrin		ug/L		0.010	40
	1582-09-8	Trifluralin		ug/L		0.010	40
	115-29-7	alpha-Endosulfan		ug/L		0.010	40
	33213-65-9	beta-Endosulfan		ug/L		0.010	40
Brominated diphenylethers							
	41318-75-6	BDE-28	CZ_SOP_ D06_06_177 except chapters: 10.2.3.2-10.2.3.7; 10.2.4; 10.2.5 (US EPA 1614, CSN EN ISO 22032)	ng/L	0.025-0.057	0.068-0.11	30
	5436-43-1	BDE-47		ng/L	0.022-0.058	0.53-1.1	30
	60348-60-9	BDE-99		ng/L	0.037-0.100	0.25	30
	189084-64-8	BDE-100		ng/L	0.028-0.073	0.078-0.15	30
	68631-49-2	BDE-153		ng/L	0.028-0.110	0.078-0.21	30
	207122-15-4	BDE-154		ng/L	0.027-0.100	0.059-0.20	30
	207122-16-5	BDE-183		ng/L	0.023-0.098	0.26	30
	1163-19-5	BDE-209		ng/L	0.15-1.8	2.6-3.6	30
Alkylphenols and their ethoxylates							
	104-40-5, 25154-52-3	4-Nonylphenol, mixture of isomers	CZ_SOP_ D06_03_178 CSN EN ISO 18857-2	ug/L		0.10	40
	104-35-8	4-Nonylphenol monoethoxylates, mixture of isomers		ug/L		0.10	40
	20427-84-3	4-Nonylphenol diethoxylate, mixture of isomers		ug/L		0.10	40
		4-Nonylphenol triethoxylate, mixture of isomers		ug/L		0.10	40
	1806-26-4	4-n-Octylphenol		ug/L		0.010	40
	140-66-9	4-t-Octylphenol		ug/L		0.010	40
	51437-90-2	4-t-Octylphenol diethoxylate		ug/L		0.010	40
	51437-89-9	4-t-Octylphenol monoethoxylate		ug/L		0.010	40
		4-t-Octylphenol triethoxylate		ug/L		0.010	40
Perfluorooctylsulphonic acid							
.	1763-23-1	PFOS	Subcontractor's internal method	ug/L		0.2	25
Chlorinated paraffins							
	85535-84-8	C10-13 chloroalkanes (SCCP)	Subcontractor's internal method	ug/L		0.1 – 0.5	20
	85535-85-9	C14-17 chloroalkanes (MCCP)		ug/L		0.1 – 0.5	20

The list of industry branches and other objects which potentially emit selected hazardous substances is presented in Table 1.1.1.2

- **Sampling sites**

The sampling sites for source tracking activities in Latvia were chosen according to findings of HS screening in sewage sludge of WWTPs. Screening showed relatively high concentrations of selected substances in sewage sludge from Riga, Liepāja, Dobele, Valmiera and Ventspils WWTP. Also stakeholders were interested to analyse incoming Saldus WWTP sewage from cattle utilization company, that caused activity decrease of sludge. Focus was on potentially sources of the hazardous substances entering with wastewater from different industrial companies (discharged to combined sewage system) and sewage water from household (residential areas). Sampling of storm waters was not possible because long dryness period before sampling.

All together 14 samples of sewage (waste water) were taken in 6 – 9 June 2011:

- 2 samples were taken at the pipe-end of industrial companies located in Ventspils;
- 2 samples were taken in Liepaja
  - 1 sample at the pipe-end of industrial company,
  - 1 sample of municipal waste waters;
- 2 samples were taken at the pipe-end of industrial companies located in Dobele;
- 1 sample was taken from container of industrial company located in Saldus;
- 1 sample was taken at the pipe-end of industrial company located in Valmiera;
- 6 samples were taken in Riga from combined sewage system – mainly mix of industrial and waste waters from household are discharged to combined sewage system; selection of sampling sites was done according proportion of discharge industrial or municipal waste waters – 3 samples from industrial area, 3 samples from residential areas. The descriptions of spots are presented in Table 1.2.1.2.

The scopes of observed companies are: textiles production (sewing, dyeing, printing, impregnation, other finishing), cattle utilization, production of household chemistry, storage and transportation of oil and oil products, production of candles, fire-extinguishers and metal cans.

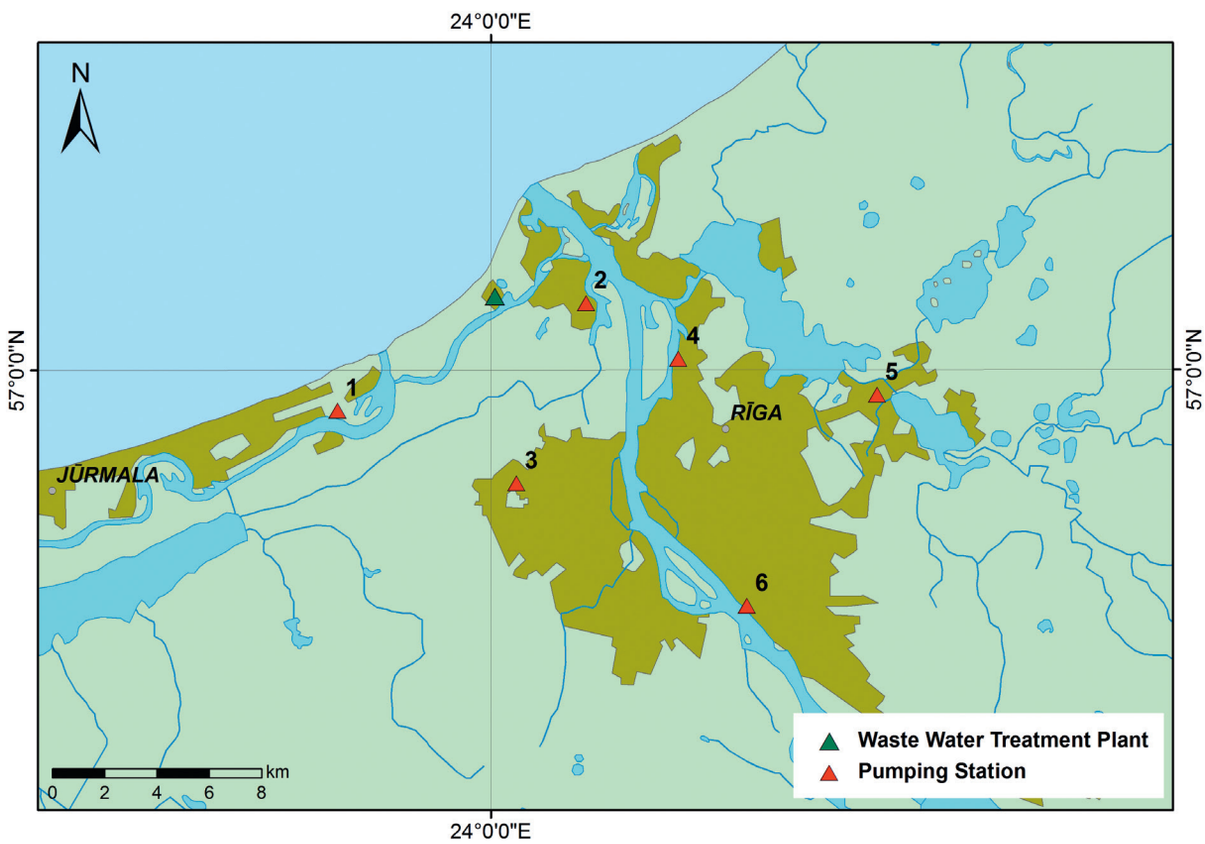
The location of sampling sites over Latvia is presented in Picture 1.2.1.1. The distribution of sites over Riga is presented in Picture 1.2.1.2.

Picture 1.2.1.1. The location of WWTPs

Table 1.2.1.2. Description of the sampling spots (pumping stations) in sewage system of Riga

Spot Nr.	Discharged waters from different sources to sewage system of Riga	Mainly
Rīga 1 JRM	Household effluents from residential area of Jurmala Eastern part	Household
Rīga 2 BOL	Shipyard, harbour, fishing industry, furniture company, timber-processing, production of plywood, production of synthetic resin and phenol films, surface run-off from industrial areas, household effluents from residential areas	Industrial
Rīga 3 IMA	Household effluents from residential area	Household
Rīga 4 SAR	Storage and transportation of oil, oil products and bulk cargo, warehouses, quayside, brewery, hospital, surface run-off from industrial areas, household effluents from residential area	Industrial
Rīga 5 JUG	Textiles production, household effluents from residential area	Household
Rīga 6 KEN	Pharmacy, metal-processing, production of electrical equipment, metal constructions and metal wires, meat-packing plant, warehouses, surface run-off from industrial areas, household effluents from two big residential areas	More household than industrial

Picture 1.2.1.2. The location of WWTP and observed sewage pumping stations (spots) in Riga



1.2.2. Quality assurance issues

- **Sampling and handling of the samples**

Sampling was performed in 6 – 9 June 2011 by the trained specialist of the Latvian Institute of Aquatic Ecology and by the specialist of the wastewater treatment plant who has been trained to take samples. Sampling was performed following Standard Activity Procedures, which are based on ISO/EN standards:

- LVS ISO 5667-10:1992 Water quality. Guidance on sampling of wastewater samples.
- LVS EN ISO 5667-1:2007 Water quality -- Sampling -- Part 1: Guidance on the design of sampling programmes and sampling techniques.
- LVS EN ISO 5667-3:2007 Water quality -- Sampling -- Part 3: Guidance on the preservation and handling of water samples.

The waste water samples analysed at ALS Laboratory Group Ltd were collected in precleaned amber glass bottles of 1 L with plastic screw-cap and polytetrafluoroethylene insertion. All bottles for the samples were delivered precleaned by the subcontracted laboratory and did not require further preparation. Plastic screw-cap and polytetrafluoroethylene insertion for PFOS analyses were isolated from the cap by aluminium foil.

Wastewater samples were taken from the specially established sampling sites:

- pipe end of factories or their pre-treatment station before waste water discharge to combined sewage system;
- waste water collecting containers;
- waste water pumping stations.

Waste water samples were taken manually with scoop/cord and bucket. Sampling dishes were washed with waste water from the site before taking the sample. One sample was collected from automatic 24-hours sampler.

From the sampling spot to the laboratory of LIAE samples were transported in the mobile cool boxes filled with a frozen cooling agent cartridges right after sampling. Samples were kept 3 – 7 days in the fridge at the temperature of 4 – 8 ºC until transportation to ALS Laboratory Group Ltd in the mobile cool boxes filled with a frozen cooling agent cartridges.

- **Analysis of the samples**

Analyses of the waste water samples were carried out by ALS Laboratory Group Ltd, the Czech Republic: alkylphenols and their ethoxylates, brominated diphenylethers, chlorinated paraffins, PFOS, chloroorganic pesticides.

Laboratory is accredited in the Czech Accreditation Institute (Standard EN ISO/IEC 17025:2005). Certificate of Accreditation No. 521/2008 from 24.11.2008, valid to 31.03.2012.

Scope of Accreditation: Chemical, radiochemical and microbiological analyses of water, soils, waste, sludge, oils, insulating liquids, sediments, rocks, solid samples, air, emission, immission, gases, working environment, biological materials (vegetable and animal tissues), food, animal feeding stuffs; ecotoxicological testing of waste, water and chemical agents; analyses of lubricants and fuels; water sampling.

Laboratory applied flexible accreditation type 2 to the 4-n-nonylphenol (expansion of range of determined parameter). The method was conferred flexible accreditation type 2 and is mentioned on Annex of Certificate of Accreditation No. 521 dated 24th November 2008.

All methods of analysis applied have to be based on an uncertainty of measurement of 50% or below (k = 2). Within source tracking round the LOD, LOQ and MU of analytical methods did not exceeded limits mentioned in legislation of Latvia (22.01.2002. Cabinet of Ministers Regulation Nr.34 "Regulation regarding discharge of polluting substances into water") (Table 1.2.2.1).

Table 1.2.2.1. Comparison of minimum required LOQ according Latvian legislation and LOQ proposed by laboratory

Substances	LOD for water discharged to sewage system	LOQ mg/l proposed by laboratory
DDT	1 ug/L	0.01 ug/L
Sum of aldrin, dieldrin, endrin and isodrin	0.4 ug/L	0.01 ug/L separately for each substance
Hexachlorobenzene (HCB)	0.5 – 1 ug/L	0.005 ug/L
Hexachlorobutadiene	0.5 – 1 ug/L	0.01 ug/L

1.2.3. Results of analysis

- **Basis for the evaluation of results**

Screening and source tracking was done in different time. The results of screening and source tracking could show different status of potential pollution source and quality of sewage sludge. Therefore it is rather difficult to conclude on source of pollution and impact to discharge waters from WWTPs due to only one source tracking observation.

There is no legal basis for the evaluation of the results except Regulation Nr.34 of Cabinet of Ministers mentioned in Chapter 2.2. The current and proposed EQS values under WFD consider waste waters discharged to natural environment and they are not suitable for sewage waters entering WWTP.

- **Overview of the results by investigated types of sites**

The results of source tracking showed that concentrations of chloroorganic pesticides and PFOS were below LOQ.

