



# PROPOSALS FOR THE STATE MONITORING PROGRAMME

2011



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## 1. 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 screening of hazardous substances in the environment, WWTPs as well as investigation of potential sources of hazardous substances in Estonia, Latvia and Lithuania are described in the separate reports, which are available for download on the project website **[www.baltacthaz.bef.ee](http://www.baltacthaz.bef.ee)**.

So far many of those substances were not really monitored in the Baltic countries due to the different reasons, i.e. lack of resources, lack of laboratory capacities etc. Therefore one of the project activities is focused on the **elaboration of proposal for the improvements with regard to detection and monitoring of hazardous substances, including the analysis of state-of-the-art of current environmental monitoring system**. The proposals are mainly based on the results from the screening activities performed within the project. However, also other available data are considered.

This report focuses on the following issues:

- legal framework for the monitoring of hazardous substances and the purpose of monitoring in general,
- analytical requirements for the chemical analysis and monitoring of water status and related challenges,
- analysis of current practices on monitoring of hazardous substances in Latvia,
- proposals for improvement of the current monitoring system.

The report is mainly targeted to the authorities that are responsible for the implementation and enforcement of policies for the control of hazardous substances (WFD and HELCOM BSAP), especially those developing environmental monitoring programmes.

## 2. BACKGROUND ON THE MONITORING OF HAZARDOUS SUBSTANCES IN THE WATER

### 2.1. LEGAL FRAMEWORK FOR THE MONITORING OF HAZARDOUS SUBSTANCES

#### 2.1.1. EU REQUIREMENTS FOR THE CHEMICALS MONITORING

A strategy for dealing with **pollution of water from chemicals is set out in Article 16 of the Water Framework Directive 2000/60/EC (WFD)**. As a first step of this strategy, a list of priority substances was adopted identifying 33 substances of priority concern at Community level. It has the objective to ensure a high level of protection against risks to or via the aquatic environment arising from these 33 priority substances by setting European environmental quality standards. In addition, the WFD requires Member States to identify specific pollutants in the River Basins and to include them in the monitoring programmes. **Monitoring of both WFD priority substances and other pollutants for the purpose of determination of the chemical and ecological status shall be performed according to Article 8 and Annex V of the.**

Article 8 of WFD lays down the main requirement to establish monitoring of surface water status, groundwater status and protected areas. Member States shall ensure the establishment of programmes for the monitoring of water status in order to establish a coherent and comprehensive overview of water status within each river basin district. The programmes have to be operational at the latest by 22 December 2006, and must be in accordance with the requirements of Annex V, which provides details of how the programme should be designed, what should be monitored for and how the results should be presented.

The **main reasons** for undertaking monitoring for the WFD are to:

- establish an overview of the water status of each river basin district,
- classify individual water bodies as to their water status.

Three types of **monitoring techniques** are required for surface waters under WFD:

- **Surveillance monitoring:** to validate the characterisation pressure and impact assessments, to identify long term changes and trends → priority list substances discharged into the river basin or sub-basins must be monitored; other pollutants also need to be monitored if they are discharged in significant quantities in the river basin or sub-basin;
- **Operational monitoring:** to help classify water bodies which are at risk of failing to meet 'good status' objectives;
- **Investigative monitoring:** to assess why a waterbody is failing to achieve its objectives and decide what action is needed (it starts when data from surveillance and operational monitoring are available).

The **chemical monitoring according WFD covers:**

- all surface waters (rivers, lakes and artificial waters; transitional waters; coastal waters up to one nautical mile and territorial waters, extending to 12 nautical miles from territorial baseline of the Member State),
- groundwater.

**Parameters to be monitored:**

- **priority substances:** compliance with European Environmental Quality Standards (AA-EQS and MAC-EQS),
- other pollutants (river basin specific substances): compliance with national EQS,
- physico-chemical parameters supporting interpretation of biological data,
- parameters required for interpretation of the results of chemical measurements (e.g. DOC, Ca, SPM).

Monitoring in biota is compulsory only for mercury, HCB, and hexachlorobutadiene. Instead of checking compliance with biota EQS Member States may set up a more stringent EQS for water (replacing the one suggested by the Commission) to provide the same level of protection as the biota standard.

The monitoring frequencies given in WFD, Annex V 1.3.4 of **once-a-month for priority substances and once-per-three-months for other pollutants** will result in a certain confidence and precision. At the same time reduced monitoring frequencies, and under certain circumstances, even no monitoring may be justified by technical knowledge and expert judgement when monitoring reveals/has revealed that concentrations of substances are far below the EQS, declining or stable and there is no obvious risk of increase.

**Directive 2008/105/EC** sets the environmental quality standards for 41 substances in the water matrix, but also gives an option to the Member States to derive **EQS for sediment and/or biota**. The frequency of monitoring of priority substances in the water column (whole water or dissolved) differs from those in sediment and biota and it is clear that the choice of the matrix to be monitored is strategic in terms of costs and resources for compliance checking. The minimum frequency required for water monitoring of priority substances is once per month (once every 3 months for river-basin-specific pollutants).

Article 3 of Directive 2008/105/EC states that (point 2) Member States may opt to apply EQS for sediment and/or biota instead of those laid down in Part A of Annex I in certain categories of surface water. According that the frequency of monitoring for sediment and biota shall take place once per year if unless technical knowledge and expert judgment justify another interval. Otherwise (point 3) the frequency of monitoring for sediment and biota shall take place once per three year if unless technical knowledge and expert judgment justify another interval

An overall methodological approach to monitoring for the implementation of the WFD is provided in **guidance documents**, however they are not legally binding documents:

- Guidance Document No. 7 - Monitoring under the Water Framework Directive
- Guidance Document No. 19 - Guidance on surface water chemical monitoring
- Guidance Document No: 25 - Guidance on chemical monitoring of sediment and biota

They can be find on CIRCA site:

[http://circa.europa.eu/Public/irc/env/wfd/library?l=/framework\\_directive/guidance\\_documents](http://circa.europa.eu/Public/irc/env/wfd/library?l=/framework_directive/guidance_documents)

### **2.1.2. INTERNATIONAL REQUIREMENTS FOR THE CHEMICALS MONITORING**

The monitoring is also necessitated by the several international environmental agreements, where the most relevant for the Baltic countries are the HELCOM Convention, which sets the requirements to monitor the Baltic Sea status. The aims of the monitoring, as decided by HELCOM are:

- To identify and quantify the effects of anthropogenic discharges/activities in the Baltic Sea, in the context of the natural variations in the system, and
- To identify and quantify the changes in the environment as a result of regulatory actions.

It also provides the guidance on it, so-called COMBINE (Cooperative Monitoring in the Baltic Marine Environment) manual:

[http://www.helcom.fi/groups/monas/CombineManual/en\\_GB/Contents/](http://www.helcom.fi/groups/monas/CombineManual/en_GB/Contents/)

### **2.1.3. LEGAL FRAMEWORK FOR THE MONITORING IN LATVIA**

The environmental monitoring framework in Latvia mostly is set by "Environment protection law", where it is stated that Environment monitoring is organized and carried out by state and local government structures as well as commercial structures. Once in a four year period the Cabinet of Ministers accept framework of Environment program based of which minister of environment accepts four year State environment monitoring program which is carried out by state environment protection organizations and financed from state budget. Monitoring carried out by commercial structures basically is regulated by Cabinet of ministers rule Nr. 34 (22.01.2002) "Rules on polluting substances emissions in water", which state that monitoring frequency etc. is set by Regional environment service individually to respective commercial structure.

## 2.2. PURPOSE OF THE MONITORING OF HAZARDOUS SUBSTANCES

The overall aim of environmental monitoring is to describe the state of the environment, to show how well our environmental objectives are being met, and to warn of new environmental issues.

Despite the regulatory requirement to perform the monitoring of hazardous substances and in such a way to assess the compliance with standards and objectives, there are number of benefits what monitoring data can provide and why they are necessary:

- it describes the state of the environment and reflect whether the “good status of the environment” (pollutants concentrations not exceeding EQS, what means that it is safe for the environment and people) is achieved,
- it helps to assess the threats to the environment (as well as human health through the environment) in the early stage, i.e. to identify the substances of concern and what is the level of concern,
- it provides data that can serve as a basis for concrete remedial actions and help to monitor the progress towards changes and efficacy of action decided on and/or measures applied on (by juxtaposing current and past states we can detect changes in the environment, what enables to see whether past measures have had the desired effect, or whether further study is necessary to determine whether or not an observed change is a sign of a problem),
- allows to estimate the pollution loads transfers across international boundaries or into the sea and provide a basis for analysing the national and international environmental impacts of different emission sources,
- it helps to ascertain formerly unidentified reasons for failure to achieve environmental objectives,
- it supports in assessment of impact of accidental pollution,
- the measured environmental concentrations of harmful substances are needed in the consumer and industrial chemicals risk assessment carried out in the EU; the information gained can also be utilized in national risk assessment work and emission source identification,
- it strengthen capacity of environmental authorities for the decision making in relation to integrated planning and control of emissions of hazardous substances,

Environmental monitoring is a long-term activity. Measurements must often be taken over long periods in order to show whether a change is due to human activity or natural variation.

### 3. ANALYTICAL REQUIREMENTS FOR CHEMICAL ANALYSIS AND MONITORING OF WATER STATUS AND RELATED CHALLENGES

#### 3.1. TECHNICAL SPECIFICATIONS FOR CHEMICAL ANALYSIS ACCORDING COMMISSION DIRECTIVE 2009/90/EC

The quality and comparability of analytical results generated by laboratories to perform water chemical monitoring pursuant to Article 8 of Directive 2000/60/EC should be ensured. Therefore the Commission directive **2009/90/EC laying down technical specifications for chemical analysis and monitoring of water status was adopted**. It establishes minimum performance criteria for methods of analysis to be applied by Member States when monitoring water status, sediment and biota, as well as rules for demonstrating the quality of analytical results.

The main requirements as described in the directive 2009/90/EC:

- all methods of analysis used for the purposes of chemical monitoring programmes carried out under Directive 2000/60/EC are validated and documented in accordance with EN ISO/IEC-17025 standard or other equivalent standards accepted at international level,
- minimum performance criteria for all methods of analysis applied are based on an uncertainty of measurement of 50 % or below ( $k = 2$ ) estimated at the level of relevant environmental quality standards and a limit of quantification equal or below a value of 30 % of the relevant environmental quality standards ( $LOQ \leq 0.3 \cdot AA-EQS$ ),
- in the absence of relevant EQS for a given parameter, or in the absence of method of analysis meeting the minimum performance criteria, monitoring is carried out using best available techniques not entailing excessive costs,
- laboratories apply quality management system practices in accordance with EN ISO/IEC-17025 or other equivalent standards accepted at international level (EN ISO/IEC-17025 standard on general requirements for the competence of testing and calibration laboratories provides appropriate international standards for the validation of the methods of analysis used).
- laboratories or parties contracted by laboratories demonstrate their competences in analysing relevant physico-chemical or chemical measurands by:
  - o (a) participation in proficiency testing programmes covering the methods of analysis at levels of concentrations that are representative of chemical monitoring programmes carried out under Directive 2000/60/EC,
  - o (b) analysis of available reference materials that are representative of collected samples which contain appropriate levels of concentrations in relation to relevant environmental quality standards.

Member States shall bring into force the laws, regulations and administrative provisions necessary to comply with this Directive at the latest two years after its entry into force, it means in 2011.

#### 3.2. CHALLENGES RELATED TO TECHNICAL SPECIFICATIONS OF COMMISSION DIRECTIVE 2009/90/EC

##### 3.2.1. AVAILABILITY OF STANDARD METHODS

Some priority substances is very difficult to analyse as there is a problem also faced on EU level with regard to availability of standardized methods meeting technical specifications of the Directive 2009/90/EC:

- PBDEs: no standard for water available, problems with sensitivity of the methods (LOQ hard to meet as the sum concentration of 6 congeners has to be below 0.5 ng/l and 0.2 ng/l respectively),

- SCCP: no standard for water available, analysis not under control also in the research laboratories, most frequently applied method is GC-ECNI-MS (but with this method there are some unsolved problems: isomers with less than five chlorine cannot be detected; problems with calibration due to dependency of response on degree of chlorination),
- TBT: extremely low LOQ required due to very low EQS – 0.2 ng/l, existing standard methods not sensitive enough,
- PAH (5- and 6-ring PAH): sensitivity for some parameters (in particular for the 6-ring isomers) not sufficient with respect to the low EQS; method is not suitable to cope with samples with SPM content (requirement for whole water samples),
- Organochlorine pesticides: sensitivity of existing standard methods insufficient for cyclodiene pesticides, endosulfane and pentachlorobenzene; difficulties of meeting required LOQ for DDT, hexachlorocyclohexane and hexachlorobenzene.

