



# PROPOSALS FOR THE STATE MONITORING PROGRAMME

2011



**FUNDED BY:**

This report is prepared in the frame of the project “Baltic Actions for the Reduction of Pollution of the Baltic Sea from Priority Hazardous Substances” (BaltActHaz) supported by LIFE+ financial instrument of the European Community /Project no. LIFE07 ENV EE 000122/, Estonian Environmental Investment Centre, Ministries of Environment of Lithuania and Latvia, Ministry of Social Affairs of Estonia.



MINISTRY OF THE  ENVIRONMENT



**PREPARED BY:**

Zita Dudutyė, Baltic Environmental Forum Lithuania  
Jolanta Dvarionienė, KTU APINI  
Jolita Kruopienė, KTU APINI

© Baltic Environmental Forum Lithuania  
Užupio 9/2-17  
LT-10202 Vilnius, Lithuania  
<http://www.bef.lt>

Public organisation “Baltijos aplinkos forumas” bears full responsibility about the content of this document and it does not reflect the EU position.

## CONTENT

|   |           |
|---|-----------|
| <b>A. INTRODUCTION .....</b>  | <b>4</b>  |
| <b>B. BACKGROUND ON THE MONITORING OF HAZARDOUS SUBSTANCES IN THE WATER .....</b>   | <b>5</b>  |
| 1. LEGAL FRAMEWORK FOR THE MONITORING OF HAZARDOUS SUBSTANCES.....  | 5         |
| 2. PURPOSE OF THE MONITORING OF HAZARDOUS SUBSTANCES.....   | 6         |
| <b>C. ANALYTICAL REQUIREMENTS FOR CHEMICAL ANALYSIS AND MONITORING OF WATER STATUS AND RELATED CHALLENGES.....</b>                            | <b>8</b>  |
| 1. TECHNICAL SPECIFICATIONS FOR CHEMICAL ANALYSIS ACCORDING 2009/90/EC .....  | 8         |
| 2. CHALLENGES RELATED TO TECHNICAL SPECIFICATIONS OF 2009/90/EC.....  | 8         |
| <b>D. ANALYSIS OF PRACTICES OF MONITORING AND SCREENING OF HAZARDOUS SUBSTANCES IN LITHUANIA .....</b>  | <b>13</b> |
| <b>E. PROPOSALS FOR IMPROVEMENT OF THE MONITORING PROGRAMME BASED ON BALTAZHAZ FINDINGS.....</b>  | <b>18</b> |
| 1. SUMMARY OF THE MAIN FINDINGS ON HAZARDOUS SUBSTANCES OCCURRENCE IN BALTAZHAZ PROJECT AND OTHER HS SCREENING ACTIVITIES IN THE COUNTRY..... | 18        |
| 2. PROPOSALS FOR IMPROVEMENT OF THE CURRENT MONITORING PROGRAMME .....  | 31        |
| <b>F. SCREENING OF SUBSTANCES OF POSSIBLE CONCERN .....</b>   | <b>35</b> |
| 1. LISTS OF SUBSTANCES OF POSSIBLE CONCERN .....  | 35        |
| 2. SCREENING SURVEY AS A TOOL TO IDENTIFY EMERGING SUBSTANCES AND AN INPUT TO THE MONITORING PROGRAMME.....                                   | 38        |
| <b>G. DERIVATION OF ENVIRONMENTAL QUALITY STANDARDS .....</b>   | <b>40</b> |
| <b>H. LIST OF ABBREVIATIONS .....</b>   | <b>41</b> |
| <b>J. REFERENCES.....</b>   | <b>42</b> |

## A. 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 the **occurrence** of selected WFD, HELCOM priority substances and nationally important pollutants in the environment as well as to 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 and experiences of other countries 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 Lithuania,
- proposals for improvement of the current monitoring system,
- management of emerging substances.