PFOS

Within screening rounds relatively high concentration of PFOS was observed in the sewage sludge of Ventspils WWTP. Probable sources of pollution could be production of goods which contain PFOS or use of flame retardants in industries with high possibility of ignition. Contrary to finding within screening the results of source tracking showed that values of PFOS concentration were below LOQ at all observed spots. However, due to the matrix influence LOQ was increased.

Chlorinated paraffins

Within screening rounds relatively high concentration of chlorinated paraffins was observed in the sewage sludge of Dobele WWTP. Probable sources of pollution could be a production of goods which contain chlorinated paraffins.

SCCP (C10 – C13) were observed in 10 out of 14 sewage samples. The range of concentration was <0.1 – 1.6 ug/L, the highest concentration was measured in sewage waters from household (residential area).

MCCP (C14 – C17) were observed 11 out of 14 sewage samples. The range of concentration was <0.1 – 8.8 ug/L, the highest concentration was measured in sewage waters from household (residential area). The concentration 5.4 ug/L was measured in the sewage waters from the entity producing candles.

PBDE

Within screening rounds relatively high concentration of PBDE was observed in the sewage sludge of Valmiera WWTP and Dobele WWTP. Probable sources of pollution could be hte production of goods which contain PBDE, use of flame retardants or household dust.

The range of PentaBDE concentrations was 1.50 – 20.7 ng/L, the highest concentration was measured in sewage waters from household (residential area).

The range of OctaBDE concentrations was 0.30 – 3.7 ng/L. The highest concentration was measured in sewage waters from the entity producing candles.

The range of DecaBDE was 8.6 – 890 ng/L, the highest concentration was measured in sewage waters from household (residential area). The concentrations of DecaBDE in Riga sewage system were in the range 120 – 400 ng/l – higher than in other towns, except, Liepāja.

Alkylphenols and their ethoxylates

Within screening rounds relatively high concentrations of alkylphenols were observed in the sewage sludge and waste waters of Riga WWTP. The main source of HS is difficult to recognize since alkylphenols are widely used.

The LOD, LOQ and MU for few samples increased due to complicated matrix (matrix interferences) of sewage waters, which did not allow to reach standard limits.

The range of 4-nonylphenol concentrations in sewage waters was 0.34 – 37 ug/L. The highest concentrations 37 and 19 ug/L and relatively high concentration of 4-nonylphenol monoethoxylates 12 ug/L in sewage waters were detected at the spots near companies that produced/worked with textiles. Relatively high concentration of 4-nonylphenol monoethoxylates 8.4 ug/L and 4-nonylphenol diethoxylates 10 ug/L was measured in sewage sample collected from the plastic containers where company stored sewage waters before utilisation.

The range of 4-t-octylphenol concentrations in sewage waters was 0.13 – 4.7 ug/L. The highest concentration of 4-t-octylphenol 4.7 ug/L and 4-t-octylphenol diethoxylate 2.1 ug/L in sewage waters were detected at the spots near companies that produced/worked with textiles. The highest concentration of 4-t-octylphenol triethoxylate 3.5 ug/L was measured in sewage sample collected from the plastic containers where company stored sewage waters before utilisation.

1.2.4. Summary of results and recommendations

The results of source tracking cannot be clearly explained since only one sampling round was performed within source tracking activity and the working regime of entities was unknown. Probably the momentary samples contained "household" effluents, not "production".

The highest concentrations of alkylphenols were observed near companies that produced/worked with textiles. However according to findings in the sewage sludge and waste waters of Riga WWTP within screening round the control is necessary also for another companies that produce or use products containing alkylphenols.

The effluents from household are regular source of pollution with PBDE and chlorinated paraffins. PBDE are used mainly as flame retardants and it is well known that household dusts contain high concentration of PBDE because furniture, textiles for furniture, building materials, plastics, electronic equipment (computers, TV sets, CD players etc.) contain PBDE to avoid a risk of fire. Chlorinated paraffins are used as plasticisers in PVC, metal working fluids, paints and varnishes, adhesives/sealants, flame retardants, leather fat liquors, carbonless copy paper. Lot of products – plastics, paints, rubbers, household chemistry and leather contain chlorinated paraffins and are made for household. The waste waters discharged to environment from WWTPs should be further monitored to make sure that PBDE and chlorinated paraffins have been removed within treatment process.

The source tracking and further control of PFOS in sewage waters and waste water cannot be regarded as effective yet because analytical methods are not developed enough.

1.3. Estonia

1.3.1. Selection of the hazardous substances and sampling sites

Sampling points, substances to be surveyed and sample matrices were selected during the national project meeting, according to the proposal of specialists from the Estonian Environment Research Centre (EERC) in co-operation with specialists from the Ministry of the Environment, Ministry of Social Affairs, Environmental Board, Health Board, Estonian Environment Information Centre and Baltic Environmental Forum (Estonian branch).

Ida-Viru county was chosen as the place for carrying out the monitoring of sources of hazardous substances. Ida-Viru county is characterized by long-term industrial traditions and an array of manufacturing enterprises. Northeast Estonia (Picture 1.3.1.1) is an industrial area in which oil shale mining, an oil shale-based chemical industry, and enterprises producing electricity and thermal energy are located.

The Kohtla-Järve waste water treatment plant (Järve Biopuhastus OÜ) participated in monitoring as most of the enterprises in the area send their waste water for treatment to this plant. In addition to waste water from industrial enterprises, Järve Biopuhastus OÜ also treats household effluents (domestic wastewater) from the cities of Jõhvi, Kiviõli, Kohtla-Järve and Püssi, the parish of Kohtla-Nõmme and the village of Kukruse.

- **Investigated hazardous substances**

The substances to be surveyed and sample matrices were chosen according to the profile of the industrial enterprises and the results of analysis from wastewater and sewage sludge samples that were previously taken from the Kohtla-Järve wastewater treatment plant, which were obtained in the course of the hazardous substances screening activities in the project. The choice of substances and substance groups to be surveyed was based also on the results of previous hazardous substances inventories, monitoring programmes, research and international projects.

Picture 1.3.1.1. Map of Northeast Estonia

The following hazardous substances or substance groups were chosen for surveying (Table 1.3.1.1):

- heavy metals
- phenols, alkylphenols and their ethoxylates
- polyaromatic hydrocarbons
- volatile organic compounds
- organotin compounds
- phthalates
- polybrominated biphenyls, diphenylethers and polybrominated organic compounds
- short- and medium-chain chlorinated paraffins
- perfluoro-compounds
- petroleum products
- organochlorine pesticides
- polychlorinated biphenyls
- hexachlorobenzene.

Additionally, the following indicators in water samples were measured:

- COD
- BOD7
- total phosphorus
- total nitrogen
- suspended solids.

Table 1.3.1.1. shows all the substances or substance groups measured during the survey and the laboratory that carried out the analysis. Hazardous substances and the industries that potentially emit them are shown in the Table 1.1.1.2., respectively.

Table 1.3.1.1. Substances and substance groups measured during the survey

No No.	Substance / substance group	CAS number	Laboratory that carried out the analysis
Heavy metals			
1	Lead and its compounds	7439-92-1	EERC
2	Nickel and its compounds	7440-02-0	EERC
3	Mercury and its compounds	7439-97-6	EERC
4	Cadmium and its compounds	7440-43-9	EERC
5	Zinc and its compounds	7440-66-6	EERC
6	Chromium	7440-47-3	EERC
7	Copper and its compounds	7440-50-8	EERC
8	Arsenic and its compounds	7440-38-2	EERC
Phenolic compounds, alkylphenols and their ethoxylates			
9	4-nonylphenol	104-40-5	GALAB
10	Isononylphenol	25154-52-3	GALAB
11	Isononylphenol-monoethoxylate	27986-36-3	GALAB
12	Isononylphenol-diethoxylate	20427-84-3	GALAB
13	Isononylphenol-triethoxylate	-	GALAB
14	Isononylphenol-tetraethoxylate	-	GALAB
15	Isononylphenol-pentaethoxylate	-	GALAB
16	Isononylphenol-hexaethoxylate	-	GALAB
17	4-octylphenol	1806-26-4	GALAB
18	4-tert-octylphenol	140-66-9	GALAB
19	4-t-octylphenol-monoethoxylate	9036-19-5	GALAB
20	4-t-octylphenol-diethoxylate	-	GALAB
21	4-t-octylphenol-triethoxylate	-	GALAB
22	4-t-octylphenol-tetraethoxylate	-	GALAB
23	4-t-octylphenol-pentaethoxylate	-	GALAB
24	4-t-octylphenol-hexaethoxylate	-	GALAB
25	4-tert-butylphenol	98-54-4	GALAB
26	4-tert-pentylphenol	80-46-6	GALAB
27	Pentachlorophenol	87-86-5	EERC
28	p- and m-cresol	106-44-5, 108-39-4	EERC
29	o-cresol	95-48-7	EERC
30	Resorcin	108-46-3	EERC
31	2,5-dimethylresorcin	95-87-4	EERC
32	5-methylresorcin	504-15-4	EERC
33	Phenol	108-95-2	EERC
35	2,3-dimethylphenol	526-75-0	EERC
36	2,6-dimethylphenol	576-26-1	EERC
37	3,4-dimethylphenol	95-65-8	EERC
38	3,5-dimethylphenol	108-68-9	EERC
Polyaromatic hydrocarbons			
39	Anthracene	120-12-7	GALAB
40	Benzo(a)pyrene	50-32-8	GALAB
41	Benzo(b)fluoranthene	205-99-2	GALAB
42	Benzo[g,h,i]perylene	191-24-2	GALAB
43	Benzo(k)fluoranthene	207-08-9	GALAB
44	Indeno[1,2,3-cd]pyrene	193-39-5	GALAB
45	Naphtalene	91-20-3	GALAB
46	Fluoranthene	206-44-0	GALAB

Volatile organic compounds			
47	Benzene	71-43-2	EERC
48	1,2-dichloroethane	107-06-2	EERC
49	Dichloromethane	75-09-2	EERC
50	Tetrachloromethane	56-23-5	EERC
51	Chloroform (trichloromethane)	67-66-3	EERC
52	Trichloroethylene (TCE)	79-01-6	EERC
53	Perchloroethylene (PCE)	127-18-4	EERC
54	Dichlorobromomethane	75-27-4	EERC
55	Bromoform	75-25-2	EERC
Chlorobenzenes			
56	Hexachlorobenzene	118-74-1	EERC
Organotin compounds			
57	Tributyltin	3664-73-3	GALAB
58	Monobutyltin	78763-54-9	GALAB
59	Dibutyltin	1002-53-5	GALAB
60	Tetrabutyltin	1461-25-2	GALAB
61	Monooctyltin	-	GALAB
62	Dioctyltin	94410-05-6	GALAB
63	Tricyclohexyltin	6056-50-4	GALAB
64	Monophenyltin	2406-68-0	GALAB
65	Diphenyltin	6381-06-2	GALAB
66	Triphenyltin	668-34-8	GALAB
Phthalates			
67	Di(2-ethylhexyl)phthalate	117-81-7	GALAB
68	Dibutylphthalate	84-74-2	GALAB
69	Dimethylphthalate	113-11-3	GALAB
70	Diethylphthalate	84-66-2	GALAB
71	Benzylbenzoate	120-51-4	GALAB
72	Diisobutylphthalate	84-69-5	GALAB
73	Dimethoxyethylphthalate	117-82-8	GALAB
74	Diisohexylphthalate	-	GALAB
75	Di-2-ethoxyethylphthalate	605-54-9	GALAB
76	Dipentylphthalate	131-18-0	GALAB
77	Benzylbutylphthalate	85-68-7	GALAB
78	Hexyl-2-ethylhexylphthalate	-	GALAB
79	Dibutoxyethylphthalate	117-83-9	GALAB
80	Dicyclohexylphthalate	84-61-7	GALAB
81	Diisononylphthalate	28553-12-0	GALAB
82	Di-n-octylphthalate	117-84-0	GALAB
83	Diisodecylphthalate	26761-40-0	GALAB
84	Di-n-butylphthalate	-	GALAB
Polybrominated biphenyls, diphenylethers and polybrominated organic compounds			
85	Pentabromodiphenylether, PBDE-99	60348-60-9	GALAB
	Pentabromodiphenylether, PBDE-100	189084-66-0	GALAB
86	Octabromodiphenylether, PBDE-203	32536-52-0	GALAB
87	3,3',5,5'-tetrabromobisphenol A, TBBPA	79-94-7	GALAB
88	Tetrabromobiphenyl, PBB-52	59080-37-4	GALAB
89	Pentabromobiphenyl, PBB-101	67888-96-4	GALAB
90	Hexabromobiphenyl, PBB-153	59080-40-9	GALAB
91	Tribromodiphenylether, PBDE-28	-	GALAB
92	Tetrabromodiphenylether, PBDE-47	5436-43-1	GALAB

93	Hexabromodiphenylether, PBDE-138	182677-30-1	GALAB
94	Hexabromodiphenylether, PBDE-153	68631-49-2	GALAB
95	Hexabromodiphenylether, PBDE-154	207122-15-4	GALAB
96	Heptabromodiphenylether, PBDE-183	207122-16-5	GALAB
97	Heptabromodiphenylether, PBDE-190	189084-68-2	GALAB
98	Decabromodiphenylehter, PBDE-209	1163-19-5	GALAB
99	Total of pentabromodiphenylethers	-	GALAB
100	Total of octabromodiphenylethers		GALAB
101	Hexabromobenzene	87-82-1	GALAB
102	Hexabromocyclododecane	25637-99-4	GALAB
103	Bromocyclene	1715-40-8	GALAB
Short- and medium-chain chlorinated paraffins			
104	C10-13 chloroalkanes (SCCP)	85535-84-8	GALAB
105	C14-17 chloroalkanes (MCCP)	85535-85-9	GALAB
Perfluoro-compounds			
106	Perfluorooctanoic acid (PFOA)	335-67-1	GALAB
107	Perfluorooctane sulfonate (PFOS)	1763-23-1	GALAB
Organochlorine pesticides and polychlorinated biphenyls			
108	Gamma-hexachlorocyclohexane	58-89-9	EERC
109	P,p`DDE	82413-20-5	EERC
110	P,p`DDD	72-54-8	EERC
111	Polychlorinated biphenyls	1336-36-3	EERC
Other substances			
112	Petroleum products (C10–C40 hydrocarbons)		EERC

EERC – Estonian Environmental Research Centre
GALAB – GALAB Laboratories GmbH, Max-Planck-Strasse 1, Geesthacht, Germany

• Sampling points, sample matrices and sampling time

A short review of the Kohtla-Järve wastewater treatment plant together with the industrial enterprises that send their wastewater to the treatment plant is given below.