**Table 1. Overview on the standard methods available (Source: Circa website)**

Priority Substance	Standard	Principle	LLOA Standard [µg/l]	Target LOQ (AA-QS *0,3)	Target LOQ (AA-QS *0,3)	Status	
				for inland surface waters [µg/l]	for other surface waters [µg/l]	inland surface waters	other surface waters
Alachlor <sup>1)</sup>	EN ISO 6468:1996	GC/ECD		0,1	0,1	B	B
Anthracene	ISO 17993:2002	HPLC/Fluo	0,01	0,03	0,03	A	A
Atrazine	EN ISO 11369:1997	HPLC/UV	0,1	0,18	0,18	A	A
	EN ISO 10695:2000	GC/NPD (MS for conf.)	0,05	0,18	0,18	A	A
Benzene	EN ISO 15680:2003	Purge/Trap + Therm. Desorp.	0,01	3	2,4	A	A
	ISO 11423-1:1997	Headspace-GC/FID	2			A	A
Cadmium and its compounds	ISO 17294-2:2003	ICP-MS	0,5	0,024-0,075	0,06	C	C
Chlorfenvinphos	EN 12918:1999	GC	0,01	0,03	0,03	A	A
Chlorpyrifos (-ethyl, -methyl)	EN 12918:1999	GC	0,01	0,01	0,01	A	A
1,2-Dichloroethane	EN ISO 10301:1997	GC or Headspace-GC	5	3	3	B	B
	EN ISO 15680:2003	Purge/Trap + Therm. Desorp.	0,01			A	A
Dichloromethane	EN ISO 10301:1997	GC or Headspace-GC-ECD or other	50	6	6	B	B
	EN ISO 15680:2003	Purge/Trap + Therm. Desorp.	0,01			A	A
Di(2-ethylhexyl)phthalate (DEHP) <sup>2)</sup>	ISO 18856:2004	GC/MS	0,02	0,390	0,390	C	C
Diuron	EN ISO 11369:1997	HPLC/UV	0,1	0,06	0,06	B	B
DDT (4 isomers) <sup>3)</sup>	EN ISO 6468:1996	GC/ECD	0,01	0,008	0,008	C	C
Fluoranthene	ISO 17993:2002	HPLC/Fluo	0,01	0,03	0,03	A	A
Hexachlorobenzene <sup>4)</sup>	EN ISO 6468	GC/ECD	0,01	0,003	0,003	C	C
Hexachlorobutadiene <sup>1)</sup>	EN ISO 10301:1997	GC or Headspace-GC-ECD or other	0,01	0,03	0,03	A	A
	EN ISO 15680:2003	Purge/Trap + Therm. Desorp.	0,01			A	A
	EN ISO 6468:1996	GC/ECD				B	B
Hexachlorocyclohexane <sup>5)</sup>	EN ISO 6468:1996	GC/ECD	0,01	0,006	0,0006	C	D
Isoproturon	EN ISO 11369:1997	HPLC/UV	0,1	0,1	0,1	A	A
Lead and its compounds	ISO 17294-2:2003	ICP-MS	0,1	2,2	2,2	A	A
	ISO 15586:2003	ET-AAS	10			B	B
Mercury and its compounds <sup>6)</sup>	EN 12338:1998	CV-AAS with Amalgamation	0,01	0,015	0,015	A	A
	ISO 17582:2006	Atomic fluor. spectrometry	0,01			A	A
Naphthalene	ISO 17993:2002	HPLC/Fluo	0,01	0,72	0,36	A	A
	EN ISO 15680:2003	Purge/Trap + Therm. Desorp.	0,01			A	A
Nickel and its compounds	ISO 17294-2:2003	ICP-MS	1	6	6	A	A
	EN ISO 11885:2007	ICP-AES	2-5*			A	A
	ISO 15586:2003	ET-AAS	7			B	B
Nonylphenol <sup>8)</sup>	ISO 18857-1:2005	GC/MS	0,005	0,090	0,090	C	C
Octylphenol (4-(1,1,3,3)-Tetramethylbutylphenol)	ISO 18857-1:2005	GC/MS	0,005	0,03	0,003	A	D
Pentachlorophenol	EN 12673:1998	GC/ECD/MS after Deriv.	0,1	0,12	0,12	A	A
Benzo(a)pyrene	ISO 17993:2002	HPLC/Fluo	0,01	0,015	0,015	A	A
Benzo(b)fluoranthene <sup>1)</sup>	ISO 17993:2002	HPLC/Fluo	0,01	0,005	0,005	C	C
Benzo(k)fluoranthene <sup>1)</sup>	ISO 17993:2002	HPLC/Fluo	0,01	0,005	0,005	C	C
Simazine	EN ISO 11369:1997	HPLC/UV	0,1	0,3	0,3	A	A
	EN ISO 10695:2000	GC/MS or GC/NPD	0,05			A	A
Tetrachloroethene	EN ISO 10301:1997	GC or Headspace-GC-ECD or other	0,1	3	3	A	A
	EN ISO 15680:2003	Purge/Trap + Therm. Desorp.	0,01			A	A
Tetrachloromethane	EN ISO 10301:1997	GC or Headspace-GC-ECD or other	0,1	4	4	A	A
	EN ISO 15680:2003	Purge/Trap + Therm. Desorp.	0,2			A	A
Trichlorobenzenes	EN ISO 6468:1996	GC/ECD	0,01	0,12	0,12	A	A
	EN ISO 15680:2003	Purge/Trap + Therm. Desorp.	0,01			A	A
Trichloroethene	EN ISO 10301:1997	GC or Headspace-GC-ECD or other	0,05	3	3	A	A
	EN ISO 15680:2003	Purge/Trap + Therm. Desorp.	0,05			A	A
Trichloromethane	EN ISO 10301:1997	GC or Headspace-GC-ECD or other	0,05	0,75	0,75	A	A
	EN ISO 15680:2003	Purge/Trap + Therm. Desorp.	0,01			A	A
Trifluralin	EN ISO 10695:2000	GC/MS or GC/ECD or GC/NPD	0,05	0,01	0,01	B	B
Pentabromodiphenyl Ether	No standard available						
C10-13-chloroalkanes	No standard available						
Endosulfan	Existing standard method not sensitive enough						
Pentachlorobenzene	Existing standard method not sensitive enough						
Benzo(ghi)perylene	Existing standard method not sensitive enough						
Indeno(1,2,3-cd)pyrene	Existing standard method not sensitive enough						
Tributyltin compounds	Existing standard method not sensitive enough						
Aldrin	Existing standard method not sensitive enough						
Endrin	Existing standard method not sensitive enough						
Isodrin	Existing standard method not sensitive enough						
Dieldrin	Existing standard method not sensitive enough						

\* axial viewing

1) Alachlor and hexachlorobutadiene are not within the scope of the standard but national monitoring laboratories reported that EN6468 may be used for the determination of these compounds.

2) Although the method is applicable to the analysis of DEHP in surface water and allows achieving sufficient low LoQ to conduct compliance checking in principle, many laboratories have serious blank problems and are hence, not able to meet the LoQ performance criterion.

3) According to the results of the CMA survey LoQ low enough to allow compliance checking is difficult to achieve or even impossible for DDT due to the fact that 4 isomers have to be determined.

4) Although the method is applicable to the analysis of mercury in surface water and allows achieving sufficient low LoQ to conduct compliance checking in principle, some laboratories have difficulties in meeting the LoQ performance criterion due to problems with blanks and memory effects.

5) According to the results of the CMA survey, a sufficiently low LoQ for compliance checking is difficult to achieve or even impossible for hexachlorocyclohexane and hexachlorobenzene.

6) Although the method is applicable to the analysis of NP in surface water and allows achieving sufficient low LoQ to conduct compliance checking in principle, many laboratories have serious blank problems and are hence, not able to meet the LoQ performance criterion.

7) Although benzo(k)fluoranthene and benzo(b)fluoranthene (28) are mentioned in the scope LoQ low enough to allow compliance checking is difficult to achieve or even impossible.

**Category:**

A = LLOA meets target LoQ criterion

B = LLOA does not meet target LoQ criterion but CMA survey indicated that laboratories are able to meet target LoQ criterion

C = LLOA does not meet target LoQ criterion, only well-equipped laboratories with highly qualified staff were able to meet target LoQ criterion, there are certain limitations in applicability of the standard

D = Standard not sensitive enough for the analysis of other surface waters.

### 3.2.2. LABORATORY CAPACITIES IN LATVIA

The information about capacity of national laboratories to analyse HS listed in WFD and Minister Cabinet regulations No 118 and No 475 is shown in Annex I of this report. The information includes methods quality limits and accreditation of laboratories to analyse HS in the different matrixes – water, sediments, sludge and biota.

### 3.2.3. DEVELOPMENT OF LABORATORY CAPACITIES

There are many important considerations for the development of national laboratory strategy plan. Issues to be addressed include technical, legal, quality, financial and logistical matters.

The potential way for developing national laboratory capacities is described below.

1. Analyse „mandatory“ needs for analysis by state, private and other entities based on:
  - a. Legal requirements: substances to be analysed, number of analysis per year (frequency at sites),
    - i. EU requirements where monitoring/control is needed: water, air, soil, biota,
    - ii. International Conventions: UNEP, CLRTAP, HELCOM, IPPC etc.,
    - iii. National priorities
  - b. Emission/pressure information from registers/databases about substances of concern, emerging substances.
2. Analyse test standards and methods:
  - a. Regulatory requirements for laboratory, standards (e.g. 2009/90/EC),
  - b. Availability of standardized methods,
  - c. Availability of innovative and emerging technologies,
  - d. Equipment needed and capacities.
3. Estimate the laboratory utilisation based on mandatory testing (point 1) and capacities (point 2.d).
4. Estimate the investments for the expansion of laboratory capacities for the specific substance/ substance group, potential test fee and its competitiveness in the market:
  - a. New equipment,
  - b. New standards,
  - c. Quality management and accreditation,
  - d. Training of personnel,
  - e. Correlation between laboratories, proficiency testing,
  - f. Etc.
5. Analyse existing capacities on the market (labs, substances analysed, methods used and compliance with mandatory requirements).
6. Estimate the potential forms for the laboratory and capacity raising (governmental, private, manufacturer, tests across multiple laboratories, tests in other countries).

## 4. ANALYSIS OF PRACTICES OF MONITORING AND SCREENING OF HAZARDOUS SUBSTANCES IN LATVIA

### 4.1. WATER MONITORING IN LATVIA DURING 2000 – 2009 (STATE MONITORING PROGRAMS)

Until 2002 when four river basin districts (Gauja, Daugava, Lielupe and Venta RBD) were established the surface water quality in Latvia was monitored in 7 (or 8) districts, i.e. four mentioned districts, in Salaca, Veļikaja, Irbe and the district of small rivers at the Baltic Sea Latvian coast.

Until 2004 Cu, Zn, Cd, Pb and petroleum hydrocarbons were monitored. In 2004 As and Ni were added to the list. Observed concentrations in this period were below limit values in almost all sites in all RBDs: Baltic Sea small rivers BD (Bārta, Saka rivers and Liepājas lake – 6 sites), Daugava (8 sites), Gauja RBD (Gauja 3 sites) Irbe river (1 site), Lielupe RBD (Lielupe – 5 to 7 sites, Mūsa, Mēmele, on boundary), Venta (4 sites). Frequency of the sampling for HS was 4 – 6 times per year.

The first national monitoring program (for period 2006-2008) according to the requirements of WFD was adopted in 2005. Hg, Cd, Ni, Pb, Zn, As and petroleum hydrocarbons were monitored in water objects according to this program. Number of monitored sites was 22 in 2006; 28 in 2007 and 40 in 2008; frequency – 4 to 6 times per year. Since 2006 also a number of pesticides, BTEX and PAH are monitored. Number of the monitored substances in 2008 reached 47.

In 2008 47 hazardous substances and groups of substances and pollutants were determined on boundaries and in mouths of the largest rivers, at inland sites – mostly heavy metals. 40 surface water sites (Gauja – 7, Daugava – 9, Lielupe – 9, Venta – 15) were monitored with a frequency 4 – 6 times per year.

In 2009 monitoring was performed in a reduced extent because of funding cut – at 47 sites 2-4 times. The number of monitored substances also was reduced to 27 hazardous substances/groups of substances.

Complete lists of monitored substances/groups of substances, and periods of observations is compiled in Table 4.1.