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

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

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

#### ► EU requirements for the chemicals monitoring

A strategy for dealing with **pollution of water with 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 into 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 WFD.**

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 had 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 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. Reduced monitoring frequencies, and under certain circumstances, even no monitoring may be justified 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 substance 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). Also the Member States shall determine the frequency of monitoring in sediment and/or biota so as to provide sufficient data for a reliable long-term trend analysis. As a guideline, monitoring should take place every three years, 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 found 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)

### ► 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. 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 reflects 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 load 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 strengthens 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.

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

### 1. TECHNICAL SPECIFICATIONS FOR CHEMICAL ANALYSIS ACCORDING 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 minimum environmental quality standards ( $LOQ \leq 0.3 * AA-EQS$ ),
- 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).

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.

### 2. CHALLENGES RELATED TO TECHNICAL SPECIFICATIONS OF 2009/90/EC

#### ► Availability of standard methods

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

- PBDEs: no standard for water is available, problems with sensitivity of the methods (LOQ difficult to meet as the sum concentration of 6 congeners has to be below 0.5ng/l and 0.2 ng/l respectively);
- SCCP: no standard for water is available; analysis is not under control also in the research laboratories; the most frequently applied method is GC-ECNI-MS (but with this method there are some unsolved problems: isomers with less than five chlorine atoms 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; the existing standard methods are not sensitive enough;
- PAH (5- and 6-ring PAH): sensitivity for some parameters (in particular for the 6-ring isomers) is not sufficient with regard 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.



However there are also other standardized methods (according to SOP, ISO, DIN EN ISO) used in different countries (e.g. Sweden) for analyses of the priority substances. These methods or other known methods could be also used for analyses of priority substances in Lithuania if there are no standardized methods according to 2009/90/EC.

An overall methodological approach to monitoring of surface water chemicals is provided in guidance document "Guidance Document No. 19 - Guidance on surface water chemical monitoring". It can be found 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)

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)          |                                 | 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>4)</sup>              | EN ISO 6468:1996                              | GC/ECD                          | 0,01                 | 0,006                            | 0,006                           | 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>4)</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                    |
| Nonylphenols <sup>4)</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>7)</sup>               | ISO 17993:2002                                | HPLC/Fluo                       | 0,01                 | 0,005                            | 0,005                           | C                     | C                    |
| Benzo(k)fluoranthene <sup>7)</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 is not sensitive enough for the analysis of other surface waters. For more detailed information see the main document.

► **Laboratory capacities**

Investigations of priority and other hazardous substances in Lithuania are possible only at the Laboratory of Environmental Research Department of the Lithuanian Environmental Protection Agency. Table 2 presents laboratory capacities of this laboratory.

Table 2. Laboratory capacity

| Laboratory/<br>Accreditation<br>status/<br>Contacts   | Substances                  | Water                 |   | Sediments             |                                      |
|---|-----------------------------|-----------------------|---|-----------------------|--------------------------------------|
|   |                             | Substance<br>measured | Accreditation status of method  | Substance<br>measured | Accreditation<br>status of<br>method |
| EPA<br>accredited<br><br>(Environmental<br>Research<br>Department)<br>according to LST<br>EN ISO/IEC<br>17025 | <b>Metals</b>               |                       |   |                       |                                      |
|   | Mercury                     | X                     | Accredited,<br>LST EN ISO 17852:2008  | X                     |                                      |
|   | Cadmium                     | X                     | Accredited,<br>LST EN ISO 15586:2004, except<br>annex B   | X                     |                                      |
|   | Chromium                    | X                     | Accredited,<br>LST EN ISO 15586:2004, except<br>annex B, LST ISO 9174:2003,<br>except section 3 | X                     |                                      |
|   | Copper                      | X                     | Accredited,<br>LST EN ISO 15586:2004, except<br>annex B   | X                     |                                      |
|   | Arsenic                     | X                     | Accredited,<br>LST EN ISO 15586:2004, except<br>annex B   | X                     |                                      |
|   | Lead                        | X                     | Accredited,<br>LST EN ISO 15586:2004, except<br>annex B   | X                     |                                      |
|   | Nickel                      | X                     | Accredited,<br>LST EN ISO 15586:2004, except<br>annex B   | X                     |                                      |
|   | <b>Pesticides</b>           |                       |   |                       |                                      |
|   | α-<br>hexachlorocyclohexane | X                     | Accredited,<br>LST EN ISO 6468:2000   | X                     |                                      |
|   | β-<br>hexachlorocyclohexane | X                     | Accredited,<br>LST EN ISO 6468:2000   | X                     |                                      |
|   | γ-<br>hexachlorocyclohexane | X                     | Accredited,<br>LST EN ISO 6468:2000   | X                     |                                      |
|   | δ-<br>hexachlorocyclohexane | X                     | Accredited,<br>LST EN ISO 6468:2000   | X                     |                                      |
|   | Hexachlorobenzene           | X                     | Accredited,   | X                     |                                      |