Kohtla-Järve wastewater treatment plant

Kohtla-Järve wastewater treatment plant is an enterprise that belongs to four local governments: Kohtla-Järve, Püssi, Jõhvi and Kiviõli cities. Wastewater treatment in the treatment plant is carried out according to the following steps:

1) Pre-treatment, ditto mechanical treatment

-Receiving chamber, emergency tank, screening building, grit separation tank, equalizing tank, distribution tank.

2) Biological treatment (with activated sludge).

3) Post-treatment (sedimentation)

Chemical dosing station, clarifiers, outflow chamber.

4) Sludge treatment

- Sludge dewatering devices, sludge composting site, exhaust air treatment (biofilter).

Industrial plants

Industrial plant no. 1 – chemical industry

The main field is the production of oil products from oil shale. Products:

1) Shale oil. Derived from shale oil fractions obtained through the thermal cracking of oil shale. Used as high quality fuel in boiler plants, wood preservative and to improve heavy fuel oils.

2) Oil shale phenols. Obtained by dephenolating (extraction with butyl acetate) of phenolic waters developed by the thermal processing of oil shale. Used as a raw material in the production of synthetic tanning substances, tamponing mixtures and phenol formaldehyde resins.

Industrial plant no. 2 – timber industry

Manufacturing of particle boards. Wood residues will be processed to particle boards with higher added value, characterized by a wide variety of surface finishing and high quality. Particle boards are a good alternative to solid timber.

Industrial plant no. 3 – chemical industry

Manufacturing of benzoic acid, preservatives and Benzoflexes. Benzoic acid is used to improve the resistance of paints to corrosion and to produce alkyd resins (for priming wood). Two salts are used as food preservatives: sodium and potassium benzoates, which are used against yeast-fungi, moulds and bacteria in an acid environment. Benzoflexes are used by producing plastics and PVC-products that contain softening substances (for example, window seals that also have to remain flexible in severe temperatures).

Industrial plant no. 4 – chemical industry

Producing of oil shale fuel oils, oil shale phenols, urea formaldehyde resin, 2-methylresorcin and 5-methylresorcin, mastic adhesive for construction, oil shale bitumen, resins, oil paints and other chemical products. Oil shale fuel oil is used as an additive in marine fuels and as fuel in boilers and industrial furnaces.

Oil shale phenols are extracted from gas liquor obtained by the thermal processing (pyrolysis) of oil shale and used as a raw material for producing synthetic tanning substances, tamponing mixtures and adhesive resins. Urea formaldehyde resin is produced by the polycondensation of urea and formaldehyde and is used as a binding agent by producing particle boards, as an adhesive by producing plywood, furniture, various types of laminated timber (parquet) and in cabinet making.

In addition to wastewater from the above mentioned industrial plants, effluent and sewage sludge from Kohtla-Järve wastewater treatment plant, samples were taken of domestic waste water flow from the cities of Jõhvi and Kohtla-Järve, the rural municipality of Kohtla-Nõmme and the village of Kukruse to the Kohtla-Järve wastewater treatment plant as well as leachate from semi-coke and ash deposits. In total, 12 samples were taken, of which 6 were waste water samples (4 industrial and 2 domestic wastewater), 1 was a leachate sample, 2 were effluent samples and 3 were samples of sewage sludge.

Sampling points and their description, sample matrices where the samples were taken from during the survey and sampling times are given in Table 1.3.1.2.

Table 1.3.1.3. will give a more specific overview regarding the substances or substance groups that were measured in the sampling points and matrices during the survey.

Table 1.3.1.2. Sampling points and matrices from which samples were taken during the survey and sampling time

No.	Sampling point	Description of the sampling point	Matrix	Sampling time
1.	Industrial plant no. 1	wastewater pit after flotation tank	wastewater	31/05/2011
2.	Industrial plant no. 2	last pit before wastewater pumping station	wastewater	31/05/2011
3.	Industrial plant no. 3	pressure pipe on the territory of the Kohtla-Järve wastewater treatment plant	wastewater	31/05/2011
4.	Industrial plant no. 4	pressure pipe on the territory of the Kohtla-Järve wastewater treatment plant	wastewater	31/05/2011
5.	Semi-coke and ash deposits	pressure pipe on the territory of the Kohtla-Järve wastewater treatment plant	leachate*	31/05/2011
6.	City of Kohtla-Järve, Kohtla-Nõmme municipality	pressure pipe on the territory of the Kohtla-Järve wastewater treatment plant	domestic wastewater	31/05/2011
7.	City of Jõhvi, Kukruse village, Ahtme district of the city of Kohtla-Järve	pressure pipe on the territory of the Kohtla-Järve wastewater treatment plant	domestic wastewater	31/05/2011
8.	Kohtla-Järve wastewater treatment plant (Järve Biopuhastus OÜ)	outflow pit on the territory of the wastewater treatment plant return sludge from the ball valve of the pumping station (three samples of sewage sludge, taken at 0.5 hour intervals)	effluent (no. 1: sample of 24 hours; no. 2: spot sample) sewage sludge (3 samples)	31/05/2011

*Since 2000, Järve Biopuhastus OÜ has been treating leachate.

Table 1.3.1.3. Sampling points, sample matrices and corresponding substances or substance groups with the laboratory that carried out the analysis

No	Sampling point and matrix	Analysed substances / substance groups and laboratory	
		EERC	GALAB
1.	Industrial plant no. 1; waste water	1. Heavy metals (As, Cr, Cu, Zn, Pb, Ni, Hg, Cd) 2. Volatile organic compounds 3. Mono- and dibasic phenols* 4. Pentachlorophenol 5. Petroleum products (C10–C40 hydrocarbons) In addition: COD, BOD7, total phosphorus, total nitrogen, suspended solids	1. Alkylphenols and their ethoxylates 2. Polyaromatic hydrocarbons 3. Organotin compounds 4. Phthalates 5. Polybrominated biphenyls, diphenylethers and polybrominated organic compounds 6. Short- and medium-chain chlorinated paraffins 7. Perfluoro-compounds
2.	Industrial plant no. 2; waste water	1. Heavy metals (As, Cr, Cu, Zn, Pb, Ni, Hg, Cd) 2. Volatile organic compounds 3. Mono- and dibasic phenols 4. Petroleum products (C10–C40 hydrocarbons) In addition: COD, BOD7, total phosphorus, total nitrogen, suspended solids	1. Alkylphenols and their ethoxylates 2. Polyaromatic hydrocarbons 3. Organotin compounds 4. Phthalates 5. Polybrominated biphenyls, diphenylethers and polybrominated organic compounds 6. Short- and medium-chain chlorinated paraffins 7. Perfluoro-compounds
3.	Industrial plant no. 3; waste water	1. Heavy metals (As, Cr, Cu, Zn, Pb, Ni, Hg, Cd) 2. Volatile organic compounds 3. Mono- and dibasic phenols 4. Petroleum products (C10–C40 hydrocarbons) In addition: COD, BOD7, total phosphorus, total nitrogen, suspended solids	1. Alkylphenols and their ethoxylates 2. Polyaromatic hydrocarbons 3. Organotin compounds 4. Phthalates 5. Short- and medium-chain chlorinated paraffins 6. Perfluoro-compounds
4.	Industrial plant no. 4; waste water	1. Heavy metals (As, Cr, Cu, Zn, Pb, Ni, Hg, Cd) 2. Volatile organic compounds 3. Mono- and dibasic phenols 4. Pentachlorophenol 5. Petroleum products (C10–C40 hydrocarbons) 6. Polyaromatic hydrocarbons In addition: COD, BOD7, total phosphorus, total nitrogen, suspended solids	1. Alkylphenols and their ethoxylates 2. Polyaromatic hydrocarbons 3. Organotin compounds 4. Phthalates 5. Polybrominated biphenyls, diphenylethers and polybrominated organic compounds 6. Short- and medium-chain chlorinated paraffins 7. Perfluoro-compounds
5.	Semi-coke and ash deposit; leachate	1. Heavy metals (As, Cr, Cu, Zn, Pb, Ni, Hg, Cd) 2. Volatile organic compounds 3. Mono- and dibasic phenols 4. Pentachlorophenol 5. Petroleum products (C10–C40 hydrocarbons) In addition: COD, BOD7, total phosphorus, total nitrogen, suspended solids	1. Alkylphenols and their ethoxylates 2. Polyaromatic hydrocarbons 3. Organotin compounds 4. Phthalates 5. Polybrominated biphenyls, diphenylethers and polybrominated organic compounds 6. Short- and medium-chain chlorinated paraffins 7. Perfluoro-compounds
6.	City of Kohtla-Järve, Kohtla-Nõmme municipality; domestic wastewater	1. Heavy metals (As, Cr, Cu, Zn, Pb, Ni, Hg, Cd) 2. Volatile organic compounds 3. Mono- and dibasic phenols 4. Petroleum products (C10–C40 hydrocarbons) In addition: COD, BOD7, total phosphorus, total nitrogen, suspended solids	1. Alkylphenols and their ethoxylates 2. Polyaromatic hydrocarbons 3. Organotin compounds 4. Phthalates 5. Short- and medium-chain chlorinated paraffins 6. Perfluoro-compounds

7.	City of Jõhvi, Kukruse village, Ahtme district of the city of Kohtla-Järve; domestic wastewater	1. Heavy metals (As, Cr, Cu, Zn, Pb, Ni, Hg, Cd) 2. Volatile organic compounds 3. Mono- and dibasic phenols 4. Petroleum products (C10–C40 hydrocarbons) In addition: COD, BOD7, total phosphorus, total nitrogen, suspended solids	1. Alkylphenols and their ethoxylates 2. Polyaromatic hydrocarbons 3. Organotin compounds 4. Phthalates 5. Polybrominated biphenyls, diphenylethers and polybrominated organic compounds 6. Short- and medium-chain chlorinated paraffins 7. Perfluoro-compounds
8.	Kohtla-Järve wastewater treatment plant (Järve Biopuhastus OÜ); effluent	1. Heavy metals (As, Cr, Cu, Zn, Pb, Ni, Hg, Cd) 2. Volatile organic compounds 3. Mono- and dibasic phenols 4. Polychlorinated biphenyls 5. Hexachlorobenzene 6. Petroleum products (C10–C40 hydrocarbons) In addition: COD, BOD7, total phosphorus, total nitrogen, suspended solids	1. Alkylphenols and their ethoxylates 2. Polyaromatic hydrocarbons 3. Organotin compounds 4. Phthalates 5. Polybrominated biphenyls, diphenylethers and polybrominated organic compounds 6. Short- and medium-chain chlorinated paraffins 7. Perfluoro-compounds
9.	Kohtla-Järve wastewater treatment plant (Järve Biopuhastus OÜ); sewage sludge	1. Heavy metals (As, Cr, Cu, Zn, Pb, Ni, Hg, Cd) 2. Mono- and dibasic phenols 3. Organochlorine pesticides and polychlorinated biphenyls 4. Hexachlorobenzene	1. Alkylphenols and their ethoxylates 2. Polyaromatic hydrocarbons 3. Organotin compounds 4. Phthalates 5. Polybrominated biphenyls, diphenylethers and polybrominated organic compounds 6. Short- and medium-chain chlorinated paraffins 7. Perfluoro-compounds

* Contents of mono- and dibasic phenols are delivered in results as total values. Total value of monobasic phenols includes the sum of p-, m-, o-cresols, 3,4-, 3,5-, 2,3-, 2,6-dimethylphenols and phenol. Total of dibasic phenols includes the sum of resorcin, 2,5-dimethylresorcin and 5-methylresorcin.