**Table 4.1.** Overview of the hazardous substances investigated within monitoring programs in Latvia.

Priority and hazardous substances (Cabinet Regulation No. 118)	Monitored or not monitored (N.m.)
<b>PRIORITY SUBSTANCES</b>	
Alachlor	N.m.
Anthracene	2007; 2008
Atrazine	N.m.
Benzene	2007; 2008
Brominated diphenylether	N.m.
Cd	2000 – 2009
C <sub>10-13</sub> Chloralkanes	N.m.
Chlorfenvinphos	N.m.
Chlorpyrifos	N.m.
1,2-Dichloroethane	N.m.
Dichloromethane	N.m.
Di(2-ethylhexyl)-phthalate (DEHP)	N.m.
Diuron	N.m.
Endosulfan	2006 – 2009
Fluoranthene	2007; 2008
Hexachlorobenzene	2008; 2009
Hexachlorobutadiene	N.m.
Hexachlorocyclohexanes	2006 – 2009
Izoproturon	N.m.
Pb	2000 – 2009

Priority and hazardous substances (Cabinet Regulation No. 118)	Monitored or not monitored (N.m.)
Hg	2005 – 2009
Naphthalene	2007; 2008
Ni	2001; 2004 – 2009
Nonylphenol	N.m.
Octylphenol	N.m.
Pentachloro-benzene	N.m.
Pentachloro-phenol	N.m.
Polyaromatic hydrocarbons (PAH): benzo(a) pyrene, benzo(b)fluor-anthene, benzo(k)fluor-anthene, benzo(g,h,i)-perylene, indeno(1,2,3-cd)-pyrene	2007; 2008
Simazine	N.m.
Tributyltin compounds	N.m.
Trichlorobenzenes	N.m.
Trichloromethane (chloroform)	2007; 2008
Trifluralin	N.m.
<b>HAZARDOUS SUBSTANCES</b>	
Carbon tetrachloride	N.m.
Cyclodyene-class pesticides: aldrin, dieldrin endrine isodrin	2006 –2009 2007 – 2009 2006 – 2009 N.m.
DDT total	2009
para-para-DDT	2006 – 2009
Trichloroethylene	N.m.
Tetrachloroethylene	N.m.
As	2004 – 2009
Zn	1991 – 2009
Cr	2007
Cu	2000 – 2009
2,4-dichlorophenoxyacetic acid	N.m.
Acrylonitrile	N.m.
Diethylamine	N.m.
Dimethoate or rogor	N.m.
Phenols (index of phenols)	2008; 2009
Formaldehyde	N.m.
2-, 3- and 4 chloroaniline	N.m.
Chlorobenzene	N.m.
Polychlorinated biphenyls (PHB)	N.m.
2,4,6-trichlorophenol	N.m.
Monoaromatic hydrocarbons: toluene, ethylbenzene, xylene	2007; 2008
Petroleum hydrocarbons: (C10-C40 index of hydrocarbons)	2000 - 2009

#### 4.1.1 WATER QUALITY WITH REGARD TO HS DURING 2000 – 2009

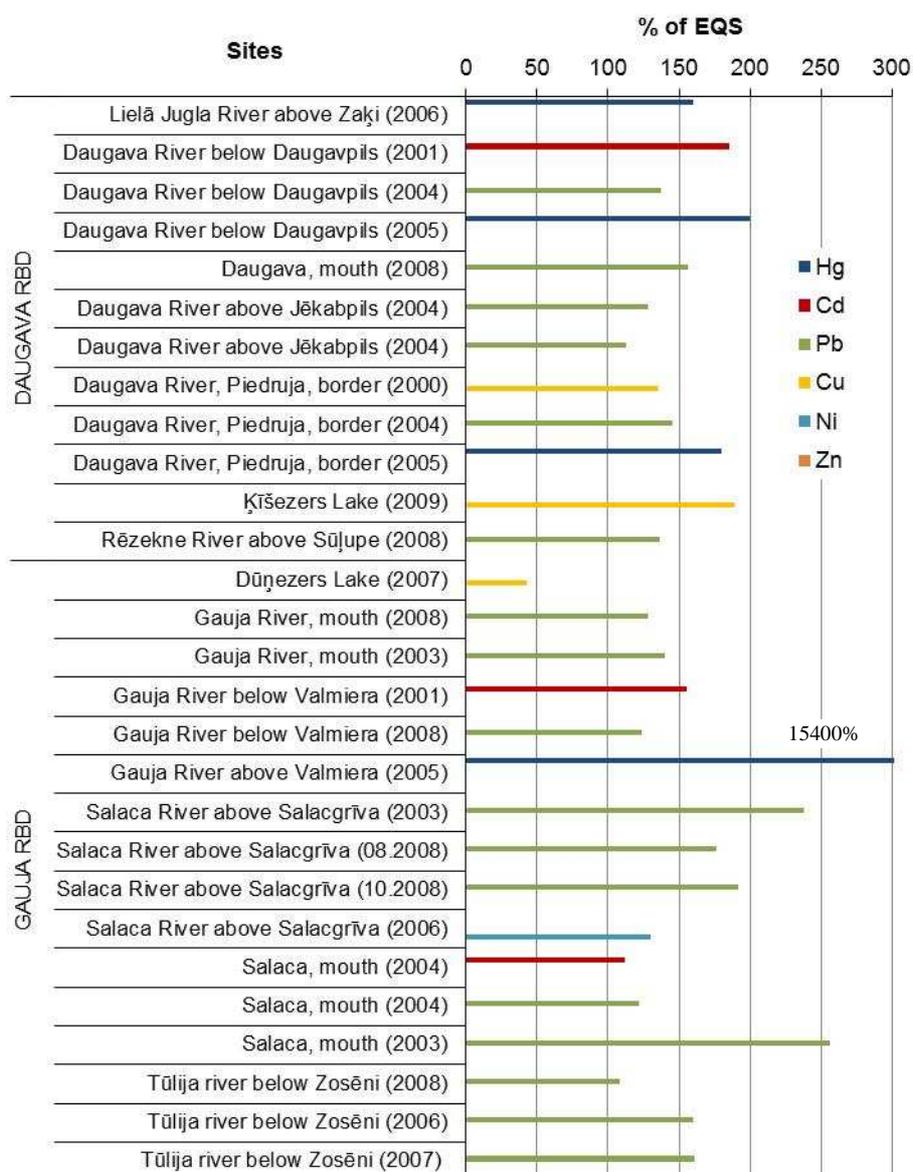
*Metals:* Seven metals – cadmium, lead, mercury, nickel, zinc, chromium and copper were monitored throughout in this period. Average annual concentrations of these metals were not exceeded during this period. In most cases exceeding values (single observations) were observed for Pb (slightly above 1.5 % of all observations). For other metals the concentrations exceeding EQS were less than 1 % of all measurements. The results of single observations – concentrations which exceeded EQS values are shown in Figure 4.1 (Daugava and Gauja RBD) and Figure 4.2 (Lielupe and Venta RBD). Observed values were calculated as percentage from following EQS values: Hg = 0.05 ug/L; Cd = 0.6 ug/L; Pb = 2.5 ug/L; Cu = 9.0 ug/L; Ni = 20 ug/l and Zn = 120 ug/L according to WFD and Cabinet Regulation No.118 "Regulations regarding the Quality of Surface Waters and Ground Waters".

**Organic substances:** During this period EQS were exceeded only for petroleum hydrocarbons (C<sub>10</sub>-C<sub>40</sub> index of hydrocarbons) and also only in few cases.

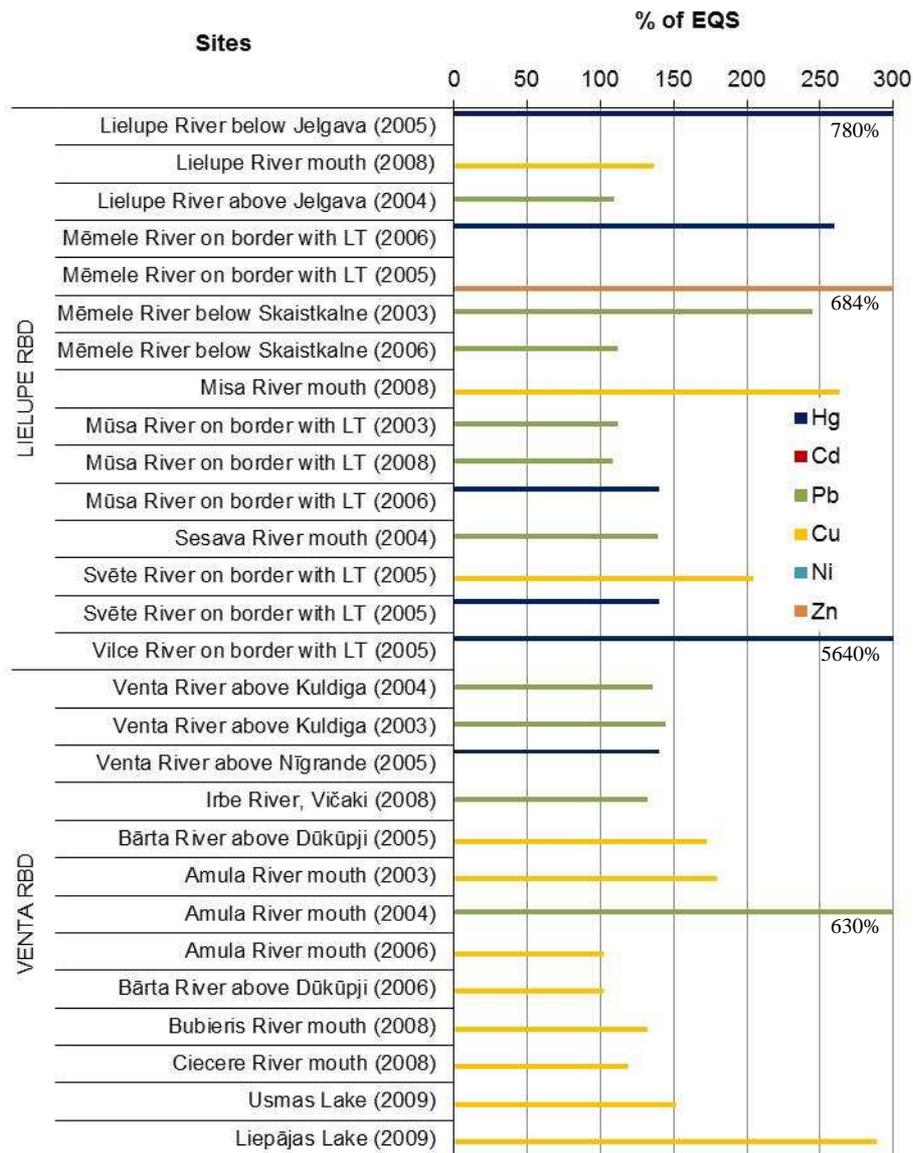
In **2001** the limit values were not exceeded.

In **2002** (December) and **2003** (January) increased concentration of petroleum hydrocarbons was determined in the water of Daugava River nearby Mīlgrāvis which is a port area with heavy water traffic. Slightly exceeded Pb concentrations in the water of Mēmele and Salaca rivers (limit value for Pb until 2009 was 2.5 ug/L) were observed in 2003.

In **2004** exceeded concentrations of Cd and Pb in water were observed at following sites: Cd in Salaca river; mouth nearby Salacgrīva; Pb (concentrations higher than limit value which was in force until 2009) in Daugava River at Piedruja on border with Belorussia, above and below Jēkabpils town, Salaca river mouth nearby Salacgrīva, Lielupe River above Jelgava, Sesava river mouth, Venta River above Kuldīga and at mouth of Amula river.



**Figure 4.1.** Concentrations of metals in water exceeding EQS values during period 2000-2009 in Daugava's and Gauja's RBDs.



**Figure 4.2.** Concentrations of metals in water exceeding EQS values during period 2000-2009 in Lielupe's and Venta's RBDs.

In **2005** exceeded concentration of Hg was determined once in water of Gauja river above Valmiera town (almost 8 times over limit value in this time). During 2005 sampling at this site was performed three times. It seems that it was an accidental emission, as the results of another two samplings were below LoD (0.04 µg/L). Although annual average value exceeded the permissible limit, in this case it was not objective value with respect to environmental quality. The limit values were exceeded also for Zn in Mēmele River; for Hg in Vilce River; for Cu in Svēte and Bārta rivers.

The highest average values for heavy metals (especially for Cu) among RBD were observed in Lielupe River.

In **2006** rather high Zn and Cu concentrations were observed in Lielā Jugla river (also observed previously) although limit values were not exceeded. Annual average concentrations were exceeded for Pb in Tūlija, Tērvete and Mēmele rivers and Ķemeru swamp; for Cu in Amula and Bārta rivers; for petroleum hydrocarbons in Salaca River.

Annual average concentrations were reached for Pb in Daugava River at the border with Belorussia.

Compliance to criteria of fish waters was assessed – all monitored water objects (9 sites) had good quality.

In **2007** the highest concentrations (maximal values) were observed in Tūlija river (Gauja RBD) and in Zvirbuļu stream located in Ķemeru swamp (Lielupes RBD). Pb concentration was 4 – 5 times higher than in other sites.

Investigation monitoring of petroleum hydrocarbons in Daugava River was performed after an oil spill accident in Belorussia at 23 March. Due to successful rescue actions the AA concentrations of petroleum hydrocarbons in Daugava River water did not exceed limit value.

The concentrations of monitored substances did not exceed corresponding limit value of AA concentration.

In **2008** the concentrations of monitored substances did not exceed corresponding limit values of AA concentration.

In **2009**. The MAC concentrations were exceeded for Cu in Liepājas Lake (almost 2,5 times), Ķīšezers Lake and Usmas Lake, also in Venta river (at Ventspils). Large concentrations of Pb were observed in Zvirbuļu stream located in Ķemeru swamp (the same location as in 2007) – close to EQS. These all were single observations. Due to small amount of samples (only two or three) the annual average values were not calculated.

#### 4.1.2 MONITORING PROGRAM FOR PERIOD 2009 – 2014

The monitoring program for this period was prepared in accordance with Water Management Law (12.09.2002) with further amendments and Cabinet Regulation No. 92 (17.02.2004) on Requirements for the Monitoring of Surface Water, Groundwater and Protected Areas and the Development of Monitoring Programs with further amendments. The surface water monitoring thus is divided in supervisory monitoring, operational monitoring and research monitoring (Table 4.2).

**Minimum sampling frequency for supervisory monitoring** for all water types (rivers, lakes, transitional waters and coastal waters) was established:

- once a month for priority substances and
- once every three months for other polluting substances.

For **operational monitoring** sampling must be not less frequent than above mentioned terms for supervisory monitoring. Frequency for supervisory monitoring may be changed if the variability of the physico-chemical criteria values is observed under the influence of natural and anthropogenic conditions and seasonal variations.