|  |    |                                      |      |  |
|--|----|--------------------------------------|------|--|
| e (HCB)                                    |    | LST EN ISO 6468:2000                 |      |  |
| α-endosulfan                               | X  | Accredited,<br>LST EN ISO 6468:2000  | X    |  |
| β-endosulfan                               | X  | Accredited,<br>LST EN ISO 6468:2000  | X    |  |
| Pentachlorobenzen<br>e                     | X  |                                      | X    |  |
| Alachlor                                   | No |                                      | No** |  |
| Aldrin                                     | X  | Accredited,<br>LST EN ISO 6468:2000  | X    |  |
| Dieldrin                                   | X  | Accredited,<br>LST EN ISO 6468:2000  | X    |  |
| Endrin                                     | X  | Accredited,<br>LST EN ISO 6468:2000  | X    |  |
| Izodrin                                    | X  |                                      | X    |  |
| p,p'-DDT                                   | X  | Accredited,<br>LST EN ISO 6468:2000  | X    |  |
| o,p'-DDT                                   | X  | Accredited,<br>LST EN ISO 6468:2000  | X    |  |
| p,p'-DDE                                   | X  | Accredited,<br>LST EN ISO 6468:2000  | X    |  |
| p,p'-DDD                                   | X  | Accredited,<br>LST EN ISO 6468:2000  | X    |  |
| Diuron                                     | X  |                                      | X    |  |
| Isoproturon                                | X  |                                      | X    |  |
| Simazine                                   | X  |                                      | X    |  |
| Atrazine                                   | X  |                                      | X    |  |
| Trifluralin                                | X  |                                      | X    |  |
| Chlorfenvinphos                            | X  |                                      | X    |  |
| Chlorpyrifos                               | X  |                                      | X    |  |
| <b>VOC</b>                                 |    |                                      |      |  |
| Hexachlorobutadie<br>ne                    | X  |                                      | N*   |  |
| Benzene                                    | X  |                                      | X    |  |
| Tetrachloromethan<br>e                     | X  |                                      | X    |  |
| 1,2-dichloroethane                         | X  |                                      | X    |  |
| Methylene<br>chloride<br>(dichloromethane) | X  |                                      | X    |  |
| Tetrachloroethylen<br>e                    | X  |                                      | X    |  |
| Trichloroethylene                          | X  |                                      | X    |  |
| 1,2,4-<br>trichlorobenzene                 | X  |                                      | N*   |  |
| 1,3,5-<br>trichlorobenzene                 | X  |                                      | N*   |  |
| 1,2,3-<br>trichlorobenzene                 | X  |                                      | N*   |  |
| Trichloromethane                           | X  |                                      | X    |  |
| <b>PAH</b>                                 |    |                                      |      |  |
| Benzo(a)pyrene                             | X  | Accredited,<br>LST EN ISO 17993:2004 | X    |  |
| Benzo(b)fluoroant<br>hene                  | X  | Accredited,<br>LST EN ISO 17993:2004 | X    |  |
| Benzo (k)<br>fluoroanthenas                | X  | Accredited,<br>LST EN ISO 17993:2004 | X    |  |
| Benzo(g, h, i)                             | X  | Accredited,                          | X    |  |