1.3.2. Quality assurance issues

- **Sampling and handling of the samples**

Samples were taken by EERC specialists accredited according to the requirements of 11 January 2002 Regulation no. 3 of the Minister of the Environment "The Procedure for the Accreditation of People Responsible for Taking Samples for Water Research." The Estonian Environmental Research Centre is accredited in the field of sampling by the Estonian Accreditation Centre.

Wastewater, leachate, effluent and sewage sludge samples were taken, stored and handled in accordance with the requirements of 6 May 2002 Regulation no. 30 of the Minister of the Environment "Sampling Methods". The regulation lays down the methods for taking samples from sea water, surface water, ground water, wastewater, effluent and sewage sludge in the process of water research. The above mentioned regulation is based on Estonian standard EVS-EN 5667, parts 1, 2, 3, 4, 6, 9, 10, 13, 15. Standard EVS-EN 5667 complies with the requirements of the respective ISO 5667 standard.

Samples were taken from the inlets and outlets of Kohtla-Järve wastewater treatment plant. One effluent sample was taken as a spot sample from the outlet of Kohtla-Järve wastewater treatment plant. The other sample was taken as a medium of 24 hours using the time-proportional sampling mode with the help of a stationary automatic sampler owned by Kohtla-Järve wastewater treatment plant.

From the inlets, the wastewater sample of industrial plant no. 1 was taken from the wast water pit after the flotation tank (where the shale oils are separated). The wastewater sample of industrial plant no. 2 was taken from the last pit before the inlet to the pumping station. The wastewater samples of the other industrial plants and the leachate sample were taken from the inlet maintenance chamber located underground and before the wastewater treatment plant. The pressure pipings of all pumping stations that pump wastewater to the treatment plant pass through this chamber. The pipings are equipped with one or more sensors for the continuous registering of wastewater quality. There are four types of sensors and they automatically register the following parameters: temperature, pH, redox potential, dissolved oxygen content. Pressure pipes equipped with ball valves for taking water samples are situated near the outlet-side wall of the maintenance chamber. Samples were also taken through these for this survey. As a small amount of sludge collects on the bottom of the pressure pipes, despite the rapid movement of water, a sufficient amount of water was let flow into the bucket before sampling, to ensure that the sample was representative. Next, the bottles were filled straight from the valves as spot samples.

Sewage sludge samples were taken from fresh return sludge directly to the sampling container. Separating and compacting the excess sludge did not occur during the sampling.

The samples were transported to the laboratory in thermo boxes equipped with cold batteries and were placed into the refrigerator upon arrival. The analysis of those substances in samples that were measured in the EERC laboratory were commenced on the day of arrival. In order to analyse the substances at the GALAB laboratories, the samples were delivered by a courier to Germany in thermo boxes equipped with cold batteries.

From the wastewater, leachate and effluent samples, heavy metal samples were collected into 500 ml plastic bottles. The remainder of the water samples were collected into 1 litre glass bottles; for the samples of the cresols analysis, 500 ml glass bottles were used.

All three sewage sludge samples were collected into 500 ml glass jars.

- **Analysis of the samples**

Technical operations that ensure the quality and comparability of the results were made in compliance with internationally recognised quality management system practices. Commission directive no. 2009/90/EC of 31 July 2009 stipulates that laboratory methods of analysis must be validated and documented according to standard EN ISO/IEC-17025.

Chemical analyses were carried out in two laboratories: the laboratory of the Estonian Environmental Research Centre (Marja 4D, 10617 Tallinn) and the GALAB laboratories (GALAB Laboratories GmbH, Max-Planck-Strasse 1, Geesthacht, Germany).

The scope of accreditation of both chosen laboratories is in compliance with the list and specifics of the analysis, and the requirement stipulated in article 6 "Quality Assurance and Control" of the above mentioned directive on applying standard EN ISO/IEC-17025 has been met by them.

The quality management system of the Estonian Environmental Research Centre has been accredited by the Estonian Accreditation Centre since 1998. In 2009, it was certified by AS Metrosert and declared to be in compliance with the requirements of standards ISO 9001 and ISO 14001. The Estonian Accreditation Centre has declared the activity of the laboratory of Estonian Environmental Research Centre to be in conformity with the requirements of standard EN ISO/IEC 17025. The laboratory has also been appointed as the reference laboratory in the field of wastewater and effluent by the Minister of the Environment.

The activity of GALAB has been declared to be in line with the requirements of standards EN ISO/IEC 17025 and DAC-PL-0114-00-10 by the Accreditation Centre of Germany.

Table 1.3.2.1. The methods of analysis used in different matrices by the laboratories of the Estonian Environmental Research Centre and GALAB

Substance / substance group / laboratory	Wastewater/effluent/leachate	Sewage sludge
Heavy metals except mercury; EERC	Inductively coupled plasma mass-spectrometry (ICP-MS), EVS EN ISO 17294-2:2004; flame atomic absorption spectrophotometry (FAAS), ISO 8288	Inductively coupled plasma mass-spectrometry (ICP-MS), STJ no. M/U 91(EN ISO 11885)
Heavy metals: mercury; EERC	Cold vapour method (EVS-EN 1483)	Cold vapour method (EVS-EN 1483)
Benzene; EERC	Gas chromatography, flame ionisation detector (GC-FID), ISO 11423-2, STJ no. U62B	-
Volatile organic compounds, including chlorobenzenes; EERC	Gas chromatogaphy, electron capture detector (GC-ECD), EVS-EN ISO 10301, STJ no. V75	-
Organochlorine pesticides and polychlorinated biphenyls; EERC	Gas chromatography, electron capture detector (GC-ECD) (EN ISO 6468), STJ no. U63	Gas chromatography, electron capture detector (GC-ECD) (EN ISO 6468), STJ no. U63
Petroleum products (C10–C40 hydrocarbons); EERC	Gas chromatography, flame ionisation detector (GC-FID) EVS-EN ISO 9377-2: 2001	-
Pentachlorophenol; EERC	Liquid chromatography, diode array detector (HPLC-DAD), STJ no. U12A	Liquid chromatography, diode array detector (HPLC-DAD), STJ no. U12A
Phenols; EERC	Liquid chromatography, electrochemical detector (HPLC-ECD), STJ no. U12	Liquid chromatography, electrochemical detector (HPLC-ECD), STJ no. U12
Alkylphenols and their ethoxylates; GALAB	Gas chromatography, mass-spectrometric detector (GC-MCD), SOP no. 23, 156	Gas chromatography, mass-spectrometric detector (GC-MCD), SOP no. 23
Polyaromatic hydrocarbons (PAH); GALAB	Gas chromatography, mass-spectrometric detector (GC-MCD), SOP no. 103	Gas chromatography, mass-spectrometric detector (GC-MCD), DIN 38414-21
Organotin compounds; GALAB	Gas chromatography (GC-AED), DIN EN ISO 17353	Gas chromatography (GC-AED), DIN EN ISO 19744
Polybrominated biphenyls, diphenylethers and polybrominated organic compounds; GALAB	Gas chromatography, mass-spectrometric detector (GC-MCD), SOP no. 42	Gas chromatography, mass-spectrometric detector (GC-MCD), SOP no. 42
Phthalates and their ethoxylates; GALAB	Gas chromatography, mass-spectrometric detector (GC-MCD), SOP no. 154	Gas chromatography, mass-spectrometric detector (GC-MCD), SOP no. 154
Short- and medium-chain paraffins (chloroalkanes) C10-13 chloroalkanes (SCCP) C14-17 chloroalkanes (MCCP); GALAB	Gas chromatography with negative chemical ionisation, mass-spectrometry (GC-MS(NCI))	Gas chromatography with negative chemical ionisation, mass-spectrometry (GC-MS(NCI))
Perfluoro-compounds (PFOA, PFOS); GALAB	Liquid chromatography - mass-spectrometry (LC-MS/MS), SOP no. 229	Liquid chromatography - mass-spectrometry (LC-MS/MS)

All limits of quantification of the methods used for the analysis of the substance groups chosen for the survey, and substances belonging to those groups, fulfilled the requirements laid down by law, i.e. they were comparable with corresponding limit values either for effluent discharged into a water body or wastewater discharged into a public sewerage system.

Table 1.3.2.2. includes the substances measured in the laboratory of the Estonian Environmental Research Centre, limits of detection, limits of quantification and measurement uncertainties of the analysis methods.

Substances analysed in the laboratories of GALAB, limits of quantification and measurement uncertainties of the analysis methods are shown in Table 1.3.2.3.

Table 1.3.2.2. Substances measured in the laboratory of the Estonian Environmental Research Centre, limits of detection, limits of quantification and measurement uncertainties of the analysis methods

		Wastewater/leachate/effluent			Sewage sludge		
CAS Nr.	Substance / substance group	LOQ (µg/l)	LOD (µg/l)	MU %	LOQ (µg/kg)	LOD (µg/kg)	MU %
Heavy metals							
7439-92-1	Lead and its compounds	1	0.3	12	2000	1500	28
7440-02-0	Nickel and its compounds	1	0.3	12	1000	500	23
7439-97-6	Mercury and its compounds	0.05	0.02	29	20	10	17
7440-43-9	Cadmium and its compounds	0.1	0.007	11	1000	500	38.5
7440-66-6	Zinc and its compounds	10	4	9	1000	500	25
7440-47-3	Chromium	0.1	0.05	16	1000	500	17.6
7440-50-8	Copper and its compounds	1	0.2	13	1000	500	16.5
7440-38-2	Arsenic and its compounds	1	0.02	12	2500	1250	42
Phenols							
106-44-5	p- and m-cresol	2	0.4	20	100	50	20
95-48-7	o-cresol	2	0.4	25	100	50	20
108-46-3	Resorcin	10			500		
95-87-4	2,5-dimethylresorcin	10			500		
504-15-4	5-methylresorcin	10			500		
108-95-2	Phenol	2			100		
526-75-0	2,3-dimethylphenol	2			100		
87-86-5	Pentachlorophenol	0.4			1		
Volatile organic compounds							
71-43-2	Benzene	0.2	0.05	20	-	-	-
107-06-2	1,2-dichloroethane	0.1	0.08	45	-	-	-
75-09-2	Dichloromethane	0.1	0.08	45	-	-	-
56-23-5	Tetrachloromethane	0.1	0.08	35	-	-	-
127-18-4	Perchloroethylene (PCE)	0.1	0.08	44	-	-	-
67-66-3	Chloroform (trichloromethane)	0.1	0.08	35	-	-	-
79-01-6	Trichloroethylene (TCE)	0.1	0.08	30	-	-	-
118-74-1	Hexachlorobenzene	0.005	0.0037	32	1	0.8	20
608-93-5	Pentachlorobenzene	0.005	0.0037	32	1	0.8	23
75-27-4	Dichlorobromomethane	0.1			-		
75-25-2	Bromoform	0.1			-		
Organochlorine pesticides and polychlorinated biphenyls							
58-89-9	Gamma-hexachlorocyclohexane	0.003	0.002		1	0.8	
82413-20-5	P,p`DDE		0.0012		1		
72-54-8	P,p`DDD		0.0017		1		
1336-36-3	Polychlorinated biphenyls	0.005 (as single component)		7-32	1 (as single component)	7-19	
Other substances							
	Petroleum products (C10-C40 hydrocarbons)	20		20**			
87-68-3	Hexachlorobutadiene	0.1	0.08	12	-	-	-

LOQ – limit of quantification
LOD – limit of detection
MU – measurement uncertainty
** Expanded uncertainty (k=2)

Table1 1.3.2.3. Substances analysed in the laboratories of GALAB, limits of quantification and measurement uncertainties of the analysis methods

		Waste water/leachate/effluent		Sewage sludge	
CAS Nr.	Substance / substance group	LOQ (µg/l)	MU %	LOQ (mg/kg)	MU %
Alkylphenols and their ethoxylates					
104-40-5	4-nonylphenol	0.01	15	0.1	15
25154-52-3	Isononylphenols	0.1	15	0.1	15
27986-36-3	Isononylphenol-monoethoxylate	0.1		0.1	
20427-84-3	Isononylphenol-diethoxylate	0.1		0.1	
-	Isononylphenol-triethoxylate			0.1	
-	Isononylphenol-tetraethoxylate			0.1	
-	Isononylphenol-pentaethoxylate			0.1	
-	Isononylphenol-hexaethoxylate			0.1	
1806-26-4	4-octylphenol	0.01	15	0.01	15
140-66-9	4-tert-octylphenol	0.01	15	0.01	15
9036-19-5	4-t-octylphenol-monoethoxylate	0.01		0.01	
-	4-t-octylphenol-diethoxylate	0.01		0.01	
-	4-t-octylphenol-triethoxylate			0.01	
-	4-t-octylphenol-tetraethoxylate			0.01	
-	4-t-octylphenol-pentaethoxylate			0.01	
-	4-t-octylphenol-hexaethoxylate			0.01	
98-54-4	4-tert-butylphenol	0.01		0.01	
80-46-6	4-tert-pentylphenol	0.01		0.01	
Polyaromatic hydrocarbons					
120-12-7	Anthracene	0.01		0.01	
50-32-8	Benzo(a)pyrene	0.01	8	0.01	10
205-99-2	Benzo(b)fluoranthene	0.01		0.01	
207-08-9	Benzo(k)fluoranthene	0.01		0.01	
191-24-2	Benzo[g,h,i]perylene	0.002	8	0.002	10
193-39-5	Indeno[1,2,3-cd]pyrene	0.002	8	0.002	10
91-20-3	Naphtalene	0.01	8	0.01	
206-44-0	Fluoranthene	0.01	8	0.01	10
Organotin compounds					
3664-73-3	Tributyltin	0.0002	15	0.0002	15
78763-54-9	Monobutyltin	0.001		0.001	
1002-53-5	Dibutyltin	0.001		0.001	
1461-25-2	Tetrabutyltin	0.001		0.001	
-	Monooctyltin	0.001		0.001	
-	Dioctyltin	0.001		0.001	
-	Tricyclohexyltin	0.001		0.001	
-	Monophenyltin	0.001		0.001	
-	Diphenyltin	0.001		0.001	
668-34-8	Triphenyltin	0.001		0.001	
Phthalates					
117-81-7	Di(2-ethylhexyl)phthalate	0.05	15	0.05	15
84-74-2	Dibutylphthalate	0.05		0.05	
113-11-3	Dimethylphthalate	0.05		0.05	
84-66-2	Diethylphthalate	0.05		0.05	
120-51-4	Benzylbenzoate	0.05		0.05	
84-69-5	Diisobutylphthalate	0.05		0.05	