**Table 4.2.** Numbers of sampling sites for different kinds of monitoring.

\* may be changed depending of actual situation

\*\* in periods between operational monitoring cases – included in list of operational monitoring sites

\*\*\* additional point for research monitoring overlapping with operational monitoring points, but not included in number of research monitoring points

$P_{int}$  for intercalibration (only for lakes), may be planned also extra

Kind of monitoring:	Venta's RBD		Lielupe's RBD		Daugava's RBD		Gauja's RBD		Sum	
	Rivers	Lakes	Rivers	Lakes	Rivers	Lakes	Rivers	Lakes	Rivers	Lakes
supervisory	11	4	7	2	5	13	6	6	28	25
operational	51	26	30	6	61	146	37	26	178	204
research $P_{int}$	2*	1***	1***	3	2**	18 (2 $P_{int}$ )	2	7 (5 $P_{int}$ )	5*	29 (7 $P_{int}$ )
Sum	64	31	38	11	66	177	45	39	213	258

## 4.2 DATA FROM SCREENING PROJECT “SCREENING OF NITRATES, PRIORITY AND HAZARDOUS SUBSTANCES IN SURFACE AND GROUND WATER OBJECTS OF LATVIA” 2009 – 2010

### Sampling

Within this project sampling in rivers and lakes was carried out three times for water samples in October - November 2009, June 2010 and July 2010 and once for sediment samples in October

2009. Biota (perch) was sampled also in July 2010. 129 water samples, 45 sediment samples, 14 biota samples and 6 WWTP sludge samples (not including number of parallel samples) were taken. Sampling was performed at following sites:

- Rivers:
  - Above and below the largest cities – for assessing of urban influence.
  - On the largest rivers – three of them on border with Lithuania and Belorussia – for transboundary transport of HS – and Gauja River which is not transboundary river.
- Lakes and rivers flowing into lakes
- Sludge from waste water treatment plants (Liepāja WWTP, Rīga WWTP “Daugavgrīva”) also was sampled three times (November 2009, January 2010 and June 2010).
- Biota - perch (*Perca fluviatilis*) was sampled once in July 2010 at all above mentioned sites for transboundary transport assessment and in three lakes: Ķīšezers, Liepājas and Baltezers lakes (latter one in the Daugava's RBD).

## Analysis

Following groups of priority, hazardous substances and a number of other pollutants were analysed in water, sediment and WWTP sludge samples.

1. Elements and their compounds: Cd, Pb, Hg, Ni, Se, As, Cr, Cu, Zn, Sb, Ba, Be, Co, Mo, Sn and V.
2. Monoaromatic hydrocarbons: 17 compounds and total content of substances' groups.
3. PAH: 17 compounds and total content of substances' groups.
4. Chlorinated hydrocarbons: 83 compounds and total content of substances' groups including PHB of primary interest - PHB 28, 52, 101, 118, 138, 153, and 180.
5. Phenols and their derivatives: 44 compounds and total content of substances' groups including 22 chlorinated phenols and sums.
6. Chlorinated pesticides: 30 compounds and total content of substances' groups.
7. Phosphorylated pesticides 16 compounds.
8. Nitrogen-containing pesticides 8 compounds.
9. Other pesticides 11 compounds.
10. Other hazardous substances and pollutants: 33 compounds and total content of substances' groups including petroleum hydrocarbons.

Biota samples were tested for the content of hexachlorobenzene, hexachlorobutadiene and mercury (according to the requirements of the Directive of Priority Substances).

## Overview of results

Water quality in absolutely most cases corresponded to EQS values and content of HS was lower than LoD especially for the organic substances. Sediment quality was little worse than water quality, but also exceeding of set EQS was observed for far less than 10 % of all measurements. In most cases the sediment quality was good except at the water objects nearby urban and industrial territories.

In most cases exceeding of EQS was observed for metals and petroleum hydrocarbons.

For some substances the cases of exceeding of EQS are questionable due to LoQ of applied testing method which was comparable to or even larger than corresponding limit values, e.g. for aldrin, dieldrin, endrin, isodrin, endosulfan, pentachlorobenzene, benzo(g,h,i)perylene, BDEs, acrylonitrile and tributyl cation.

## Water quality

Results of screening for **water** show that in all cases exceeding values were single observations and probably accidental emissions of substances/groups of substances, especially for petroleum hydrocarbons (PHC). Large concentrations of PHC were observed in areas with heavy water traffic

– Lielupe River mouth, Burnieku Lake and Ķīšezers Lake. The boats with petroleum engines are widely used by fishermen, anglers and for recreational purposes here. As well the diffuse source of PHC can be the riverside or waterfront of lake covered with reeds. The reeds accumulate oil products on their surface during the low water period whereas the high water washes out oil products from reeds. All data (exceeding values) are listed in the following Table 4.3.

**Table 4.3.** Testing results for water samples investigated in project “SCREENING OF NITRATES, PRIORITY AND HAZARDOUS SUBSTANCES IN SURFACE AND GROUND WATER OBJECTS OF LATVIA” reported as values exceeding limits.

*n.d.* – Values considerably lower than LoQ of testing method

No.	Site, basin	Substance	Value, ug/L	Data	Observed once in this screening?
<b>Lielupe RBD</b>					
1	Bērze River above Dobeles	BDE	0.0246	15.07.2010	before – n.d.*
2	Lielupe River above Jelgava	BDE (deca-BDPE)	0.0083	11.06.2010	before and later – n.d. 60, <b>190</b> , n.d.
3		Zn	190		
4	Misa River below Olaine	Trichloromethane	5.0	11.06.2010	0,52; <b>5,0</b> ; 1,6
5	Mēmele River above Bauska	BDE (deca-BDPE)	0.360	23.11.2010	later - n.d.
6	Lielupe River mouth	PHC	2200	09.06.2010	before and later – n.d.
<b>Gauja RBD</b>					
7	Gauja River above Cēsis	PHC	100	28.10.2009	later - n.d.
8	Burtnieku Lake	PHC C16-C21	270 260	27.10.2009	before and later and in another site – n.d.
<b>Venta RBD</b>					
9	Ciecere River above Saldus	Chloropyrifos	0.1	12.06.2010	before – n.d.
10	Venta River above Kuldīga	PHC	130	21.06.2010	before and after – n.d.
11	Venta River on border with LT	Hexachlorobutadiene	11	21.10.2009	later – n.d.
<b>Daugava RBD</b>					
12	Sarkandaugava armlet	Hg	0.062	19.11.2009	later – n.d.
13		BDE (deca-BDPE)	0.1		
14	Hapakas ditch	BDE (deca-BDPE)	0.08	20.11.2010 08.06.2010	later – n.d.
15	Daugava River mouth	BDE (deca-BDPE)	0.012	20.11.2010	later- n.d.
16	Ķīšezers Lake	PHC	3400	08.06.2010	before and later – n.d.
17	Alūksnes Lake	Hg	0.042	17.06.2010	before and later –n.d.
18	Rēzekne River above Lubāna Lake	BDE	0.034	07.07.2010	before –n.d.

### Quality of sediments

Most of the cases with exceeded EQS proposed by WFD or designated in Regulations issued by Cabinet of Ministers Nr.475 (“Procedures regarding the Cleaning and Deepening of Surface Water Bodies and Port Basins”) occurred in **the Daugava RBD**. The most polluted samples in the Daugava RBD **originated** from waters nearby Rīga: Sarkandaugava armlet, Hapakas ditch and Ķīšezers. High concentrations of metals, petroleum hydrocarbons and sum of DDT, DDD and DDE were found there. Outside urban and industrial territories close to Rīga exceeding of EQS was observed only for Ni (1<sup>st</sup> level set by Regulation No. 475).

The quality of sediments is shown in Table 4.4; the given values were calculated as percentage of EQS set for sediments in Cabinet Regulation No. 475: 1<sup>st</sup> level (satisfactory limit) and 2<sup>nd</sup> level (highest EQS’s value allowing sediment deposition in the sea).

In the **Lielupe RBD** the most polluted samples were from Lielupe at site above Jelgava town and Babītes Lake.

The most polluted samples in the **Gauja RBD** were from Burtnieku Lake.

Liepājas Lake and Venta’s mouth were the most polluted sites in the **Venta RBD**.

**Table 4.4.** The quality of sediments in the polluted sites. The values are given as exceeding percentage of EQS 1<sup>st</sup> (satisfactory limit) and 2<sup>nd</sup> (deposit limit) level set for sediments in Cabinet Regulation No. 475.

\*Values close to 2<sup>nd</sup> level

Site	Cd		Hg		Ni		Cr		Cu		Zn	
	1 <sup>st</sup>	2 <sup>nd</sup>										
<b>Daugava RBD</b>												
Sarkandaugava armlet		277	126			152		247		145		135
Hapaka ditch	130				169							113
Ķīšezers Lake – 1	290	97*	152		237	95*	202		110		192	96*
Ķīšezers Lake – 2	150				135							
Alūksnes Lake – 2					112							
<b>Venta RBD</b>												
Slocene River above Kaņieris Lake					114							
Liepājas Lake – 3					137							
<b>Lielupe RBD</b>												
Lielupe River above Jelgava			116			106						
Babītes Lake – 1					148							
Babītes Lake – 2					168							
<b>Gauja RBD</b>												
Burtnieku Lake – 1					148							
Burtnieku Lake – 2					161							

#### Biota quality

In **biota** EQS values were exceeded for only one determinand – mercury. Hg concentrations varied in range 0.023 – 0.219 mg/kg WW. The largest values were observed in Venta River's mouth, Baltezers Lake and Ķīšezers Lake, on border with Lithuania in Mūsa and Mēmele river. A decrease of Hg concentrations in direction from boundary to river mouths was observed for Lielupe River, an increase – in Venta River probably due to the pollution from Ventspils. However, it could not be assessed as clear tendency due to very little amount of samples and number of sampling sites. Hexachlorobenzene and hexachlorobutadiene values were below LoQ.

## 5. PROPOSALS FOR IMPROVEMENT OF THE MONITORING PROGRAMME BASED ON BALTAZHAZ FINDINGS AND OTHER HS SCREENING ACTIVITIES IN THE COUNTRY

### 5.1. SUMMARY OF THE MAIN FINDINGS ON HAZARDOUS SUBSTANCES OCCURRENCE IN BALTAZHAZ

The range of pollutants measured within the project “BaltActHaz” in Latvia included analyses of 43 substances in water and 54 substances in sediments and sewage sludge. The project thus focused on the selected substances from Annex X and Annex III of WFD – all together 16 – 18 substances. In total five substances and/or groups of substances were screened in water and seven in sediments and sludge – alkylphenols and their ethoxylates, brominated diphenylethers, chlorinated paraffins, organochlorine pesticides, perfluorooctane sulphonic acid (PFOS) in water, waste water, sediments and sewage sludge; organotin compounds and cadmium in sediments and sewage sludge only. In total 22 sites were screened for the selected hazardous substances (Table 5.1 and 5.2)

**Table 5.1. Sampling sites and analysed matrixes of the first sampling round 1 – 8 June 2010.**

Matrixes: WW - waste water, SW - surface water, WS - sludge from WWTP, BS - bottom sediments.

Site No.	Sampling site	Sampling site description	Matrixes	
			WW/SW	WS/BS
1.	Rīga WWTP “Daugavgrīva”, Rīgas ūdens	WW to the Gulf of Riga	✓	✓
2.	Liepāja WWTP, Liepājas ūdens	WW to the Baltic Sea	✓	✓
3.	Daugava river	At boarder with Belarus	✓	✓
4.	Mūsa river	At border with Lithuania	✓	✓
5.	Mēmele river	At border with Lithuania	✓	✓
6.	Venta river	At border with Lithuania	✓	✓
7.	Bārta river	At border with Lithuania	✓	✓
8.	Lielupe river	below Jelgava	✓	✓
9.	Misa river	below Olaine	✓	✓
10.	Bērze river	below Dobeles	✓	✓
11.	Gauja river	below Valmiera	✓	
12.	Bulļupe river	between Daugava and Lielupe estuaries	✓	✓
13.	Venta river	above Ventspils, Venta river estuary	✓	✓
14.	Water storage lake on the Daugava river	Electricity power plant Pļaviņas storage lake above Aizkraukle town		✓
15.	Liepāja Lake	at Northern side near Liepāja city	✓	✓
16.	Ķīšezers Lake	Southern part	✓	✓
17.	Ķīšezers Lake	Northern part	✓	✓
18.	Harbour territory	Liepāja commercial harbour, Karosta	✓	✓

**Table 5.2. Sampling sites and analysed matrixes of the second sampling round 14 – 16 February 2011.**

Matrixes: WW - waste water, WS - sludge from WWTP.

Site No.	Sampling site	Sampling site description	Matrixes	
			WW	WS
1.	WWTP Daugavpils	WW to Daugava river	✓	✓
2.	WWTP Dobeles	WW to Bērze river	✓	✓
3.	WWTP Rēzekne	WW to Rēzekne river	✓	✓
4.	WWTP Saldus	WW to Ciecere river	✓	✓
5.	WWTP Valmiera	WW to Gauja river	✓	✓
6.	WWTP Ventspils	WW to the Baltic Sea	✓	✓

According to the findings within screening activities 14 samples of the municipal and industrial waste water were collected before entering to municipal WWTPs of city/town in 6 – 9 June 2011 and were analysed within HS source tracking activity:

- 6 samples at waste water transfer stations located in Riga (mix of industrial and municipal waste waters; Table 5.3),
- 1 municipal and 1 industrial waste water sample in Liepaja,
- 2 industrial waste water samples in Ventspils,
- 2 industrial waste water samples in Dobeles,
- 1 industrial waste water sample in Valmiera,
- 1 industrial waste water sample in Saldus.

The scope of respective industrial companies includes: 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.

**Table 5.3.** Description of the sampling spots (pump 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	Shipyards, 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

Sampling for screening was carried out in two phases: June 2010 and February 2011. Sampling for source tracking of HS during the project was carried out in June 2011.