|                              |      |                                      |      |  |
|------------------------------|------|--------------------------------------|------|--|
| perylene                     |      | LST EN ISO 17993:2004                |      |  |
| Indeno(1,2,3-cd)pyrene       | X    | Accredited,<br>LST EN ISO 17993:2004 | X    |  |
| Anthracene                   | X    | Accredited,<br>LST EN ISO 17993:2004 | X    |  |
| Fluoranthene                 | X    | Accredited,<br>LST EN ISO 17993:2004 | X    |  |
| Naphtalene                   | X    | Accredited,<br>LST EN ISO 17993:2004 | X    |  |
| <b>Phthalates</b>            |      |                                      |      |  |
| Di(2-ethylhexyl)phtalate     | X    |                                      | No** |  |
| Dibutylphtalate              | X    |                                      | No** |  |
| <b>Phenols</b>               |      |                                      |      |  |
| Nonylphenol                  | X    |                                      | No** |  |
| (4-(para)-nonylphenol)       | X    |                                      | No** |  |
| Octylphenol                  | X    |                                      | No** |  |
| Oil hydrocarbon              | X    |                                      | X    |  |
| <b>PBD</b>                   |      |                                      |      |  |
| Brominated diphenylether     | No** |                                      | X    |  |
| Pentabromdiphenylether       | No** |                                      | X    |  |
| <b>TBT</b>                   |      |                                      |      |  |
| Tributiltin cation           | X    |                                      | N*   |  |
| <b>Chlorinated paraffins</b> |      |                                      |      |  |
| SCCP                         | No** |                                      | No** |  |
| MCCP                         | No** |                                      | No** |  |
| <b>Chlorphenol</b>           |      |                                      |      |  |
| Pentachlorphenol (PCP)       | X    |                                      | X    |  |
| <b>PCB</b>                   |      |                                      |      |  |
| PCB isomers                  | X    |                                      | X    |  |

N\* - Method will be assimilated until the end of 2011

No\*\* – No standardized method

### ► Development of laboratory capacities

There are many important aspects to be taken into consideration when developing a national laboratory strategy plan. Issues to be addressed include technical, legal, quality, financial and logistical matters.

There are several possible scenarios for further development of laboratory capacities:

- Extension of EPA laboratory (new equipment, methods, etc.);
- Analysis of certain substances outside Lithuania;
- **Establishment of independent laboratory research center, which can provide services both to state institutions and to industrial installation.**

The potential way to take a decision on development of national laboratory capacities is the following:

1. Analyse „mandatory“ needs for analysis by state, private and other entities based on<sup>1</sup>:
  - a. Legal requirements: substances to be analysed, number of analysis per year (frequency, sites):
    - i. EU requirements where monitoring/control is needed: water, air, soil, sludge, IPPC...
    - ii. International Conventions: UNEP, CLRTAP, HELCOM...
    - iii. National priorities.
  - b. Emission/pressure information from registers/databases → other substances of concern, emerging substances;
  - c. Frequency of substance detection, occurrence in the environment.
2. Analyse test standards and methods:
  - a. Availability of standardized methods;
  - b. Equipment needed and capacities.
3. 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. Creation and development of SOP ; later possibly accreditation;
  - g. Etc.
4. Analyse existing capacities on the market (labs, substances analysed, methods used, compliance with mandatory requirements...).
5. Estimate the potential forms for the laboratory and capacity raising (governmental, private, manufacturer, tests across multiple laboratories, tests in other countries).
6. Make cost analyses for different scenarios<sup>2</sup>:
  - a. Development of the National laboratory;
  - b. Analyses of certain substances at the accredited laboratories outside Lithuania.