117-82-8	Dimethoxyethylphthalate	0.05		0.05	
-	Diisohexylphthalate	0.05		0.05	
605-54-9	Di-2-ethoxyethylphthalate	0.05		0.05	
131-18-0	Dipentylphthalate	0.05		0.05	
85-68-7	Benzylbutylphthalate	0.05		0.05	
-	Hexyl-2-ethylhexylphthalate	0.05		0.05	
117-83-9	Dibutoxyethylphthalate	0.05		0.05	
84-61-7	Dicyclohexylphthalate	0.05		0.05	
28553-12-0	Diisononylphthalate	0.05		0.05	
117-84-0	Di-n-octylphthalate	0.05		0.05	
26761-40-0	Diisodecylphthalate	1.0		1.0	
-	Di-n-butylphthalate	0.05			
Polybrominated biphenyls, diphenylethers and polybrominated organic compounds					
60348-60-9	Pentabromodiphenylether, PBDE-99	0.005	10	0.005	10
189084-66-0	Pentabromodiphenylether, PBDE-100	0.005	10	0.005	10
32536-52-0	Octabromodiphenylether, PBDE-203	0.005		0.005	
79-94-7	3,3',5,5'-tetrabromobisphenol A, TBBPA	0.005		0.005	
59080-37-4	Tetrabromobiphenyl, PBB-52	0.005		0.005	
67888-96-4	Pentabromobiphenyl, PBB-101	0.005		0.005	
59080-40-9	Hexabromobiphenyl, PBB-153				
-	Tribromodiphenylether, PBDE-28	0.005	10	0.005	10
5436-43-1	Tetrabromodiphenylether, PBDE-47	0.005	10	0.005	10
182677-30-1	Hexabromodiphenylether, PBDE-138	0.005		0.005	
68631-49-2	Hexabromodiphenylether, PBDE-153	0.02	10	0.02	10
207122-15-4	Hexabromodiphenylether, PBDE-154	0.005	10	0.005	10
207122-16-5	Heptabromodiphenylether, PBDE-183	0.02		0.02	
189084-68-2	Heptabromodiphenylether, PBDE-190	0.1		0.1	
1163-19-5	Decabromodiphenylehter, PBDE-209	0.1		0.1	
-	Total of pentabromodiphenylethers	0.05		0.05	
	Total of octabromodiphenylethers	0.05		0.05	
87-82-1	Hexabromobenzene	0.005		0.005	
25637-99-4	Hexabromocyclododecane	0.2		0.2	
1715-40-8	Bromocyclene	0.005		0.005	
Short- and medium-chain chlorinated paraffins					
85535-84-8	C10-13 chloroalkanes (SCCP)	0.3	20	0.3	
85535-85-9	C14-17 chloroalkanes (MCCP)	0.3	20	0.3	
Perfluoro-compounds					
335-67-1	Perfluorooctanoic acid (PFOA)	0.03	10		
1763-23-1	Perfluorooctane sulfonate (PFOS)	0.03	10		

LOQ- limit of quantification
MU – measurement uncertainty

For analysing some substances/substance group in industrial waste water, the limit of quantification in the GALAB laboratory was higher than in the table above. This was caused by the high content of organic compounds in the sample, which interfered with measuring (such as in the case of alkylphenols and phthalates).

1.3.3. Results of analysis

- **Contents of hazardous substances in the wastewater inlet of the Kohtla-Järve wastewater treatment plant**

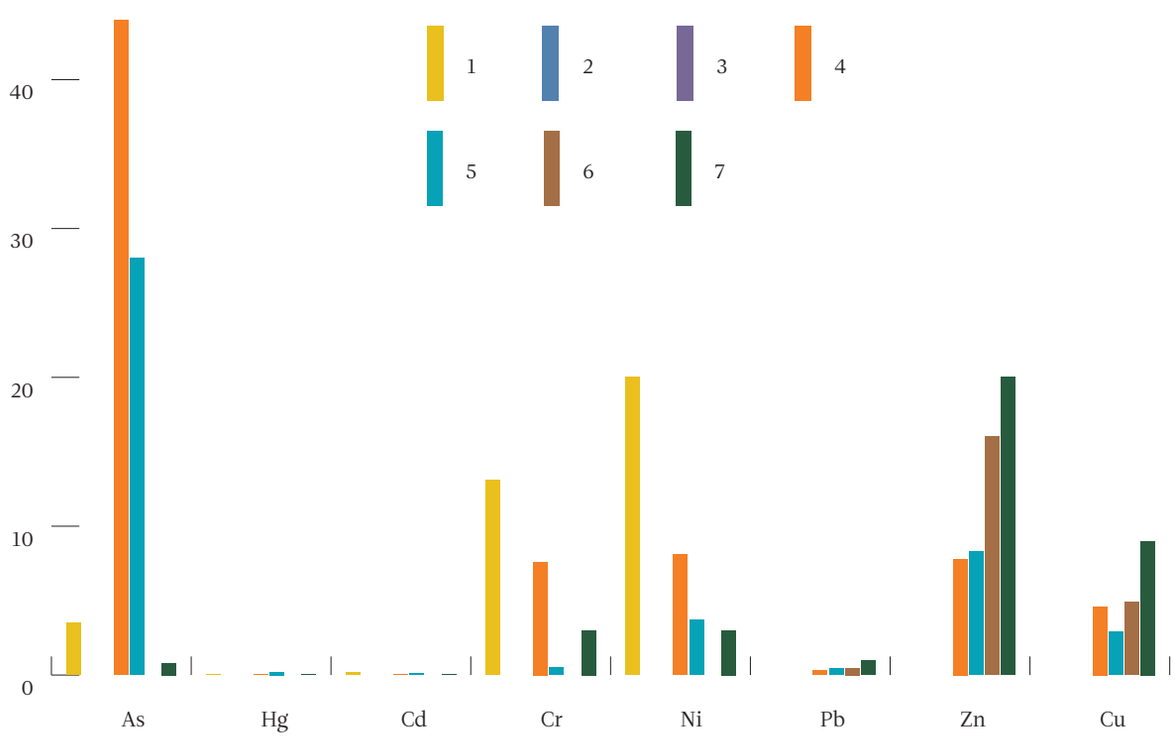
During the survey, wastewater from 4 participating industrial plants (3 chemical industries and 1 timber industry), leachate from semi-coke and ash deposits, and domestic wastewater from the cities of Jõhvi, Kiviõli, Kohtla-Järve and Püssi, the Kohtla-Nõmme municipality and Kukruse village were analysed.

The results of industrial and domestic wastewater analysis were compared to the limit values for the content of hazardous substances in the effluent discharged into the public sewerage system, laid down with the 16 October 2003 regulation of the Minister of the Environment "Establishing of requirements for the discharge of hazardous substances into a public sewerage system".

Heavy metals

None of the analysed heavy metal contents in wastewater exceeded the limit values laid down for hazardous substances discharged into the public sewerage system. The industrial wastewater from all the industry plants that participated in the survey, and domestic wastewater from cities, municipalities and villages that was discharged into the Kohtla-Järve wastewater treatment plant, fulfilled the requirements for heavy metal content (Figure 1.3.3.1). Heavy metal content (limit values are in parentheses) found in industrial wastewater samples, domestic wastewater samples and leachate of semi-coke and ash deposits are the following: arsenic: 0.31–44 µg/l (200 µg/l), mercury: 0.05–1.1 µg/l (50 µg/l), cadmium: 0.03–1.8 µg/l (200 µg/l), lead: 0.31–1.6 µg/l (500 µg/l), nickel: 3–20 µg/l (1000 µg/l), zinc: 6.9–27 µg/l (2000 µg/l), copper: 1–11 µg/l (2000 µg/l), chromium: 0.8–13.1 µg/l (100 µg/l).

Figure 1.3.3.1. Heavy metal content (µg/l) in industrial and domestic wastewater and leachate from semi-coke and ash deposits, dispatched into the Kohtla-Järve wastewater treatment plant



1 – Industrial plant no. 1; 2– Industrial plant no. 2; 3 – Industrial plant no. 3; 4 – Industrial plant no. 4; 5 – Leachate from semi-coke and ash deposits; 6 – City of Kohtla-Järve, Kohtla-Nõmme municipality; 7 – City of Jõhvi, Kukruse village, Ahtme district of the city of Kohtla-Järve.

Phenolic compounds, alkylphenols and their ethoxylates

One of the main problems in the industrial area of Northeast Estonia has been the high contents of mono- and dibasic phenols in the industrial wastewater discharged into the Kohtla-Järve wastewater treatment plant. The limit values for pollution characteristics in waste water, as laid down by the Regulation no. 269 of 31 July 2001 of the Government of the Republic, are 0.1 and 15 mg/l, respectively (wastewater purification grades respectively 75 and 70 %).

In the industrial wastewater and semi-coke and ash deposit leachate, high mono- and dibasic phenol contents were found, while the contents of dibasic phenols were remarkably higher than those of monobasic phenols. The contents of those phenols are given in Table 1.3.3.1.

Table 1.3.3.1. The contents of mono- and dibasic phenols in industrial and domestic wastewater, and leachate from semi-coke and ash deposits, dispatched into the Kohtla-Järve wastewater treatment plant

No	Source of hazardous substances	Content of monobasic phenols (mg/l)	Contents of dibasic phenols (mg/l)
1	Industrial plant no. 1 (chemical industry)	198	1044
2	Industrial plant no. 2 (timber industry)	0.047	<0.01
3	Industrial plant no. 3 (chemical industry)	0.294	1.63
4	Industrial plant no. 4 (chemical industry)	7.32	2.93
5	Leachate from semi-coke and ash deposit	13.3	2.0
6	City of Kohtla-Järve, Kohtla-Nõmme municipality	0.23	0.764
7	City of Jõhvi, Kukruse village, Ahtme district of the city of Kohtla-Järve	1.48	2.37

The content of pentachlorophenol in the wastewater discharged into the public sewerage system may not exceed 0.2 µg/l. The limit value was exceeded by the content of pentachlorophenol of semi-coke and ash deposit leachate (206.2 µg/l). The permitted limit value for pentachlorophenol in the effluent discharged into the public sewerage system was also exceeded by the contents found in the wastewater from industrial plants no.1 and no.4.

In industrial and domestic wastewater and in the leachate from semi-coke and ash deposits, the following alkylphenols and their ethoxylates were found (the corresponding limit of quantification, higher than that in the Table 1.3.2.3, is given in parentheses):

1) industrial plant no. 1 (chemical industry): 4-t-octylphenol-monoethoxylate (<30 ng/l), isononylphenol-monoethoxylate (<500 ng/l), 4-n-octylphenol (<250 ng/l), 4-tert-octylphenol (<300 ng/l), 4-n-nonylphenol (<100 ng/l), isononylphenol - 300 ng/l, 4-tert-butylphenol (<150 ng/l)

2) industrial plant no. 2 (timber industry): isononylphenol - 180 ng/l, 4-tert-butylphenol - 250 ng/l

3) industrial plant no. 3 (chemical industry): 4-tert-octylphenol – 21 ng/l

4) industrial plant no. 4 (chemical industry): 4-tert-butylphenol (<50 ng/l)

4) leachate from semi-coke and ash deposit: 4-t-octylphenol-monoethoxylate (<100 ng/l), isononylphenol-monoethoxylate (<1000 ng/l), isononylphenol-diethoxylate (<1000 ng/l), 4-n-octylphenol (<300 ng/l), 4-tert-octylphenol (<200 ng/l), 4-n-nonylphenol (<50 ng/l), 4-tert-butylphenol (<50 ng/l), 4-tert-pentylphenol (<500 ng/l)

6) city of Kohtla-Järve, Kohtla-Nõmme municipality (domestic waste water): 4-t-octylphenol-monoethoxylate - 130 ng/l, 4-t-octylphenol-monoethoxylate (<100 ng/l), 4-n-octylphenol (< 40 ng/l), 4-tert-octylphenol - 44 ng/l, 4-tert-butylphenol (<25 ng/l), isononylphenol - 2300 ng/l

7) city of Jõhvi, Kukruse village, Ahtme district of the city of Kohtla-Järve (domestic waste water): 4-t-octylphenol-monoethoxylate - 220 ng/l, isononylphenol - 1000 ng/l, 4-tert-butylphenol (<25 ng/l).