Sampling was carried out by the specialists of the Latvian Institute of Aquatic Ecology. Sewage sludge and waste water samples were taken 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.

Analyses of the samples were carried out by Laboratory of Marine Monitoring Department of Latvian Institute of Aquatic Ecology (LIAE) – cadmium in bottom sediments and sewage sludge; ALS Laboratory Group Ltd, the Czech Republic: organotin compounds in sediments and sewage sludge; alkylphenols and their ethoxylates, brominated diphenylethers, chlorinated paraffins, PFOS, organochlorine pesticides in all matrixes.

### 5.1.1. THE RESULTS OF HS SCREENING ACTIVITIES

The results of screening showed the status of quality of aquatic environment at the observation time. Therefore it is rather difficult to conclude on quality of aquatic environment and impact of discharge waters from WWTPs due to only one observation.

The technical information of sampling – sites, methods and matrixes – and technical information of selected substances – analytical methods used in laboratories, LoD, LoQ, MU and tables of results

is detailed described in report "Results on Screening of Hazardous Substances in Latvia" (www.bef.lv).

In general water quality according to selected HS could be characterized as satisfactory. The evaluation of results can be based only on concentrations in the bottom sediments since the selected hazardous substances were not detected or were below LOQ in surface water.

During the screening 5 sites on transboundary rivers at the border were included, all of them flowing into Latvia: Daugava from Byelorussia; Memele, Musa, Barta and Venta from Lithuania. Only DecaBDE were detected in the bottom sediments: Daugava River (8 ug/kg DW) and Mūsa River (0.6 ug/kg DW).

The quality of bottom sediments at 2 sites in the rivers at the estuary zones was investigated. Bullupe River is connecting estuaries of the Daugava River and Lielupe River inflowing into the Gulf of Riga. Venta River discharges waters directly to the Baltic Sea. All selected substances in the sediments were below LOQ or were not detected at all.

4 sites on the rivers below towns with manufacturing enterprises were analysed: Berze river below Dobele, Misa River below Olaine, Lielupe River below Jelgava and Gauja River below Valmiera. At the site on Gauja River below Valmiera only water samples for selected hazardous substances were taken because the river bottom is mixture of sand and gravel. The most polluted with selected HS were sediments of Misa River below Olaine town. PentaBDE (4.3 ug/kg DW) and DecaBDE (2.0 ug/kg DW) were detected in the bottom sediments. Relatively high concentration of cadmium was observed in the sediments of the river (1.17 mg/kg). The concentration of cadmium in sediments exceeded the 1<sup>st</sup> level (1 mg/kg DW) of sediment quality designated in Regulations of Cabinet of Ministers Nr.475.

5 sites in the lakes and harbour aquatories near highly industrially affected areas were analysed: one point in Liepājas Lake, two points in Kīšezers Lake, one point in Liepaja Harbour and one point in the storage lake of electrical power plant Pļaviņas on Daugava River. These areas were supposed to be highly contaminated with selected substances such as organotin compounds, PBDE and cadmium.

Since Liepaja Lake and Kisezers Lake are located close to harbours and shipyards organotin compounds were found in these lakes as well as in Liepaja Harbour area. For TBT the levels of sediment quality are (1<sup>st</sup> level – 3 ug/kg; 2<sup>nd</sup> level – 30 ug/kg) designated in Regulations of Cabinet of Ministers Nr.475.

- *Liepajas Lake.* Mono-, di- and tributyltin compounds were found in the bottom sediments of the lake. The concentration of MBT was 2.5 ug/kg DW, DBT – 7.0 ug/kg DW, TBT – 19 ug/kg DW.
- *Kisezers Lake.* Mono-, di- and tributyltin compounds were found in the bottom sediments of the lake. In the southern part of the lake the concentration of MBT was 4.4 ug/kg DW, DBT – 24 ug/kg DW, TBT – 60 ug/kg DW; in the northern part of lake the concentration of MBT was 1.6 ug/kg DW, DBT – 4.1 ug/kg DW, TBT – 11 ug/kg DW. At the same time very high concentration of cadmium was found in southern part of the lake – 3.1 mg/kg DW. Organochlorine pesticide 4,4'-DDD was found in the bottom sediments of the southern part of the lake (0.014 mg/kg). Concentration of Cd exceeded the 2<sup>nd</sup> level of sediment quality (3 mg/kg DW) and concentration of DDD exceeded 1<sup>st</sup> level of sediment quality (0.01 mg/kg DW). The concentration of 4-nonylphenol in the bottom sediments of the southern part of the lake was 0.14 mg/kg DW.
- *Liepaja harbour.* Mono-, di-, tri- and tetra butyltin compounds were found in the bottom sediments of the Liepaja harbour. The concentration of MBT was 21 ug/kg DW, DBT – 160 ug/kg DW, TBT – 190 ug/kg DW, TtBT – 3.6 ug/kg DW. The concentration of TBT in the harbour sediments exceeded 2<sup>nd</sup> level of sediment quality six times. DecaBDE in the harbour sediments was 1.9 ug/kg DW; 4,4'-DDD – 0.044 mg/kg. The concentration of DDD exceeded 2<sup>nd</sup> level of sediment quality (0.03 mg/kg DW). The concentration of 4-nonylphenol and 4-nonylphenol monoethoxylate in the bottom sediments of the harbour was 0.25 and 0.16 mg/kg DW, respectively.
- *The storage lake of the electrical power plant Pļaviņas on Daugava River.* Relatively high concentration of DecaBDE was found in the bottom sediments of the storage lake (11 ug/kg DW).

DW). This is highest concentration of DecaBDE discovered in aquatic environment within this project.

The selected hazardous substances were screened in waste water and sewage sludge of 8 WWTPs, including the biggest cities such as Riga, Liepaja, Daugavpils and Ventspils, and smaller towns – Dobele, Saldus, Valmiera and Rezekne. Analysis of waste water and sewage sludge samples from Riga and Liepaja WWTP were performed within the first sampling round in June 2010. Analysis of waste water and sewage sludge samples from Dobele, Saldus, Ventspils, Rezekne, Daugavpils and Valmiera WWTP were performed within the second sampling round in February 2011. Analytical methods of PFOS and chlorinated paraffins detection in sewage sludge differed between the both rounds. LOQ for PFOS in sewage sludge was 0.01 – 0.05 mg/kg DW within the first round and it was higher than within the second round – 0.001 – 0.005 mg/kg DW. At the same time the selectivity of analytical method for chlorinated paraffins was higher within the first round compared to the second round. The results for chlorinated paraffins analyzed within the second round are given as the sum of all chloroalkanes.

2,4-DDD, 4,4'-DDD and 4,4'-DDE from organochlorine pesticide group were detected only in Riga and Liepaja WWTP (Table. 5.4).

Only 4-t-Octylphenol was detected in the waste water of Riga WWTP (0,036 ug/L) while this value was below AA-EQS limits for inland surface waters (0.1 ug/L) but more than AA-EQS limits for saltwater (0.01 ug/L). Relatively high content of 4-nonylphenol and the highest one between all regional WWTPs was observed in sewage sludge of Riga WWTP (Table 5.4). For 4-t-octylphenol the highest concentration was estimated in the sewage sludge of Ventspils WWTP. The highest concentrations of TBT were found in the sewage sludge of Riga WWTP and Liepaja WWTP. Relatively high concentrations and the highest one between all regional WWTPs for PFOS were observed in the sewage sludge of Ventspils WWTP. Relatively high results were observed for chlorinated paraffins in sewage sludge of Dobele WWTP. Concentrations of these substances were the highest between all regional WWTPs. The highest concentrations of PentaBDE were estimated in the sewage sludge of Ventspils and Daugavpils WWTP. The highest concentrations of DecaBDE were observed in the sewage sludge of Valmiera WWTP.

**Table 5.4. Substances detected in the sewage sludge of the regional WWTPs.**

\* - result below LoQ,

\*\* - due to selectivity problems, the results for chlorinated paraffins are given as the sum of all SCCP, MCCP and LCCP.

Group of Substances	Substances	Unit to DW	Riga WWTP	Liepāja WWTP	Daugavpils WWTP	Dobele WWTP	Rēzekne WWTP	Saldus WWTP	Valmiera WWTP	Ventspils WWTP
<b>Alkylphenols</b>	4-Nonylphenol	mg/kg	32	0.83	0.78	0.23	0.53	0.32	0.49	0.67
	4-Nonylphenol monoethoxylate	mg/kg	8.6	2.19	0.93	0.30	*	*	*	1.19
	4-Nonylphenol diethoxylate	mg/kg	*	*	1.19	*	*	*	*	1.04
	4-t-Octylphenol	mg/kg	0.54	0.024	0.036	*	0.035	0.047	*	0.64
	4-t-Octylphenol monoethoxylate	mg/kg	0.042	*	*	*	*	*	*	*
	4-t-Octylphenol triethoxylate	mg/kg	*	0.28	*	*	*	*	*	*
<b>Chlorinated Paraffins</b>	Chloroalkanes C10-C13	mg/kg	1.2	0.75	**	**	**	**	**	**
	Chloroalkanes C14-C17	mg/kg	2.0	2.20	**	**	**	**	**	**
	Sum of SCCP, MCCP, LCCP	mg/kg	x	x	3.0	15	2.0	2.0	2.0	5.0
<b>Organochlorine Pesticides</b>	2,4-DDD	mg/kg	0.041	0.020	*	*	*	*	*	*
	4,4'-DDD	mg/kg	0.040	0.034	*	*	*	*	*	*
	4,4'-DDE	mg/kg	0.042	0.021	*	*	*	*	*	*
<b>Organotin compounds</b>	Monobutyltin	mg/kg	0.12	0.054	0.15	0.15	0.12	0.064	0.0098	0.13
	Monooctyltin	mg/kg	0.060	0.020	0.024	0.026	0.018	0.015	0.034	0.036
	Dibutyltin	mg/kg	0.16	0.059	0.071	0.11	0.073	0.075	0.079	0.072
	Diocetyl tin	mg/kg	0.034	0.021	0.025	0.026	0.019	0.0069	0.018	0.023
	Tributyltin	mg/kg	0.028	0.018	*	0.0036	0.0014	*	*	0.0049
<b>PBDE</b>	PentaBDE	ng/g	10.3	4.18	15.4	10.1	12.9	14.9	14.3	17.0
	OctaBDE	ng/g	0.12	0.076	0.51	0.53	0.56	0.45	0.36	0.38
	DecaBDE	ng/g	190	74	410	510	110	120	700	250
<b>PFOS</b>	PFOS	ug/kg	<10	<10	6.1	2.8	3.5	3.2	3.8	19.8
<b>Metals</b>	Cd	mg/kg	1.38	0.99	1.35	0.57	0.77	0.54	1.35	0.87

## 5.1.2. THE RESULTS OF HS SOURCE TRACKING ACTIVITIES

The technical information of sampling – sites, methods and matrixes – and technical information of selected substances – analytical methods used in laboratories, LoD, LoQ, MU and tables of results is detailed described in report “Investigation of Sources of Hazardous Substances in Lithuania, Latvia and Estonia” (www.bef.lv).

Screening and source tracking was done in different time. The results of screening and source tracking thus 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. 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 the "production" ones.

The results of source tracking showed that concentrations of **organochlorine pesticides** and **PFOS** were below LoQ. However, due to the matrix influence LoQ for PFOS analytical method was significantly increased. Probably it did not allow tracking the source of PFOS which was observed in the sewage sludge of Ventspils WWTP within the screening round.

### ***Chlorinated paraffins***

SCCP (C<sub>10</sub> – C<sub>13</sub>) 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 (C<sub>14</sub> – C<sub>17</sub>) 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***

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.

The concentrations of PBDE in the sewage sample at a pipe-end of the entity producing fire-extinguishers were the lowest among all samples.

### ***Alkylphenols and their ethoxylates***

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

The range of **4-nonylphenol** concentrations in the 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 the sewage sample collected from the plastic containers where the company stored sewage waters before their utilisation.

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

## **5.2. PROPOSALS FOR IMPROVEMENT OF THE CURRENT MONITORING PROGRAMME**

Taking into account the legal frame of Latvia in respect to the environmental monitoring, where monitoring requirements for commercial companies are elaborated individually depending on their characteristic, the proposals listed in this chapter are aiming to improve only State monitoring program.

The more specific monitoring programs for port areas (sediments periodically are removed and deposited elsewhere) and areas directly impacted by agricultural lands can be addressed only after specific targeted project has generated required information and knowledge. Furthermore, in both cases a clarification of legal framework is needed as well.

In the light of the results of this project we propose to divide the state monitoring program in three mutually complimentary parts. Additionally we propose several recommendations in concluding remarks based on findings.