#### D. ANALYSIS OF PRACTICES OF MONITORING AND SCREENING OF HAZARDOUS SUBSTANCES IN LITHUANIA

The list of substances investigated within the monitoring programmes is provided in the Table 3.

Table 3. Overview of the hazardous substances covered by monitoring programmes

| HS | EMP<br>1997 - 2004 |      | EMP<br>2005-2010 |      | EMP<br>2011 -2017 |
|----|--------------------|------|------------------|------|-------------------|
|    | 1997               | 2004 | 2005             | 2009 |                   |
| Fe | X                  |      |                  |      |                   |
| Mn | X                  |      |                  |      |                   |
| Hg | X                  | X    | X                | X    | X                 |
| Cd | X                  | X    | X                | X    | X                 |

<sup>1</sup> Various water quality parameters, including organic substances, need to be investigated not only for the purposes of the state monitoring. Also, for example, companies discharging hazardous chemical substances have a need to monitor these substances in their emissions.

<sup>2</sup> E.g. prices for analysis at GALAB laboratory are comparable with prices at EPA laboratory. The list of laboratories questioned during the project is presented in Annex 1.

|   |   |   |   |           |           |
|---|---|---|---|-----------|-----------|
| Cu  | X | X | X | X         | X         |
| Cr  | X | X | X | X (b, VI) | X (b, VI) |
| Zn  | X | X | X | X         | X         |
| Pb  | X | X | X | X         | X         |
| Ni  | X | X | X | X         | X         |
| Sn  |   |   | X | X         | X         |
| V   |   |   | X | X         | X         |
| Al  |   |   | X | X         | X         |
| As  |   |   | X | X         | X         |
| Sr  |   | X | X |           |           |
| Cs  |   | X | X |           |           |
| 3,4-dichlorbenzoic acid                   | X |   |   |           |           |
| 2-chlorphenol                             | X |   |   |           |           |
| 2, 4-chlorphenol                          | X |   |   |           |           |
| 2, 4, 6-trichlorphenol                    | X |   |   |           |           |
| 2, 3-dimethylphenol                       | X |   |   |           |           |
| 3, 4-dimethylphenol                       | X |   |   |           |           |
| 4-chlor-3-methylphenol;                   | X |   |   |           |           |
| o,p'-DDT                                  | X | X | X | X         | X         |
| p,p'-DDT                                  | X | X |   | X         | X         |
| o,p'-DDE                                  | X | X |   | X         | X         |
| p,p'-DDE                                  | X | X |   | X         | X         |
| o,p'-DDD                                  | X | X |   | X         | X         |
| p,p'-DDD                                  | X | X |   | X         | X         |
| Hexachlorocyclohexane<br>( $\alpha$ -HCH) | X |   |   |           | X         |
| Hexachlorocyclohexane<br>( $\beta$ -HCH)  | X |   |   |           | X         |
| Hexachlorocyclohexane<br>( $\gamma$ -HCH) | X | X | X |           | X         |
| Endosulfan (beta)                         |   |   | X | X         | X         |
| Endosulfan (alfa)                         |   |   | X | X         | X         |
| Aldrin                                    |   |   | X | X         | X         |
| Dieldrin                                  |   |   | X | X         | X         |
| Endrin                                    |   |   | X | X         | X         |
| Izodrin                                   |   |   | X | X         | X         |
| Hexachlorobenzene<br>(HCB)                |   |   | X | X         | X         |
| Pentachlorobenzene                        |   |   |   | X         | X         |
| Tributyltin                               |   |   |   | X         | X         |
| Di(-2-ethylhexil)phtalate -<br>DEHP       |   |   |   | X         | X         |
| Dibutylphtalate                           |   |   |   |           | X         |
| 4-n-nonylphenol                           |   |   |   | X         | X         |
| 4-n-octylphenol                           |   |   |   | X         | X         |
| 4-tert-octylphenol                        |   |   |   | X         | X         |
| Nonylphenol (mixture) CAS<br>25154-52-3   |   |   |   | X         | X         |
| Bisphenol A                               |   |   |   |           | X         |
| Chlorphenvinphos                          |   |   |   | X         | X         |
| Chlorpyriphos                             |   |   |   | X         | X         |
| Tetrachloromethane (CCl4)                 |   |   | X | X         | X         |
| Trichloromethane                          |   |   | X | X         | X         |
| 1,2-dichloroethane<br>(EDC)               |   |   | X | X         | X         |
| Trichloroethylene (TRI)                   |   |   | X | X         | X         |
| Perchloroethylene                         |   |   | X | X         | X         |
| Benzene                                   |   |   | X | X         | X         |
| Methylenechloride<br>(Dichloromethane)    |   |   | X | X         | X         |
| 1,3,5-trichlorobenzene                    |   |   |   |           | X         |
| 1,2,3- trichlorobenzene                   |   |   |   |           | X         |
| 1,2,4- trichlorobenzene                   |   |   |   | X         | X         |
| Heksachlorobutadiene                      |   |   |   |           | X         |