Polyaromatic hydrocarbons (PAH)

The following contents of PAHs exceeded the limit of quantification of methods used for analysis: anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, fluoranthene, benzo[g,h,i]perylene, indeno[1,2,3-cd]pyrene, naphthalene, total of benzo[g,h,i]perylene and indeno[1,2,3-cd]pyrene. In the wastewater of the industrial enterprise no. 2 (timber industry) the content of all polyaromatic hydrocarbons were below the limit of quantification of the used methods. In the wastewater of the industrial enterprise no. 1 (chemical industry) the content of all PAHs were above the limit of quantification. The total content of polyaromatic hydrocarbons in the wastewater discharged into the public sewerage system may not exceed 10 µg/l. The total content was above the limiting value in the wastewater of the industrial enterprise no. 1 and in the leachate of semi-coke and ash deposit.

The following amounts of polyaromatic hydrocarbons were found:

1) industrial plant no. 1 (chemical industry): anthracene – 1441 ng/l, benzo(a)pyrene – 235 ng/l, benzo(b) fluoranthene – 81 ng/l, benzo(k)fluoranthene – 50 ng/l, fluoranthene – 757 ng/l, benzo[g,h,i]perylene – 141 ng/l, naphthalene – 76635 ng/l, total of benzo[g,h,i]perylene and indeno[1,2,3-cd]pyrene – 199 ng/l

2) industrial plant no. 3 (chemical industry): naphthalene – 20 ng/l

3) industrial plant no. 4 (chemical industry): naphthalene – 52 ng/l

4) leachate from semi-coke and ash deposit: anthracene – 142 ng/l, benzo(a)pyrene – 19 ng/l, fluoranthene – 72 ng/l, benzo[g,h,i]perylene – 17 ng/l, indeno[1,2,3-cd] pyrene – 4.2 ng/l, naphthalene – 14486 ng/l, total of benzo[g,h,i]perylene and indeno[1,2,3-cd]pyrene – 21 ng/l

5) city of Kohtla-Järve, Kohtla-Nõmme municipality (domestic waste water): benzo[g,h,i]perylene – 6.9 ng/l, fluoranthene – 23 ng/l, indeno[1,2,3-cd]pyrene – 3 ng/l, naphthalene – 28 ng/l, total of benzo[g,h,i] perylene and indeno[1,2,3-cd]pyrene – 9.9 ng/l

6) city of Jõhvi, Kukruse village, Ahtme district of the city of Kohtla-Järve (domestic waste water): benzo[g,h,i]perylene – 3 ng/l, fluoranthene – 17 ng/l, total of benzo[g,h,i]perylene and indeno[1,2,3-cd] pyrene – 4 ng/l.

Along the analyses conducted in the laboratory of GALAB, PAH was analysed also in EERC laboratory, and most of the results were higher than those of GALAB.

Organotin compounds

In industrial and domestic wastewater and in the leachate from semi-coke and ash deposits, the following high contents of organotin compounds were found:

1) industrial plant no. 2 (timber industry): monobutyltin – 3.6 ng/l, dibutyltin – 1.4 ng/l, monooctyltin – 2.4 ng/l, dioctyltin – 5.3 ng/l

2) industrial plant no. 3 (chemical industry): monobutyltin – 2.3 ng/l

3) leachate from semi-coke and ash deposit: monobutyltin – 3.1 ng/l, monooctyltin – 5.7 ng/l

4) city of Kohtla-Järve, Kohtla-Nõmme municipality (domestic wastewater): monobutyltin – 3.0 ng/l, dibutyltin – 2.5 ng/l, monooctyltin – 2.1 ng/l

5) city of Jõhvi, Kukruse village, Ahtme district of the city of Kohtla-Järve (domestic waste water): monobutyltin – 5.1 ng/l, dibutyltin – 4.5 ng/l, monooctyltin – 11 ng/l, dioctyltin – 1.6 ng/l.

Phthalates

In industrial and domestic wastewater and in the leachate from semi-coke and ash deposits, the following high contents of phthalates were found (the corresponding limit of quantification, higher than that in the Table 1.3.2.3, is given in parentheses):

1) industrial plant no. 1 (chemical industry): diisobutylphthalate – 5500 ng/l, dibutylphthalate – 1900 ng/l, di-2-ethoxyethylphthalate – 430 ng/l

2) industrial plant no. 2 (timber industry): diethylphthalate – 690 ng/l, diisobutylphthalate – 750 ng/l, dibutylphthalate – 310 ng/l, di-2-ethoxyethylphthalate – 690 ng/l

3) industrial plant no. 3 (chemical industry): di-2-ethoxyethylphthalate – 1100 ng/l

4) leachate from semi-coke and ash deposit: di-2-ethoxyethylphthalate – 180 ng/l; diethylphthalate (<6000 ng/l), diisobutylphthalate (<500 ng/l), dibutylphthalate (<350 ng/l)

5) city of Kohtla-Järve, Kohtla-Nõmme municipality (domestic waste water): dimethylphthalate – 120 ng/l, diethylphthalate – 2900 ng/l, diisobutylphthalate – 1400 ng/l, dibutylphthalate – 520 ng/l, di-2-ethoxyethylphthalate – 29000 ng/l, diisononylphthalate – 6700 ng/l

6) city of Jõhvi, Kukruse village, Ahtme district of the city of Kohtla-Järve (domestic waste water): dimethylphthalate – 110 ng/l, diethylphthalate – 4600 ng/l, diisobutylphthalate – 1300 ng/l, dibutylphthalate – 320 ng/l, di-2-ethoxyethylphthalate – 17000 ng/l, diisononylphthalate – 8300 ng/l.

Volatile organic compounds

In industrial and domestic wastewater and in the leachate from semi-coke and ash deposits, the following high contents of volatile organic compounds were found:

1) industrial plant no. 1 (chemical industry): trichloromethane – 900 ng/l

2) industrial plant no. 2 (timber industry): trichloromethane – 300 ng/l, dichloromethane – 5800 ng/l, 1,2-dichloroethane – 6000 ng/l, perchloroethylene – 100 ng/l

3) industrial plant no. 3 (chemical industry): trichloromethane – 190 ng/l, perchloroethylene – 120 ng/l, dichlorobromomethane – 110 ng/l

4) industrial plant no. 4 (chemical industry): trichloromethane – 250 ng/l, perchloroethylene – 380 ng/l, bromoform – 1480 ng/l

5) leachate from semi-coke and ash deposit: benzene – 88000 ng/l, trichloromethane (chloroform) – 200 ng/l, 1,2-dichloroethane – 5200 ng/l

6) city of Kohtla-Järve, Kohtla-Nõmme municipality (domestic waste water): trichloromethane – 600 ng/l, trichloroethylene – 2100 ng/l, perchloroethylene – 140 ng/l, bromoform – 1100 ng/l

1) city of Jõhvi, Kukruse village, Ahtme district of the city of Kohtla-Järve (domestic waste water): trichloromethane – 220 ng/l, perchloroethylene – 120 ng/l.

Other substances

The contents of naphtha products (C10–C14 hydrocarbons) remained below the limit of quantification of the analysing method in the wastewater sample from industrial plant no. 2 and the domestic wastewater sample from the city of Jõhvi, Kukruse village and the Ahtme district of the city of Kohtla-Järve. In the rest of the samples, the following contents were found: industrial plant no. 1 (chemical industry) – 619 µg/l; industrial plant no. 3 (chemical industry) – 1066 µg/l; industrial plant no. 4 (chemical industry) – 81 µg/l; leachate from the semi-coke and ash deposits – 96 µg/l; domestic waste water from the city of Kohtla-Järve and Kohtla-Nõmme municipality – 576 µg/l.

- **The content of hazardous substances in the effluent and sewage sludge of Kohtla-Järve wastewater treatment plant**

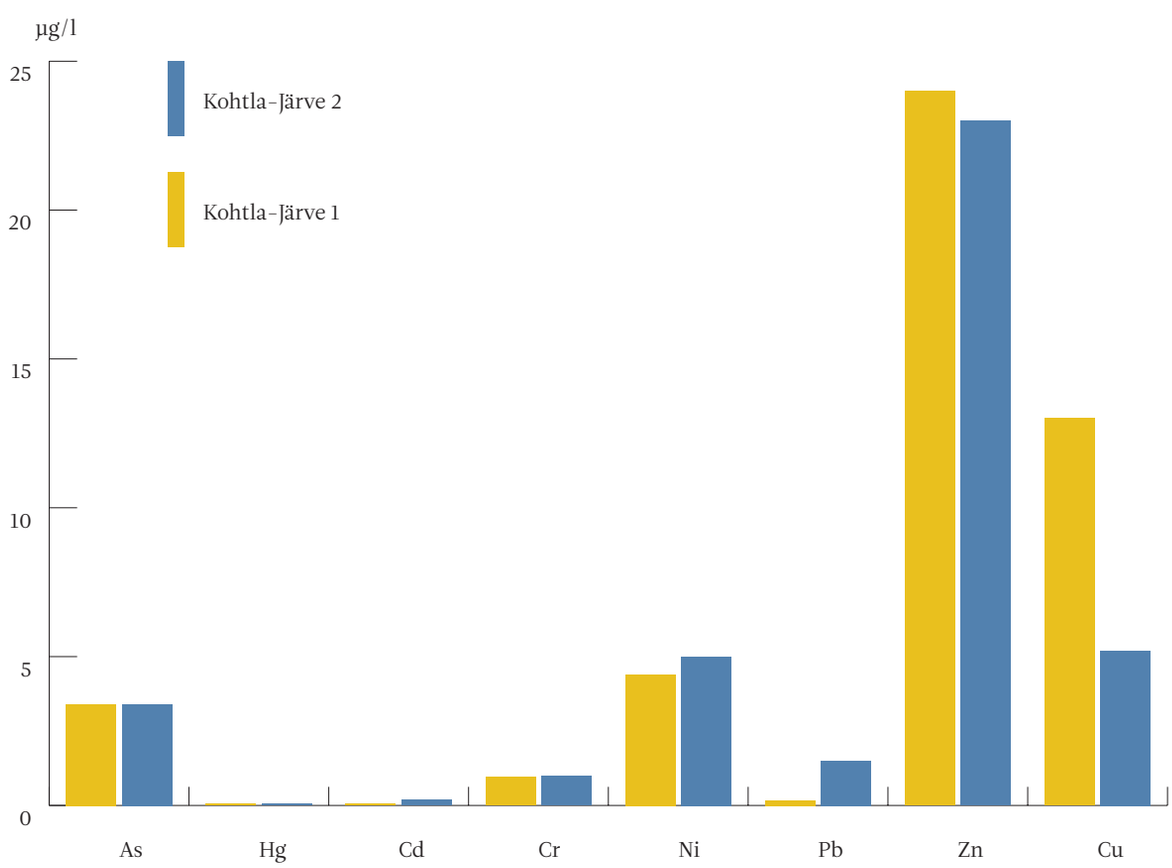
EFFLUENT

The analysis results of the effluent of the Kohtla-Järve wastewater treatment plant were compared to the limit values of the content of hazardous substances in the effluent discharged into a water body, as laid down by Regulation no. 269 of 31 July 2001 of the Government of the Republic "Requirements for Waste Water Discharged into Water Bodies or into Soil".

Heavy metals

None of the analysed heavy metal contents in the effluent exceeded the limit values, as laid down for heavy metal contents in the effluent discharged into a water body. The heavy metal content of the two effluent samples are as follows (limit values are given in parentheses): 1) in the 24 hours sample was found arsenic –3.4 µg/l (200 µg/l), cadmium – 0.06 µg/l (200 µg/l), lead – 0.17 µg/l (500 µg/l), nickel – 4.4 µg/l (1000 µg/l), zinc – 24 µg/l (2000 µg/l), copper – 13 µg/l (2000 µg/l) ja chromium – 0.94 µg/l (100 µg/l); 2) in the spot sample arsenic was found – 3.4 µg/l, cadmium – 0.19µg/l, lead – 1.5 µg/l, nickel – 5 µg/l, zinc – 23 µg/l, copper – 5.2 µg/l, chromium – 0.98 µg/l; the mercury content in both effluent samples remained below the limit of quantification 0.05 µg/l.

Figure 1.3.3.2. Heavy metal content (µg/l) in the effluent of the Kohtla-Järve wastewater treatment plant (Kohtla-Järve 1 is a 24 hours sample, Kohtla-Järve 2 is a spot sample).



The biggest differences between the heavy metal content in the 24 hours sample and the spot sample were in Pb, Cd and Cu content; as for the other heavy metals, big content differences did not occur. In the spot sample, the Pb content was 8.8 times and the Cd content more than 3 times higher than in 24 hours sample (Figure 1.3.3.2). The heavy metal content in the effluent of the Kohtla-Järve wastewater treatment plant remained at the same order of magnitude with results obtained with a screening that was carried out in the scope of the same project in 2010. Only the copper content was more than ten times higher in the screening results, at 59.4 µg/l, respectively.