### **5.2.1. SCREENING FOR OCCURRENCE**

This part can be viewed as part of Surveillance monitoring, however, technically this type of pre-monitoring screening exercise is generating information on basis of which monitoring program can be amended. All priority substances should be addressed. A scope might vary from exercise to exercise since the list of priority substances is constantly updated, therefore we will not nominate the substances at this stage. Once in at least 12 year period screening exercise should be carried out for HS in current list, once in 4 year period – for new HS included in the updated list. Monitoring stations should represent all four river drainage basins and in minimum water from 13 stations should be sampled in spring (as close to spring flood as possible) and summer (representing low level water conditions). We recommend that water sampling stations should be located in Salaca, Gauja, Daugava, Lielupe and Venta (upstream of river mouths where marine water influence is absent or negligible), in Daugava, Mūsa, Mēmele, Bārta, Venta, (close to the State border), and in Ķīšezers, Liepājas and Burtnieku Lake. In addition to that sediment samples should be taken once in Ķīšezers, Liepājas, Burtnieku Lake and the storage lake of the electrical power plant Pļaviņas and analyzed for priority substances taking in account coefficient  $\log K_{OW}$  of substance.  $\log K_{OW} \geq 3$  (in circa website) are relevant for lipophilic substances that accumulate in sediments. Sediments which accumulated constantly would clearly show potential continuous pollution and problematic HS. Since this type of screening, with exception to sediment sites, will allow to identify HS only if continuous pollution source is presented the biota (Eurasian perch, *Perca fluviatilis*) should be sampled in Daugava, Gauja, Lielupe and Venta as well and analyzed for priority substances (mercury, hexachlorobutadiene and hexachlorobenzene) and taking in account biomagnification factor ( $BMF > 1$ ) or bioconcentration factor ( $BCF \geq 100$ ) (in circa website) or  $K_{OW} \geq 3$  in a case of lack BMF or BCF.

### **5.2.2. SURVEILLANCE MONITORING**

In areas where relatively substantial concentrations of contaminants were estimated we propose to establish a surveillance monitoring. Since the abovementioned concentrations were recorded in the sediments and sediments are accumulating with a slow rate and the concentration changes are expected only over longer time periods, we propose to analyze organotin compounds, cadmium, mercury, lead, organochlorine pesticides, phenols and brominated diphenylethers twice per monitoring program period (that is once per 3 years) in the sediments of Liepājas, Ķīšezers and Burtnieku Lake as well as in the storage lake of the electrical power plant Pļaviņas. Three replicates should be sampled at each sampling point in order to confirm statistically significant increase/decrease of the concentrations.

### **5.2.3. MONITORING OF RIVER LOADS TO MARINE ENVIRONMENT**

Existing monitoring program already foresees monitoring of heavy metals in the water of the transboundary rivers and in the rivers discharging in the Baltic Sea and the Gulf of Riga. However, current sampling frequency is not satisfactory to achieve desired accuracy in load calculations. Therefore we suggest to increase sampling frequency of heavy metals (at least Cd, Hg and Pb) to 12 times per year (minimum 10 times per year) in Salaca, Gauja, Daugava, Lielupe and Venta (upstream of river mouths where marine water influence is absent or negligible), and in Daugava, Mūsa, Mēmele, Bārta, Venta (close to State border).

#### 5.2.4. MONITORING OF HS IN SEDIMENTS AND BIOTA

The alarming concentrations of HS in the waters of Latvia are not observed often because of the poor solubility of these substances in the water. Since most of HS are lipophilic ( $\text{Log } K_{\text{OW}} \geq 3$ ) it is advisable for the State monitoring program to focus on HS observations in sediments and biota. As it is pointed out in Directive 2008/105/EC the monitoring of HS in sediments and biota is required for providing sufficient data for a reliable long-term trend analysis of those priority substances that tend to accumulate in sediment and/or biota. According to results and findings within several projects (as well HELCOM exercises) in time period from 2009 it is important to include sediment and biota analyses for HS.

The sediments from constant accumulation sites, mainly lakes – Ķīšezers, Liepājas, Burtnieku Lake and the storage lake of the electrical power plant Pļaviņas and Riga as well as other lakes close to industrial centres – Riga (Jugla and Baltezers Lake), Liepāja (Tosmares Lake) and Daugavpils (Stropu Lake) should be monitored. For monitoring of HS in sediments it would be beneficial to analyse metals - mercury, cadmium, lead and nickel – as well as organic substances – alkylphenols, PAHs, DDT/DDD/DDE, phthalates, PBDEs, TBT/TPhT and oil products. The supporting parameters – aluminium, iron and organic carbon should be measured in sediments.

According to the previous experience and knowledge on biota collection and occurrence in rivers and lakes of Latvia we propose to focus on one species for HS monitoring in biota – Eurasian perch (*Perca fluviatilis*). The monitoring of HS in biota should be done pursuant to HELCOM recommendations about amount, age and body part of fishes as well as sampling season. The proposed sampling sites are following:

- the transboundary sites on rivers Daugava, Mūsa, Mēmele, Venta and Bārta,
- the mouth of rivers Daugava, Gauja, Venta, Lielupe, Salaca,
- the lakes - Ķīšezers, Liepājas, Burtnieku, Lubānas Lake and the storage lake of the electrical power plant Pļaviņas and Riga as well as other lakes close to industrial centres – Riga (Jugla and Baltezers Lake), Liepāja (Tosmares Lake) and Daugavpils (Stropu Lake),
- the potentially polluted sites – Bērze River below Dobeles, Misa River below Olaine, Hapaka Ditch, Lielupe River above Jelgava.

The occurrence of perch at some of proposed sites for biota monitoring Jugla Lake, Tosmares Lake, Stropu Lake as well as Misa below Olaine and Bērze below Dobeles is unknown. Therefore additional data gathering or study on fish occurrence is needed before inclusion of these stations/locations in State monitoring program.

The analyses in biota (Eurasian perch, *Perca fluviatilis*) for metals - mercury, cadmium, lead, nickel – and for organic substances – hexachlorobenzene, hexachlorobutadiene, PAHs, phthalates, PBDEs, TBT/TPhT, fluoranthene, benzene, dioxins and furans, PFOS and hexabromocyclododecane should be done on a regular basis described in WFD.

#### 5.2.5. ALTERNATIVES AND NEW METHODS IN MONITORING

Concerning the capacity of national laboratories to analyse HS listed in WFD and Minister Cabinet regulations No 118 and No 475, the Annex I of this report includes method quality limits in comparison with set EQS values and accreditation of laboratories to analyse HS in the different matrixes – water, sediments, sludge and biota. The improvement and development of current and new analytical methods are important part in proposal for National monitoring program. Only a reasonable number of samples monitored within the program make sense for further development of methods and capacity building in national laboratories. Otherwise it just creates enormous expenses in contrast with funds for chemical analyses at the external accredited laboratories. Sensitive analytical equipment and sensitive analytical methods are required for detection of several HS as mentioned in Chapter 3.1. and 3.2.1. It is well known from the previous laboratory practice especially in chromatography that each item of the analytical equipment requires routine maintenance, stable conditions and specific analytes or analyte groups to avoid contamination of sample supply and/or detection system within measurement. This circumstance distinguishes necessity of separate analytical equipment items for selected HS with following increase of

expenses for maintenance of equipment, accreditation and educated staff. The economic possibilities of new selected analytic method development and capacity building in national laboratories must be assessed within separate studies.

According to analytical method quality limits applied in national laboratories (Annex I of this report), determination of HS in water are problematic while the same problems for determination of TBT, SCCP (C10- C13), phthalates, few cloroorganic pesticides, PBDE etc. are problematic for a number of routine laboratories in Europe. Most of these organic substances as well as metals have affinity to attach suspended particles with sequent accumulation in sediments and biota tissues. The most relevant monitoring of HS would be in sediments and biota. Lack of EQS for HS in sediments and biota (except Hg, hexachlorbenzene and hexachlorbutadiene) set by WFD does not allow determining the state of waterbody, however it clearly illustrates the tendency of pollution.

The waste water effluents are mainly controlled by chemical analyses – identifying selected hazardous substances or substances groups and their concentrations according to the legal frame. As it was mentioned before, LoD and LoQ of analytical methods for detection of several substances cannot reach the level of EQS, these methods will be improved. A mixture of different substances or unidentified substances can cause unexpected and/or poorly known effects. A bioassay tests or whole effluent assessment (WEA) comply together with chemical analyses could indicate the toxicity of the effluents and their overall environmental effects. The bioassay tests can be used for waste water surveillance and routine control before effluents are discharged in the environment. For example, the *Daphnia magna* acute tests can be useful analytical tool for early warning system to monitor various operational units of waste water treatment plant and can have additional value to hazard and risk assessment of effluent discharges to ambient aquatic ecosystem. However the use of WEA is not currently supported by the legal frame in Latvian legislation, although, Germany legislation adapted WEA and contains whole effluent toxicity limit values for several industry sectors. Many countries around the Baltic Sea are going forward to develop and establish WEA in their legislation in nearest future, so we suggest that Latvian authorities consider possibility of WEA inclusion in National legislation.

Numerous other biological tests can be considered to be used for support of the chemical analyses in a case if LoD and LoQ of analytical methods for concentration detection of several substances cannot reach the level of EQS; for example determination of PAHs metabolites in fish, imposex index for molluscs and whelks whether TBT be present in water body.

#### **5.2.6. CONCLUDING REMARKS**

Relatively significant concentrations of brominated diphenylethers and cadmium in Misa river sediments below Olaine town indicate that Olaine as well as other cities/towns with industrial enterprises is a source of hazardous substances. However, not always substances from such cities/towns are discharged in such concentrations which are measurable in the water.

The screening results show different problematic substances for different regional WWTPs – perfluorooctane sulphonate (PFOS), alkylphenols and their ethoxylates, chlorinated paraffins, PBDE and orngotin compounds. These substances were detected in the sewage sludge of WWTPs. Similarly the findings within source tracking illustrate that the effluents from household are a regular source of pollution with PBDE and chlorinated paraffins. High concentrations of alkylphenols were detected in sewage sludge of WWTP and waste waters discharged from WWTP. The waste waters discharged from WWTPs to the environment should be further monitored to make sure that alkylphenols, chlorinated paraffins, PBDE, TBT and PFOS have been removed within the treatment process. It is also strongly recommended to monitor PAHs in waste waters from WWTPs indicated by findings in another screening project “Screening of nitrates, priority and hazardous substances in surface and ground water objects of Latvia”.

Some monitoring options might be considered to follow discharge trends. However, the respective company providing water and canalization service for city and industries located there should be responsible for that monitoring. Therefore, it would be an operator monitoring for which individual monitoring requirements should be set by the regional environment service according to permits.

New or updated legal framework for the management of the sewage sludge used on agricultural land in Latvia is required. In addition to current EC Directive 86/278/EEC and Cabinet Regulations

No 362 (02.05.2006.) "Regulations Regarding Utilization, Monitoring and Control of Sewage Sludge and the Compost thereof" it should include limit values and quality criteria for list of inorganic and organic HS in sewage sludge from WWTPs used on agricultural land.

There are several officially known dumpsites for toxic waste in Latvia. Two most polluted locations are the open ponds of toxic waste goudron in Inčukalns and the liquid toxic waste dumpsite in Olaine. Previous monitoring showed that the groundwater around few officially known dumpsites is polluted, and the pollution tends to progress toward rivers. Monitoring of selected HS in the groundwater around these sites must be continued or launched.

## 6. LIST OF ABBREVIATIONS

AA-EQS	Environmental Quality Standard expressed as an annual average value
AAS	Atomic Absorption Spectroscopy
BCF	Bioconcentration factor
BDE / PBDE	Brominated diphenylethers / Poly Brominated diphenylethers
BMF	Biomagnification factor
BS	Bottom sediments
BTEX	Acronym that stands for benzene, toluene, ethylbenzene, and xylenes
DBT	Dibutyltin
DDD	Dichlorodiphenyldichloroethane
DDE	Dichlorodiphenyldichloroethylene
DDT	Dichlorodiphenyltrichloroethane
DOT	Diocetyl tin
DW	Dry weight
EQS	Environmental quality standard
EU	European Union
GC	Gas Chromatography
HCB	Hexachlorobenzene
HCH	Hexachlorocyclohexane
HELCOM	Baltic Marine Environment Protection Commission (Helsinki Commission)
HS	Hazardous substances
K <sub>ow</sub>	Partition coefficient K octanol - water
LCCP	Long chain chlorinated paraffins
LOD	Limit of detection
LOQ	Limit of quantification
LOR	Limit of reporting
MAC	Maximum allowable concentration
MAC-EQS	Environmental Quality Standard expressed as a maximum allowable concentration
MBT	Monobutyltin
MCCP	Medium chain chlorinated paraffins
MOT	Monooctyltin
MS	Mass spectrometry
MU	Measurement uncertainty
NCI	Negative chemical ionization
NP	Nonylphenols
NPE	Nonylphenoethoxylate
OP	Octylphenols
OPE	Octylphenoethoxylate
PAH	Polycyclic aromatic hydrocarbons
PCB	Polychlorinated biphenyls
PFOS	Perfluorooctane sulphonic acid
PHC	Petroleum hydrocarbons
RBD	River Basin District
SCCP	Short chain chlorinated parafins
SW	Surface water
TBT	Tributyltin
TCDD	2,3,7,8-Tetrachlorodibenzo- <i>p</i> -dioxin
US EPA	The United States. Environmental Protection Agency
WEA	Whole effluent assessment
WFD	Water Framework Directive (2000/60/EC)
WS	Sludge from WWTP
WW	Wastewater
WWTP	Wastewater treatment plant

## 7. REFERENCES

Cabinet Regulation **No. 92** adopted on 17.02.2004 "Requirements for the Monitoring of Surface Water, Groundwater and Protected Areas and the Development of Monitoring Programmes", with amendments until 27.07.2010.

Cabinet Regulation **No. 118** adopted on 12.03.2002 "Regulations regarding the Quality of Surface Waters and Groundwaters", with amendments until 22.12.2009.

Cabinet Regulations **No 362** "Regulations Regarding Utilization, Monitoring and Control of Sewage Sludge and the Compost thereof " 02.05.2006.

Cabinet Regulation **No.475** "Procedures regarding the Cleaning and Deepening of Surface Water Bodies and Port Basins" 13.06.2006.