|                                       |   |   |   |   |   |
|---------------------------------------|---|---|---|---|---|
| (HCBD)                                |   |   |   |   |   |
| Benzo(a)pyrene                        |   |   | X | X | X |
| Benzo(b)fluoroantene                  |   |   | X | X | X |
| Benzo(g,h,i)perylene                  |   |   | X | X | X |
| Benzo(k)fluoranthene                  |   |   | X | X | X |
| Fluoranthene                          |   |   | X | X | X |
| Inden(1,2,3-cd)pirene                 |   |   | X | X | X |
| Naphtalene                            |   |   | X | X | X |
| Alachlor                              |   |   |   |   | X |
| Pentabromodiphenylether               |   |   |   |   | X |
| C10-13-chloroalkanes                  |   |   |   |   | X |
| PCB (28, 52, 101, 118, 138, 153, 180) | X | X | X | X | X |
| Simazine                              |   |   | X | X | X |
| Atrazine                              |   |   | X | X | X |
| Diuron                                |   |   |   | X | X |
| Isoproturon                           |   |   |   | X | X |
| Heptachlor                            |   |   |   | X |   |
| Transchlordan                         |   |   |   | X |   |
| Oxichlordan                           |   |   |   | X |   |
| Mirex                                 |   |   |   | X |   |
| Toxafen P26                           |   |   |   | X |   |
| Toxafen P50                           |   |   |   | X |   |
| Toxafen P62                           |   |   |   | X |   |
| Cischlordan                           |   |   |   | X |   |
| Trifluraline                          |   |   |   | X | X |
| Pentachlorophenol (PCP)               | X | X | X | X | X |

Some of the substances in water (e.g. C10-13-chloroalkanes, brominated diphenylethers) still cannot be analysed in the Environmental Research Department of EPA (due to the lack of method assimilation, see Table 2), although they have already been included into the monitoring system.

Also some substances in sediments (e.g. di(2-ethylhexyl)phthalate, dibutylphthalate, nonylphenol (mixture), 4-n-nonylphenol, 4-n-octylphenol, C10-13-chloroalkanes) still cannot be analysed in the Environmental Research Department of EPA (due to the lack of method assimilation, see Table 2), although they have already been included into the monitoring system as well.

### ► Water quality with regard to hazardous substances

#### 1997 – 2004

**Metals:** Five metals: zinc, copper, chromium, lead and nickel were monitored throughout the period of 1995-2003. During this period the average annual concentrations of heavy metals were exceeding AA-MAC only in one river – Kulpė for Cr and Ni. In 2002 concentration of lead in Nemunas below Smalininkai and Sidabra river at the border exceeded AA-MAC. In 2003 there were few cases when concentrations of Cu, Zn, Cr, Ni and Pb exceeded AA-MAC. Higher concentrations of these metals occurred in the rivers Nemunėlis, Kulpė, Šventoji, Jūra, Buka and Birvėta.