Phenolic compounds, alkylphenols and their ethoxylates

The concentration of alkylphenols and their ethoxylates in the effluent did not exceed the limit of quantification of the used methods of analysis. The same results were also obtained by screening. The total concentration of monobasic phenols in the effluent was 12.4 µg/l in the first sample and 40.9 µg/l in the second sample. Neither of those values, however, exceeded the limit value (100 µg/l) set for the concentration of monobasic phenols in effluent. The concentration of dibasic phenols was considerably higher than those of the monobasic phenols, especially in the second effluent sample – 14.2 µg/l and 273 µg/l respectively. The concentration of pentachlorophenol in the effluent that is discharged into a water body may not exceed 0.2 µg/l, and the excess of this limit value was not detected in the effluent.

Polyaromatic hydrocarbons

PAH contents of the effluent did not exceed the limit of quantification; the total content of PAHs in the effluent did not exceed the limit value of 10 µg/l, as laid down for the total of those substances in the effluent discharged into a water body.

Organotin compounds

Most of the contents of organotin compounds did not exceed the limit of quantification of the methods used for analysis. Only the value for monobutyltin (MBT) content in effluent was obtained – 3.9 ng/l.

Phthalates

The contents of phthalates remained below the limit of quantification (0.05 µg/l) of the methods used for analysis.

Volatile organic compounds

Most of the contents of volatile organic compounds remained below the limit of quantification of the methods used for analysis. Above the limit of quantification, only the contents of trichloromethane (chloroform), 1,2-dichloroethane and dichloromethane were analysed in the effluent. In the first effluent sample, the limit of quantification was only exceeded by the contents of trichloromethane (chloroform) – 0.32 µg/l, dichloromethane – 2.4 µg/l and 1,2-dichloroethane – 2.1 µg/l; in the second sample only by the content of trichloromethane (chloroform) – 0.17 µg/l. The content of trichloromethane in the effluent discharged into a water body may not exceed 1000 µg/l, contents of 1,2-dichloroethane and trichloromethane 3 µg/l and 1000 µg/l, respectively. Levels above those limit values were not detected.

Polychlorinated biphenyls

The total content of polychlorinated biphenyls was high in two effluent samples – 43.4 and 35.5 ng/l respectively, but did not exceed the limit value laid down for these compounds in the effluent discharged into a water body (50 ng/l).

Other substances

The content of naphtha products (C10–C40 hydrocarbons) remained below the limit of quantification (20 µg/l) in both effluent samples.

SEWAGE SLUDGE

The contents of polybrominated biphenyls, diphenylethers and polybrominated organic compounds as well as short- and medium-chain chlorinated paraffins and perfluorocompounds in the waste water sludge of the Kohtla-Järve waste water treatment plant were below the limit of quantification of the methods used for analysis.

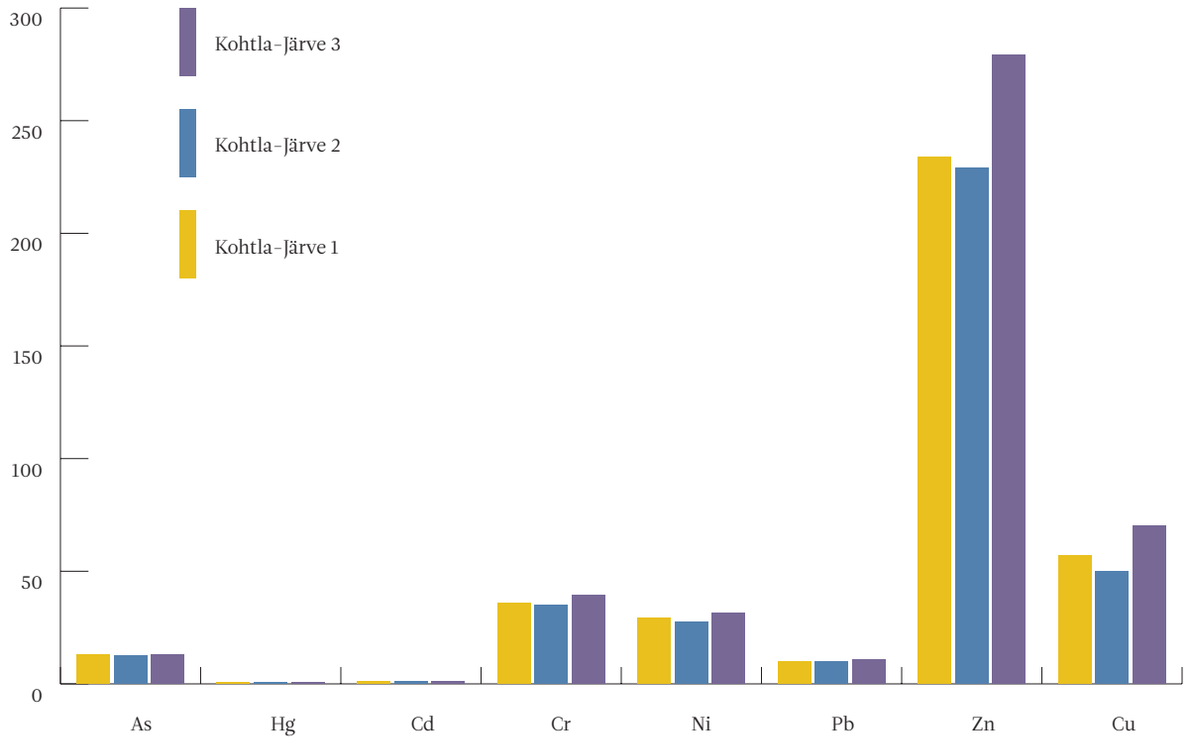
Heavy metals

Big differences between the heavy metal content in three sewage sludge samples were not found. The heavy metal content in three sewage sludge samples remained at the following limits: zinc 229–279 mg/kg dry matter (DM), copper 50–70 mg/kg DM, chromium 35.1–39.4 mg/kg DM, nickel 27.6–31.4 mg/kg DM, arsenic 12.4–13.2 mg/kg DM and mercury 0.69–0.84 mg/kg DM. The cadmium content of all three sewage sludge samples remained below the limit of quantification 1 mg/kg DM. The heavy metal content in three sewage sludge samples from the Kohtla-Järve wastewater treatment plant are also shown in Figure 1.3.3.3.

Phenolic compounds, alkylphenols and their ethoxylates

The contents of alkylphenols and their ethoxylates in all three sewage sludge samples remained below the limits of quantification (the limits of quantification of different substances being between 10–100 µg/kg DM). The contents of alkylphenols and their ethoxylates also remained below the limit of quantification in the sludge samples that were collected during the earlier screening. The total content of monobasic phenols in three sewage sludge samples remained between 2.84–9.53 mg/kg DM and of dibasic phenols between 30.1–73.1 mg/kg DM. The contents of pentachlorophenol measured in the sludge of the wastewater treatment plant remained between 3.4–10.6 mg/kg DM. The obtained results are a little bit higher than the screening results, in which the

Figure 1.3.3.3. Heavy metal content (mg/kg dry matter) in three sewage sludge samples from Kohtla-Järve wastewater treatment plant



contents of pentachlorophenol did not exceed the limit of quantification (1 mg/kg DM).

Polyaromatic hydrocarbons

The following contents of PAHs exceeded the limit of quantification of methods used for analysis: anthracene, benzo(a)pyrene, benzo(b)fluoranthene, fluoranthene, benzo[g,h,i]perylene, indeno[1,2,3-cd]pyrene, total of benzo(g,h,i)perylene and indeno(1,2,3-c,d)pyrene. The contents of naphthalene and benzo(k)fluoranthene remained below the limit of quantification. The following quantities of polyaromatic hydrocarbons were found in the sludge: anthracene – 15 µg/kg DM (was found above the limit of quantification in one sludge sample), benzo(a)pyrene – 50–73 µg/kg DM, benzo(b)fluoranthene – 24–26 µg/kg DM, fluoranthene – 29–85 µg/kg DM, benzo[g,h,i]perylene – 17–39 µg/kg DM, indeno[1,2,3-cd]pyrene – 6.4–12 µg/kg DM, total of benzo(g,h,i)perylene and indeno(1,2,3-c,d)pyrene – 23–51 µg/kg DM.

Organotin compounds

From the organotin compounds, monobutyltin, dibutyltin, monooctyltin and dioctyltin were found above the limit of quantification of the methods used for analysis. The contents of the other organotin compounds in the sludge remained below the limits of quantification of the methods used for analysis. In the sludge, the following quantities of organotin compounds were found: monobutyltin (MBT) 249–308 µg/kg DM, dibutyltin (DBT) – 57–68 µg/kg DM, monooctyltin – 41–58 µg/kg DM, dioctyltin – 88–191 µg/kg DM.

Phthalates

Very high contents of di(2-ethylhexyl)phthalate and diisononylphthalate were found. The contents of other phthalates did not exceed the limits of quantification of the methods used for analysis. The highest content of di(2-ethylhexyl)phthalate was found in the first and second sludge sample, 2.8 mg/kg DM in both cases; in the third sample, the content of phthalate was somewhat lower – 2.0 mg/kg DM. The contents of diisononylphthalate were somewhat lower, between 0.63–0.73 mg/kg DM.

Organochlorine pesticides, polychlorinated biphenyls and hexachlorobenzene

Above the limits of quantification of the methods used for analysis small quantities of degradation compounds of DDT were also found: p,p`DDE and p,p`DDD, but their contents did not exceed 2 µg/kg DM. In one sludge sample, lindane (gamma-hexachlorocyclohexane) was measured – 2.9 µg/kg DM. The contents of polychlorinated biphenyls in three separate sludge samples were remarkably different from each other, 4.6, 34.3 and 121 µg/kg DM, respectively. The content of hexachlorobenzene was 1.4 µg/kg DM. and only exceeded the limit of quantification (1 µg/kg DM) in one sludge sample. p,p`DDE and p,p`DDD, but their content did not exceed 2 µg/kg DM. In one sludge sample, lindane (gamma-hexachlorocyclohexane) was measured – 2.9 µg/kg DM. The contents of polychlorinated biphenyls in three separate sludge samples were remarkably different from each other, 4.6, 34.3 and 121 µg/kg DM, respectively. The content of hexachlorobenzene was 1.4 µg/kg DM and only exceeded the limit of quantification (1 µg/kg DM) in one sewage sludge sample.

1.3.4. Summary of results and recommendations

In the table below, there is a brief outline of which hazardous substances were mainly contained in the wastewater of the industrial enterprises that participated in survey, in the leachate of semi-coke and ash deposits, or the domestic waste water, and what should be considered as the source of such hazardous substances.

Table 1.3.4.1. Occurrence and significance of hazardous substances for country

Source	Hazardous substances
Chemical industry	Mono- and dibasic phenols, pentachlorophenol, polyaromatic 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-tert-butylphenol), phthalates (di(2-ethylhexyl)phthalate, diisobutylphthalate).
Semi-coke and ash deposit	Mono- and diphenols, arsenic, pentachlorophenol, polyaromatic hydrocarbons (naphthalene, fluoranthene, anthracene), volatile organic compounds (benzene), organotin compounds (monooctyltin, monobutyltin).
Domestic waste water (household effluents)	Phthalates (di(2-ethylhexyl)phthalate, diisononylphthalate, diethylphthalate, diisobutylphthalate), alkylphenols and their ethoxylates (isononylphenol, 4-t-octylphenol-monoethoxylate), organotin compounds (monobutyltin, monooctyltin).

Based on this research, the most problematic hazardous substances in the industrial area of Northeast Estonia turned out to be mono- and dibasic phenols, pentachlorophenol, from polyaromatic hydrocarbons naphthalene, anthracene and fluoranthene as well as organotin compounds and phthalates.

Considering the high quantities of hazardous substances in the wastewater of industrial plants in Northeast Estonia, in the leachate from semi-coke and ash deposits as well as in the domestic wastewater discharged into the Kohtla-Järve wastewater treatment plant, the treatment plant copes with the cleaning of wastewater relatively well, because the contents of those hazardous substances in effluent, for which the limit values have been laid down by Estonian law, met the requirements. However, a high quantity of organotin compound monobutyltin was found in the effluent during the survey, and it should be considered that all the hazardous substances present in the effluent are discharged into the Gulf of Finland. At the same time, the sewage sludge was contaminated by hazardous substances – organotin compounds, polychlorinated biphenyls and phthalates – and it is not recommended to use such sludge in the agriculture.

The domestic wastewater should definitely be regarded as an equal source of hazardous substances compared to industrial wastewater. Domestic wastewater contained alkylphenols and their ethoxylates, phthalates and also organotin compounds in very high concentrations.

2. Summary of the results from all Baltic States

The aim was to track the sources of the most widely spread or polluting substances (e.g. which were found in high concentrations in the environment - in surface water bodies, coastal areas or in the effluents or sewage sludge of WWTPs).

Sampling covered different types of sites, which could potentially emit the hazardous substances:

- different industries
- commercial facilities (e.g. laundries, supermarkets, car washing)
- run-off from specific areas (e.g. car shredding facilities, industrial areas)
- filtrate from landfills
- leakage from shipyards
- residential areas - household effluents

The substances for investigation on their sources were chosen based on the results from the BaltActHaz project screening of hazardous substances in Estonia and Latvia, and in Lithuanian environment in 2006. In table below the overview on analysed substances is given.