Cabinet Regulation **No. 646** "Regulations on river basin management plans and programmes of measures" 04.07.2009.

Directive **2000/60/EC** of the European Parliament and of the Council of 23 October 2000 establishing framework for Community action in the field of water policy.

Directive **2006/11/EC** of the European Parliament and of the Council of 15 February 2006 on pollution caused by certain dangerous substances discharged into the aquatic environment of the community.

Directive **2008/105/EC** of European Parliament and Council on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/419/EEC, 86/280/EEC and amending Directive 2000/60/EC.

Commission Directive **2009/90/EC** of 31 July 2009 laying down, pursuant to Directive 2000/60/EC of the European Parliament and of the Council, technical specifications for chemical analysis and monitoring of water status.

**ISO/IEC 17025:2005**. General requirements for the competence of testing and calibration laboratories.

The Law On Pollution of 15.03.2001 with amendments until 25.10.2007.

Water Management Law of 12.09.2002 with amendments until 03.03.2011.

## ANNEXES

- Annex I Overview on the national laboratories covering HS analysis in water and technical specification of those analyses (on 1<sup>st</sup> October 2011).
- Annex II Overview on the national laboratories covering HS analysis in sediments, soils and sewage sludge and technical specification of those analysis (on 1<sup>st</sup>October 2011).
- Annex III Overview on the national laboratories covering HS analysis in biota and technical specification of those analysis (on 1<sup>st</sup>October 2011).

Overview on the national laboratories covering HS analysis in water and technical specification of those analyses (on 1<sup>st</sup> October 2011)

Laboratory/ Accreditation status/ Contacts	Substances analysed	Method used	A	Technical specifications			Compliance with 2009/90/EC			
				LoD, ug/L	LoQ, ug/L	MU, %	AA-EQS for Inland surface waters, ug/L*		MAC-EQS for Inland surface waters, ug/L*	
							EQS	LoQ (30% from EQS)	EQS	LoQ (30% from EQS)
Latvian Environment, Geology and Meteorology Centre (LEGMC) Environmental laboratory LATAK-KT-105 Ošu street 5, Jūrmala, Latvia LV-2015	Anthracene	US EPA 550.1: 1990	A	0.003	0.009	15	0.1	0.03	0.4	0.12
	Fluorantene	PAHs in drinking water by Liquid-Solid Extraction and HPLC with Coupled UV and Fluorescence Detection	A	0.004	0.015	12	0.1	0.03	1	0.3
	Naphthalene		A	0.04	0.13	12	2.4	0.72	n.a.	
	Benzo-a-pyrene		A	0.0082	0.027	25	0.05	0.015	0.1	0.03
	Benzo-b-fluoranthene	US EPA 8270C: 1996 GC/MS detection with mass selective detector	A	0.0048	0.016	25	Sum = 0.03	0.009	n.a.	
	Benzo-k-fluoranthene		A	0.019	0.063	25				
	Benzo-g,h,i-perylene		A	0.0075	0.025	25	Sum = 0.002	0.0006	n.a.	
	Indeno(1,2,3-cd) pyrene		A	0.0091	0.03	25				
	Aldrin		A	0.0003	0.001	37	Sum = 0.01	0.003	n.a.	
	Dieldrin	A	0.0002	0.001	24					
	Endrin	A	0.0002	0.001	32					
	Isodrin	LVS EN ISO 6468:1996	A	0.0003	0.001	40	0.005	0.0015	0.01	0.003
	alpha-Endosufan	Water quality - Determination of certain organochlorine insecticides, polychlorinated biphenyls and chlorobenzenes - Gas chromatographic (GC) method after liquid-liquid extraction	A	0.0002	0.001	30				
	beta-Endosulfan		A	0.0002	0.001	55				
	alpha-HCH		A	0.0006	0.002	23				
	beta-HCH		A	0.0002	0.001	44				
	gamma-HCH (Lindane)		A	0.0006	0.002	30				
	DDT sum	A	0.002	0.01	50	0.025	0.0075	n.a.		
	DDT, p,p'	A	0.0002	0.001	34	0.01	0.003	n.a.		
	Hexachlorobenzene (HCB)	A	0.0002	0.001	24	0.01	0.003	0.05	0.015	
	As	A	0.3	1	8	150	45			
	Cd (depending of water hardness class)	LVS EN ISO 17294-2:2005 Water quality - Application of inductively coupled plasma mass spectrometry (ICP-MS) - Part 2: Determination of 62 elements	A	0.06	0.2	12	≤ 0.08 (1)	≤ 0.02	≤ 0.45 (1)	≤ 0.14
			A				0.08 (2)	0.02	0.45 (2)	0.14
			A				0.09 (3)	0.03	0.6 (3)	0.18
			A				0.15 (4)	0.05	0.9 (4)	0.27
			A				0.25 (5)	0.08	1.5 (5)	0.45
	Cu	A	1	4	6	9.0	2.7	--		
Pb	A	0.4	1.3	6	7.2	2.16	n.a.			
Ni	A	0.9	3	8	20	6	n.a.			
Zn	A	8	26	6	120	36	--			
Cr	A	0.5	2.0	12	11	3.3	--			
Hg	LVS EN 1483:2007 Water quality - AAS in supercooled steam	A	0.07	0.22	13	0.05	0.015	0.07	0.021	
Petroleum hydrocarbons (C <sub>10</sub> -C <sub>40</sub> index of hydrocarbons)	LVS EN ISO 9377-2:2001 Water quality - Determination of hydrocarbon oil index - Part 2: Method using solvent extraction and GC	A	20	50		100	30	--		

Laboratory/ Accreditation status/ Contacts	Substances analysed	Method used	A	Technical specifications			Compliance with 2009/90/EC			
				LoD, ug/L	LoQ, ug/L	MU, %	AA-EQS for Inland surface waters, ug/L*		MAC-EQS for Inland surface waters, ug/L*	
							EQS	LoQ (30% from EQS)	EQS	LoQ (30% from EQS)
LEGMC Environmental laboratory (cont.)	Phenols (index of phenols)	LVS ISO 6439:1990 Water quality - Determination of phenol index - 4- Aminoantipyrine spectrometric methods after distillation	A	3	9.5	19	300	90	--	
	Benzene	ISO 11423-1:1997 Water quality - Determination of benzene and some derivatives – Part 1: Head-space GC method	A	1.0	2.0	21	10	3	50	15
	Toluene		A	1.0	2.0	19	10	3	--	
	Ethylbenzene		A	1.0	2.0	20				
	Xylenes		A	1.0	2.0	19				
	Trichloromethane	EN ISO 10301: 1997 Water quality - Determination of highly volatile halogenated hydrocarbons - GC methods	A	0.2	2.0	15	2.5	0.75	n.a.	
	Carbon tetrachloride		A	0.4	4	15	12	3.6	--	
	Trichloroethylene		A	0.2	2	10	10	3	--	
	Tetrachloroethylene		A	0.2	2	15	10	3	--	
	Dichloromethane		A	0.5	5	20	20	6	n.a.	

Laboratory/ Accreditation status/ Contacts	Substances analysed	Method used	A	Technical specifications			Compliance with 2009/90/EC			
				LoD, ug/L	LoQ, ug/L	MU, %	AA-EQS for Inland surface waters, ug/L*		MAC-EQS for Inland surface waters, ug/L*	
							EQS	LoQ (30% from EQS)	EQS	LoQ (30% from EQS)
Diagnostic Centre of Institute of Food Safety, Animal Health and Environment „BIOR”	Benzo(a)pyrene	NDC-T-012-030-2006 Determination of PAHs in food products and water by GC/MS	A	0.0011	0.0036	32	0.05	0.015	0.1	0.03
	Benzo(b)fluoranthene		A	0.0010	0.0034	32	Sum = 0.03	0.009	n.a.	
	Benzo(k)fluoranthene		A	0.0013	0.0042	32				
	Indeno(1,2,3-c,d)pyrene		A	0.0012	0.0040	32	Sum = 0.002	0.0006	n.a.	
	Benzo(g,h,i)perylene		A	0.0015	0.0050	32				
LATAK-T-012	Hg	LVS EN 1483:2007 Water quality - Determination of Hg - Method using AAS	A	0.1	0.3	32	0.05	0.015	0.07	0.021
Lejupes street 3, Rīga, Latvia LV-1076	Aldrin	NDC-T-012-066-2009 Determination of organochlorine pesticides' residues in water	A	0.004	0.012	18.2	Sum = 0.01	0.003	n.a.	
	Dieldrin		A	0.003	0.011	18.8				
	HCH-alpha		A	0.003	0.009	10.5	0.02	0.006	0.04	0.012
	HCH-beta		A	0.001	0.003	16.3				
	HCH-gamma		A	0.002	0.005	19.6				
	Alpha-endosulfan		A	0.003	0.009	28.3	0.005	0.0015	0.01	0.003
	Beta-endosulfan		A	0.002	0.005	28.1				
	Heptachlorepoxyde***		A	0.0002	0.0006	17.9	$2.1 \cdot 10^{-7}$	$0.6 \cdot 10^{-7}$	$3 \cdot 10^{-4}$	$0.9 \cdot 10^{-4}$
	Dicofol***		A	0.026	0.056	26.5	$1.5 \cdot 10^{-4}$	$0.5 \cdot 10^{-4}$		
	p,p-DDT		A	0.001	0.005	18.8	0.01	0.003	n.a.	
	Pb		A	0.8	2.6	23	7.2	2.16	n.a.	
	Cr		A	0.7	2.5	18	11	3.3		
	Ni		A	0.7	2.5	23	20	6	n.a.	
	As		A	1	3	17	150	45		
	Cd (depending of water hardness class)		A	LVS EN ISO 15586:2003 Water quality - Determination of trace elements by AAS with graphite furnace	A	0.12	0.5	17	$\leq 0.08$ (1)	$\leq 0.024$
A		0.08 (2)	0.024		0.45 (2)				0.135	
A		0.09 (3)	0.027		0.6 (3)				0.18	
A		0.15 (4)	0.045		0.9 (4)				0.27	
A		0.25 (5)	0.075		1.5 (5)				0.45	
1,2-dichloroethane	A	SMWW, 21th.Ed. 2005, 6200 B Purge and trap capillary-column GC/MS method	A	0.04	0.2	20	10	3	n.a.	
Benzene	A		0.04	0.2	20	10	3	50	15	
Trichloroethylene	A		0.02	0.1	20	10	3	n.a.		
Tetrachloroethylene	A		0.02	0.1	20	10	3	n.a.		
Trichloromethane	A		0.04	0.2	20	2.5	0.75	n.a.		
Cu	A	LVS ISO 8288:1986	A	10	30	25	9,0	2,7		
Zn	A	Water quality - Determination of Co, Ni, Cu, Zn, Cd and Pb - Flame AAS	A	7	21	20	120	36		
Dichlorvos***	A	NDC-T-012-067-2006	A	0.010	0.035	20.4	$6 \cdot 10^{-4}$	$1.8 \cdot 10^{-4}$	$7 \cdot 10^{-4}$	$2.1 \cdot 10^{-4}$
Dimethoate	A	Determination of organophosphorous pesticides' residues in water	A	0.0002	0.0006	29.2	1	0,3		
Chlorpyrifos	A		A	0.002	0.007	21.0	0.03	0.009	0.1	0.03

Laboratory/ Accreditation status/ Contacts	Substances analysed	Method used	A	Technical specifications			Compliance with 2009/90/EC			
				LoD, ug/L	LoQ, ug/L	MU, %	AA-EQS for Inland surface waters, ug/L*		MAC-EQS for Inland surface waters, ug/L*	
							EQS	LoQ (30% from EQS)	EQS	LoQ (30% from EQS)
Vides audits, Ltd. LATAK-T-261 Dzērbenes street 27, Rīga, Latvija LV-1006	Benzene	US EPA 5030C:2003/ US EPA 8021B:1996 Purge-and-Trap for aqueous samples. Aromatic and halogenated volatiles by GC using PI and/or EC detectors.	A	0.01	0.10	20	10	3	50	15
	Phenols (index of phenols)	LVS ISO 6439:1990 Water quality - Determination of phenol index - 4-Aminoantipyrine spectrometric methods after distillation	A	1	5	8	300	90		
	Petroleum hydrocarbons (C <sub>10</sub> -C <sub>40</sub> index of hydrocarbons)	LVS EN ISO 9377-2:2001 Water quality - Determination of hydrocarbon oil index - Part 2: Method using solvent extraction an GC	A	20	100	9	100	30		
	Benzene	ISO 11423-1:1997 Water quality - Determination of benzene and some derivatives -- Part 1: Head-space GC method	A	0.4	1.2	9	10	3	50	15
	Toluene		A	0.3	0.9	5	10	3		
	Ethylbenzene		A	0.4	1.2	7	10	3		
	m-xylene		A	0.4	1.2	7	10	3		
	p-xylene		A	0.3	1.0	7	10	3		
	o-xylene		A	0.3	1.0	6	10	3		
	Hg		LVS ISO 5666:2000 Water quality - Determination of Hg	A	0.16	0.54	11	0.05	0.015	0.07
	As	LVS EN ISO 11969:2001 Water quality - AAS (hydride techn.)	A	1.0	2.0	14	150	45		
	Zn	LVS EN ISO 15586:2003 Water quality - Determination of trace elements by AAS with graphite furnace	A	5.0	10.0	12	120	36		
	Cu		A	0.8	2.5	12	9,0	2,7		
	Cr		A	2.2	6.5	16	11	3,3		
	Cd (depending of water hardness class)	LVS EN ISO 15586:2003 Water quality - Determination of trace elements by AAS with graphite furnace	A	0.12	0.4	20	≤ 0.08 (1)	≤ 0.024	≤ 0.45 (1)	≤ 0.135
A			0.08 (2)				0.024	0.45 (2)	0.135	
A			0.09 (3)				0.027	0.6 (3)	0.18	
A			0.15 (4)				0.045	0.9 (4)	0.27	
A			0.25 (5)				0.075	1.5 (5)	0.45	
	Ni		A	2.0	2.3	17	20	6	n.a.	
	Pb		A	0.9	2.0	17	7.2	2.16	n.a.	
	As		A	1.0	5.0	19	150	45		
	1,2-dichlorethane	EN ISO 10301:1997 Water quality - Highly volatile halogenated hydrocarbons - GC meth.	A	0.1	0.3	12	10	3	n.a.	
	Naphtalene	US EPA 8100:1986 Polynuclear Aromatic Compounds	A	0.09	0.28	12	2.4	0.72	n.a.	
	Anthracene		A	0.39	1.17	12	0.1	0.03	0.4	0.12
	Fluoranthene		A	0.14	0.42	12	0.1	0.03	1	0.3
	Benzo(b)fluoranthene		A	0.17	0.51	12	Sum = 0.03	0.009	n.a.	
	Benzo(k)fluoranthene		A	0.18	0.53	12	0.05	0.015	0.1	0.03
	Benzo(a)pyrene		A	0.24	0.71	12	Sum = 0.002	0.0006	n.a.	
	Benzo(ghi)perylene		A	0.22	0.65	12				
	Indeno(1,2,3-cd)pyrene		A	0.21	0.64	12				

Laboratory/ Accreditation status/ Contacts	Substances analysed	Method used	A	Technical specifications			Compliance with 2009/90/EC			
				LoD, ug/L	LoQ, ug/L	MU, %	AA-EQS for Inland surface waters, ug/L*		MAC-EQS for Inland surface waters, ug/L*	
							EQS	LoQ (30% from EQS)	EQS	LoQ (30% from EQS)
"AND resources" Ltd, LATAK-T-246 Olīvu street 9, Rīga, Latvia LV-1004	Petroleum hydrocarbons (C <sub>10</sub> -C <sub>40</sub> index of HC)	LVS EN ISO 9377-2:2001 Water quality - Hydrocarbon oil index - Part 2: Solvent extraction an GC	A	20	50	±15	100	30		
	Benzene	ISO 11423-1:1997 Water quality - Benzene and some derivatives – P. 1: Head-space GC	A	1	3	±15	10	3	50	15
	Toluene		A	1	3	±15	10	3		
	Ethylbenzene		A	1	3	±15	10	3		
	Xylenes		A	1	3	±15	10	3		

A Accreditation status of method.

\* Cabinet Regulation No. 118 adopted on March 12. 2002 "Regulations regarding the Quality of Surface Waters and Groundwaters", with amendments until 14.08.2009., as well Directive **2008/105/EC** of European Parliament and Council on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/419/EEC, 86/280/EEC and amending Directive 2000/60/EC.

\*\*\* Proposals for including new HS and setting new EQS (Working Group E (EC), January 2011).

n.a. EQS value is not applicable.

-- EQS value is not available.

EQS values/required values for testing methods' LoQ which are lower than LoQ of certain method are marked with yellow (methods do not comply with requirements of Directive 2009/90/EC).

Overview on the national laboratories covering HS analysis in sediments, soils and sewage sludge and technical specification of those analysis (on 1<sup>st</sup> October 2011)

Laboratory/ Accreditation status/ Contacts	Substances analysed	Method used	A	Technical specifications			Compliance with 2009/90/EC			
				LoD, mg/kg	LoQ, mg/kg	MU, %	EQS for soil, 1 <sup>st</sup> limit**, mg/kg		EQS for soil, 2 <sup>nd</sup> limit**, mg/kg	
							EQS	LoQ (30% from EQS)	EQS	LoQ 30% from EQS
Latvian Environment, Geology and Meteorology Centre Environmental laboratory  LATAK-KT-105,  Ošu street 5, Jūrmala, Latvia LV-2015	Alpha-endosulfan	US EPA 8081:1990 Organochlorine pesticides and PCBs as arochlors by GC: capillary column technique	A	1.1-3.6	3.6-12	50	--		--	
	Beta-endosulfan		A	1.1-3.6	3.6-12	50	--		--	
	HCH-alpha		A	1.1-3.6	3.6-12	50	--		--	
	HCH-beta		A	1.1-3.6	3.6-12	50	--		--	
	HCH-gamma		A	1.1-3.6	3.6-12	50	--		--	
	DDT, DDD, DDE		A	1.1-3.6	3.6-12	50	0.01		0.03	
	p,p-DDT		A	1.1-3.6	3.6-12	50	--		--	
	Hexachlorobenzene (HCB)		A	1.1-3.6	3.6-12	50	--		--	
	Trichloromethane		A	1.1-3.6	3.6-12	50	--		--	
	Heptachlor		A	1.1-3.6	3.6-12	50	--		--	
	Heptachlorepoide		A	1.1-3.6	3.6-12	50	--		--	
	PCB 28		A	1.1-3.6	3.6-12	50	0.001		0.03	
	PCB 52		A	1.1-3.6	3.6-12	50	0.001		0.03	
	PCB 101		A	1.1-3.6	3.6-12	50	0.004		0.03	
	PCB 118		A	1.1-3.6	3.6-12	50	0.004		0.03	
	PCB 138		A	1.1-3.6	3.6-12	50	0.004		0.03	
	PCB 153	A	1.1-3.6	3.6-12	50	0.004		0.03		
	PCB 180	A	1.1-3.6	3.6-12	50	0.004		0.03		
	Anthracene	US EPA 8270C Semivolatile organic compounds by GC/MS	A	0.010	0.033	25	0.01		0.1	
	Benz(a)anthracene		A	0.016	0.053	25	0.03		0.4	
	Benzo-a-pyrene		A	0.010	0.029	25	0.3		3	
	Benzo-b-fluoranthene		A	0.014	0.047	25	--		--	
	Benzo-k-fluoranthene		A	0.010	0.029	25	0.2		2	
	Benzo-g,h,i-perylene		A	0.010	0.033	25	0.8		8	
	Chrysene		A	0.040	0.133	25	1.1		11	
	Indeno(1,2,3-cd) pyrene		A	0.012	0.040	25	0.6		6	
	Fluorantene		A	0.026	0.087	25	0.3		3	
Phenanthrene	A		0.020	0.067	25	0.05		0.5		
Naphthalene	A		0.012	0.040	25	0.01		0.1		
Toluene	ISO 22155:2005 Soil quality - GC quantitative determ. of volatile arom. and halogenated hydrocarbons and selected ethers - Static headspace method	A	0.3	1	25	--		--		
Ethylbenzene		A	0.3	1	25	--		--		
m,p-xylene		A	0.3	1	25	--		--		
o-xylene		A	0.3	1	25	--		--		
Cd	LVS ISO 11047:1998 Soil quality - Determination of Cd, Cr, Co, Cu, Pb, Mn, Ni and Zn in aqua regia extracts of soil - Flame and ET AAS methods	A	0.006	0.021	15	1	0.3	3	0.9	
Cr		A	0.06	0.21	16	100	30	300	90	
Cu		A	0.3	1	10	100	30	200	30	
Pb		A	0.06	0.2	13	100	30	200	60	
Ni		A	0.14	0.48	11	20	6	50	15	
Zn		A	2	7	6	200	60	400	120	
Hg	LVS 346:2005. Soil quality - Cold vapour AAS	A	0.08	0.27	10	0.5	0.15	1.5	0.45	

Laboratory/ Accreditation status/ Contacts	Substances analysed	Method used	A	Technical specifications			Compliance with 2009/90/EC			
				LoD, mg/kg	LoQ, mg/kg	MU, %	EQS for soil, 1 <sup>st</sup> limit**, mg/kg		EQS for soil, 2 <sup>nd</sup> limit**, mg/kg	
							EQS	LoQ (30% from EQS)	EQS	LoQ 30% from EQS
Vides audits, Ltd. LATAK-T-261 Dzērbenes street 27, Rīga, Latvia LV-1006 <a href="mailto:info@videsaudits.lv">info@videsaudits.lv</a>	Cu	LVS ISO 11047:1998 Soil quality - Determination of Cd, Cr, Co, Cu, Pb, Mn, Ni and Zn in aqua regia extracts of soil - Flame and ET AAS methods	A	0.15	0.36	7	100	30	200	30
	Zn		A	1.0	2.7	9	200	60	400	120
	Cr		A	0.24	0.65	10	100	30	300	90
	Cd		A	0.008	0.026	18	1	0.3	3	0.9
	Ni		A	0.23	0.64	14	20	6	50	15
	Pb		A	0.93	3.0	9	100	30	200	60
	Hg	LVS 346:2005 Soil quality - Cold vapour AAS	A	0.2	0.6	11	0.5	0.15	1.5	0.45
	Benzene	ISO 22155:2005 Soil quality - GC quantitative determination of volatile aromatic and halogenated hydrocarbons and selected ethers - Static headspace method	A	0.01	0.05	12	--		--	
	Toluene		A	0.05	0.10	9	--		--	
	Ethylbenzene		A	0.02	0.05	12	--		--	
	m-Xylene		A	0.01	0.04	12	--		--	
	p- Xylene		A	0.01	0.04	11	--		--	
	o- Xylene		A	0.01	0.04	10	--		--	
	Petroleum hydrocarbons	ISO 16703:2004 Soil quality - Content of hydrocarbons in the range C <sub>10</sub> to C <sub>40</sub> by GC	A	3	10	9	100	30	400	120
Latvian Institute of Aquatic Ecology (LIAE), LATAK-T-169 Daugavgrīvas street 8, Rīga, LV-1007	Cd	US EPA 7000B:2007 Flame AAS	A	0.07	0.24	25	1	0,3	3	0,9
	Cu		A	3	10	25	100	30	200	30
	Ni		A	1	4	25	20	6	50	15
	Pb		A	2	6	25	100	30	200	60
	Zn		A	3	11	25	200	60	400	120
	Cr		A	1	3	25	100	30	300	90
	Hg	US EPA 7471B:2007 Hg in solid or semisolid waste (manual cold- vapour techn.)	A	0.02	0.06	25	0.5	0.15	1.5	0.45
"AND resources" LATAK-T-246 Olīvu street 9, Rīga, LV-1004	Petroleum hydrocarbons	ISO 16703:2004 Soil quality- Determination of content of hydrocarbons in the range C <sub>10</sub> to C <sub>40</sub> by GC	A	10	30	18	100	30	400	120

A Accreditation status of method.

\*\* Cabinet Regulation No. 475 "Procedures regarding the Cleaning and Deepening of Surface Water Bodies and Port Basins".

-- EQS value is not available.

EQS values/required values for testing methods' LoQ which are lower than LoQ of certain method are marked with yellow (methods do not comply with requirements of Directive 2009/90/EC).

Overview on the national laboratories covering HS analysis in biota and technical specification of those analysis (on 1<sup>st</sup> October 2011)

Laboratory/ Accreditation status/ Contacts	Substances analysed	Method used	A	Technical specifications				Compliance with 2009/90/EC	
				LoD	LoQ	Unit	MU %	EQS for biota (surface water organisms)*, µg/kg	
								EQS	LoQ, (30% from EQS)
Diagnostic Centre of Institute of Food Safety, Animal Health and Environment „BIOR” LATAK-T-012 Lejupes street 3, Rīga, Latvia LV-1076	Dioxins	PVO-1998-PHDD/F/PHB-TEK Determination of dioxins and dioxin like PCBs in food and feed by gas chromatography with high resolution masspectrometry (GC-HRMS)	A	0.0001	0.001	ng/kg whole body	20		
	Hexachlorbenzene	LVS EN 1528-4:1996 Fatty food - Determination of pesticides and polychlorinated biphenyls (PCBs) - Part 4: Determination, confirmatory tests, miscellaneous.	A		3	µg/kg whole body	50	10 WW	3 WW
	Hexachlorbutadiene	LVS EN 1528-4:1996 Fatty food - Determination of pesticides and polychlorinated biphenyls (PCBs) - Part 4: Determination, confirmatory tests, miscellaneous.	A		3	µg/kg whole body	50	55 WW	18 WW
Latvian Institute of Aquatic Ecology, LATAK-T-169 Daugavgrīvas street 8, Rīga, Latvia LV-1007	Hg	US EPA 245.6:1991:1991 Determination of Hg in tissues by cold vapour atomic AAS	A	10	20	µg/kg WW	25	20 WW	6 WW
	Cu	US EPA 7000B:2007 Flame AAS	A	10	30	mg/kg	25	--	
	Pb	US EPA 7000B:2007 Flame AAS	A	200	650	µg/kg	25	--	
	Zn	US EPA 7000B:2007 Flame AAS	A	10	35	mg/kg	25	--	
	Cd	US EPA 7010:2007 Graphite Furnace AAS	A	100	350	µg/kg	25	--	

A Accreditation status of method.

\* Directive **2008/105/EC** of European Parliament and Council on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/419/EEC, 86/280/EEC and amending Directive 2000/60/EC.

\*\*\* Proposals for including new PS and setting new EQS (Working Group E (EC), January 2011).

-- EQS value is not available.

WW wet weight

EQS values/required values for testing methods' LoQ which are lower than LoQ of certain method are marked with yellow (methods do not comply with requirements of Directive 2009/90/EC).