Table 2.1. Substances analysed in the source tracking activity in all Baltic States

Estonia: 134 substances	Latvia: 43 substances	Lithuania: 104 substances
organotin compounds polybrominated diphenylethers (PBDEs) phtalates alkylphenols and their ethoxylates volatile organic compounds (VOC) chlorinated paraffins perfluorinated compounds pesticides polycyclic aromatic hydrocarbons (PAH) pentachlorphenol heavy metals mono- and dibasic phenols PCB	polybrominated diphenylethers (PBDEs) alkylphenols and their ethoxylates chlorinated paraffins perfluorinated compounds pesticides	organotin compounds polybrominated diphenylethers (PBDEs) phtalates alkylphenols and their ethoxylates volatile organic compounds (trichloromethane) chlorinated paraffins perfluorinated compounds HBCDD

In the table below, there is an overview of the results which hazardous substances were mainly contained in the wastewater of the industrial plants and other facilities that participated in survey, in surface run-off from industrial areas, in the leakages of landfills or semi-coke and ash deposits, or in the domestic wastewater, and what should be considered as the source of such hazardous substances.

Table 2.2. Occurrence and significance of hazardous substances in Baltic States

Industries/industrial wastewater	HS
Metal processing industry and galvanic	MBT, DBT, Monooctyltin, Dioctyltin, MCCP, SCCP, Octylphenol, Nonylphenol & ethoxylates, DEHP
Production of building materials	Dioctyltin, MBT, DEHP, HBCDD
Wood and pulp industry	MCCP, SCCP, Octylphenol, Nonylphenol& ethoxylates, MBT, DBT
Leather industry	MCCP, Octylphenol, Nonylphenol& ethoxylates, MBT, DBT, TBT, Monooctyltin, Dioctyltin, Perfluorinated compounds
Rubber industry	MCCP, Octylphenol, Nonylphenol & ethoxylates, MBT, DBT
Oil Shale Processing & production of chemicals	One- and dibasic phenols, pentachlorophenol, naphthalene, anthracene, fluoranthene, DEHP
Pharmaceutical industry	Octylphenol, Nonylphenol, Monobutyltin, Dibutyltin
Production of industrial cleaning chemicals	Octylphenol, Nonylphenol & ethoxylates
Production of cement/concrete/asphalt	Octylphenol, Nonylphenol, MBT
Textile industry	Octylphenol, Nonylphenol &ethoxylates, MBT, DBT, Monooctyltin, Dioctyltin
Plastic industry	Octylphenol, Nonylphenol & ethoxylates, MBT, PFOA, DEHP
Production of panels	MBT, TBT, Monooctyltin, Dioctyltin
Production of semiconductors	Perfluorinated compounds, Trichloromethane
Paint industry	DEHP, 4-tert-octylphenol, 4-nonylphenol, NPE
Printing houses	MCCP, Octylphenol, Nonylphenol&ethoxylates
Household effluents/wastewater from residential areas	DEHP, Diisononylphthalate, Diethylphthalate, Diisobutylphthalate, Isononylphenol, 4-t-octylphenol-monoethoxylate, MCCP,MBT, Monooctyltin
Other objects/commercial facilities	
Laundries	MCCP, SCCP, Octylphenol, Nonylphenol& ethoxylates, Perfluorinated compounds
Car washing effluents	MCCP, Octylphenol, Nonylphenol & ethoxylates, DEHP, DEP, Di-iso-butylphthalate, Di-n-butylphthalate
Car shredding facilities	MBT, DBT, Perfluorinated compounds
Supermarkets	MCCP, SCCP, DEHP, DEP, Di-iso-butylphthalate, Di-n-butylphthalate
Regeneration of used oil	Octylphenol, Nonylphenol& ethoxylates, DEHP, Di-n-butylphthalate
Landfills	
Leakage from landfills	Octylphenol, Nonylphenol&ethoxylates, MBT, DBT, TBT, Monooctyltin, Dioctyltin, PFOS,PFOA, DEHP, Di-iso-butylphthalate, Di-n-butylphthalate
Leachate water from semicoke landfill and ash depository (remains from oil shale processing)	One- and dibasic phenols, pentachlorophenol, arsenic, naphthalene, anthracene, fluoranthene,benzene, MBT, Monooctyltin
Surface run-off from industrial areas	Octylphenol, Nonylphenol, MBT, DBT
Shipyards	
Leakage from shipyards	MBT, DBT, TBT, Monophenyltin, Diphenyltin, Monooctyltin, Dioctyltin, DEHP, MCCP

3. Further recommendations for identification of sources of hazardous substances

This chapter will introduce the method used to track or to check concrete source discharging hazardous substances into combined sewage system, which is often called sewer film sampling. In Germany this method is sufficient to prove the company discharges certain hazardous substances. The method employs investigation of sewer films or sewer slime.

Sewer films are known as microbial layers on the inside of sewer pipes, which are formed by deposition of organic matters. Due to their high content of lipids, they trap lipophilic compounds and particulate matter and can be used as indicators for organic and inorganic pollutants. This material has a memory effect because it enriches numerous pollutants appearing in the wastewater. The capability of sewer slime to accumulate different hazardous substances from municipal wastewater can be exploited to identify the sources of sewage system/sludge pollution.

How it works? Biofilm samplers are the artificial growth surface for bacteria and microorganisms. There are different types of samplers, e.g. it can consist of plastic-foil-stripes (1-2 m long) to generate biofilms on the foil-surfaces. They are installed at appropriate places in the sewer canal as a growth surface for the sewer film. After a growth time of approx. 1 – 3 weeks the sewer film has the same composition as the natural sewer film in the canal grown in the same time. Therefore the analysis results of these two sewer films will show the same pollutant content. After the exposure of the sampling devices in the sewers the biofilms get extracted from the foils and the extracts analysed by appropriate method, e.g. LC-MS-MS for pharmaceutical residues and PFTs.

If there is a wish to check specific source, then biofilm samplers should be installed before the wastewater from this source enters the sewage system and after. If the analysis indicates increase of concentration of hazardous substance after the pipe from the potential pollution source, it indicates the hazardous substance discharged from this source.

What pollutant discharge can be detected? Heavy metals, organic pollutants such as AOX, PCB, dioxins, PAH, PCP, organotin compounds or perflourated compounds (PFC/PFT), chlorinated paraffins, pharmaceutical residues can be measured.

What could be the application of the method? Typical fields of application are violation of legal limits in the sewage sludge, high drain levels or preventive protection against unexpected pollutant discharge. For a systematic monitoring of the sewer system biofilms samplers should be taken out and the sewer film extracted periodically (e.g. every 1-3 months or in the same intervals as the sludge or waste water analyses).

What is approximate cost? The prices of biofilm samplers are dependant on the laboratory. For example:

- German laboratory Agrolab (www.agrolab.de): the reusable sewer film growth body costs € 29.00 excluding VAT;
- ALS Sweden (www.alsglobal.se): the cost of the samplers (2 m long foils) are €35.

Advantages of the method

- Usually certain hazardous substances are used in specific process, operation and as not all the operations in company are continuous, therefore it is difficult to "catch" the moment when wastewater from the process of interest is discharged. Sewer films allow a detailed localization of a specific input in a time scale of at least weeks. THerefore also temporally limited emissions are covered.
- It provides a consistent, cost-effective option for monitoring and tracking hazardous dischargers into the sewer system of waste water treatment plant.
- Extensively branching sewers make it difficult to locate a specific polluter, because the control of every branch would be much too costly.

Other considerations. The intervals of the sampling and the related possibility of tracking the discharger comply with the enrichment and binding of the pollutant measured. This should therefore be discussed with the laboratory.

List of abbreviations

AA-EQS	Environmental Quality Standard expressed as an annual average value
AA-MAC	Maximum alowable concentration expressed as an annual average value
APE	Alkylphenol ethoxylates
BS	Bottom sediments
BBP	Benzyl butyl phthalate
CAS	Unique numerical identifiers assigned by the “Chemical Abstracts Service“
DBP	Dibutylphtalate
DBT	Dibutyltin
DCHP	Di-cyclohexyl-phthalate
DEHP	Di-2-ethylhexylphtalate
decaBDE	2,3,3’,4,4’,5,6-Heptabromodiphenyl Ether
DEP	Diethylphthalate
DM	Dry matter
DMP	Dimethylphthalate
DPP	Dipropylphthalate
DPP (iso)	Di-iso-propylphthalate
DPT	Diphenyltin
DOP	Dioctylphenol
DOT	Dioctyltin
EC	European Commission
ELV	Emission limit values
EQS	Environmental quality standard
HBCDD	Hexabromcyclo dodecane
HELCOM	Baltic Marine Environment Protection Commission (Helsinki Commission)
HS	Hazardous substances
IPPC	Integrated pollution prevention and control
LC	Limit concentration
LOD	Limit of detection
LOQ	Limit of quantification
MAC	Maximum alowable concentration
MAC-EQS	Environmental Quality Standard expressed as a maximum allowable concentration
MBT	Monobutyltin
MCCP	Medium chain chlorinated parafins
MOT	Mono-octyltin
MPT	Mono-pentyltin
MU	Measurement uncertainty
NBDE	Nonabromodiphenylether
NP	Nonylphenols
NPE	Nonylphenolethoxylate
NP1EO	Nonylphenol mono-ethoxylate
NP2EO	Nonylphenol di-ethoxylate
NP3EO	Nonylphenol tri-ethoxylate
OP	Octylphenols
OPE	Octylphenolethoxylate
OP1EO	Octylphenol mono-ethoxylate
OP2EO	Octylphenol di-ethoxylate
OP3EO	Octylphenol tri-ethoxylate

OT	Organotin compounds
PBDE	Brominated diphenylethers
PBDE17	2,2',4-Tribromodiphenyl Ether
PBDE28	2,4,4'-Tribromodiphenyl Ether
PBDE47	2,2',4,4'-Tetrabromodiphenyl Ether
PBDE66	2,3',4,4'-Tetrabromodiphenyl Ether
PBDE71	2,3',4',6-Tetrabromodiphenyl Ether
PBDE85	2,2',3,4,4'-Pentabromodiphenyl Ether
PBDE99	2,2',4,4',5-Pentabromodiphenyl Ether
PBDE100	2,2',4,4',6-Pentabromodiphenyl Ether
PBDE138	2,2',3,4,4',5'-Hexabromodiphenyl Ether
PBDE153	2,2',4,4',5,5'-Hexabromodiphenyl Ether
PBDE154	2,2',4,4',5,6'-Hexabromodiphenyl Ether
PBDE183	2,2',3,4,4',5',6-Heptabromodiphenyl Ether
PBDE190	2,3,3',4,4',5,6-Heptabromodiphenyl Ether
PBDE196	2,2',3,3',4,4',5,6'-Octabromodiphenyl ether
PBDE197	2,2',3,3',4,4',6,6'-Octabromodiphenyl ether
PBDE203	2,2',3,4,4',5,5',6-Octabromodiphenyl Ether
PBDE209	2,3,3',4,4',5,6-Heptabromodiphenyl Ether, decaBDE
pentaBDE	Pentabromodiphenyl ether
PFBS	Perfluorobutanesulfonic acid
PFC	Perfluoro Compounds
PFDA	Perfluorodecanoic acid
PFDoDA	Perfluorododecanoic acid
PFDS	Perfluoro-n-dodecanoic acid
PFHpA	Perfluoro-n-heptanoic acid
PFHxS	Perfluoro-1-hexanesulfonate
PFNA	Perfluoro-n-nonanoic acid
PFOA	Perfluoro-n-octanoic acid
PFOS	Perfluoro-1-octanesulfonate
PFOSA	Perfluorooctanesulfonamide
PTFE	Polytetrafluoroethylene (Teflon)
PFUnDA	Perfluoro-n-undecanoic acid
PVC	Polyvinylchloride
REPD	Regional Environmental Protection Departments
SCCP	Short chain chlorinated parafins
SW	Surface water
TBT	Tributyltin
TCHM	Trichloromethane
TCHT	Tricyclohexyltin
TPhT	Triphenyltin
TTBT	Tetrabutyltin
WFD	Water Frameworkk Directive (2000/60/EC)
WS	Sludge from WWTP
WW	Wastewater
WWTP	Wastewater treatment plant

Project website

www.baltacthaz.bef.ee

Estonia
Kertu-Kirit Sild
Project Manager
Tel.: + 372 6597 028
Fax: + 372 6597 027
E-mail: kertukirit.sild@bef.ee
Homepage: www.bef.ee

Latvia
Valters Toropovs
Project Coordinator
Tel.: + 371 6735 7546
Fax: + 371 6750 7071
E-mail: valters.toropovs@bef.lv
Homepage: www.bef.lv

Lithuania
Justė Buzelytė
Project Coordinator
Tel.: +370 5215 9287
Fax: +370 5213 5068
E-mail: juste.buzelyte@bef.lt
Homepage: www.bef.lt

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LIETUVOS RESPUBLIKOS APLINKOS MINISTERIJA

MINISTRY OF ENVIRONMENTAL PROTECTION AND REGIONAL DEVELOPMENT

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