**Pesticides:** Simazine was once detected in the Nemunas river (1,15 µg/l) and exceeded AA-MAC (1µg/l). Lindane was detected in Nemunas, Lokysta and Nemunėlis water, where concentrations ranged from 0,01 µg/l to 0,06 µg/l. Also Lindane was detected in bottom sediments in 4 rivers, where concentrations varied from 0,004 mg/kg to 1.000 mg/kg. There was only one lake Lūkšto, were lindane was detected in bottom sediments (0,002 mg/kg). DDT was detected 23 times in 15 rivers, where concentrations varied from 0,01 to 0,96 µg/l. DDT in bottom sediments was detected in 6 rivers: here concentrations of DDT varied from 0,0003 µg/kg to 0,010 mg/kg. DDT in bottom sediments in lakes was detected in Šventas, Lūkštas and Vištytis. DDE was detected 31 time in 17 rivers, where concentrations ranged from 0,005 mg/kg to 0,120 mg/kg.

**Phenols:** Pentachlorophenol was detected in 9 rivers, where concentrations varied from 0,01 µg/l to 0,4 µg/l, and in two lakes (Tauragnų and Žuvinto).

Other hazardous substances included in the monitoring programme in rivers were detected rarely or never.

## **2005 – 2010**

Water monitoring according to the new monitoring programme was first carried out in 2005. Samples of water and bottom sediments for analysis of dangerous substances were taken in 51 station (42 rivers).

As in previous years, the AA-MAC for all parameters was not exceeded, except Zn. When speaking about the parameters, included in the water monitoring for the first time, only concentrations of trichloromethane (chloroform) exceeded AA-MAC (12 µg/l) in few monitoring stations (Šušvė at estuary - 48,3 µg/l; Venta below Mažeikiai – 149,2 µg/l; Varduva at Griežė – 38,8 µg/l; Ašva at the border - 117,3µg/l). It was also detected in some more places, but in lower concentrations.

Some other hazardous substances were also detected (trichlorethylene, perchloroethylene, endosulphan(alpha), anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, fluoranthene, naphthalene), however their concentrations were low and not exceeded AA-MAC.

The number of monitored substances was increased in 2010 compared to the monitoring programme for 2009. However, only part of the analysed organic compounds, namely naphthalene, fluoranthene, benzo(a)pyrene, benzo(b)fluoroantene, benzo(g,h,i)perylene, benzo(k)fluoranthene, and anthracene, were detected in surface waters. Their concentrations were low and not exceeded AA-MAC.

## **2011 – 2017**

A new monitoring programme was prepared in 2011. Among the added substances were HCH, nonylphenol (mixture), bisphenol A, trifluralin, 1,3,5-trichlorobenzene, 1,2,3-trichlorobenzene, hexachlorbutadiene (HCBD), alachlor, pentabromdiphenylether, and C10-13-chloralkanes. Monitoring results are not published yet. However, the preliminary information received from Lithuanian EPA indicates that these newly added substances are present in surface waters and sediments.

## **Screening of hazardous substances in Lithuania**

Some priority and hazardous priority substances that are either not monitored during the State environmental monitoring programme, either are suspected to be substances of bigger concern were investigated during surveys carried out in the frame of the following projects:

- Screening of dangerous substances in the aquatic environment of Lithuania;
- Screening study on occurrence of hazardous substances in the eastern Baltic sea.

In addition to these, there have been projects, which investigated emissions from various sources, e.g. from industries, WWTPs, landfills, etc:

- BaltActHaz;
- COHIBA.

“Screening of dangerous substances in the aquatic environment of Lithuania” has been carried out by Lithuanian EPA, Finish Environmental Institute, Baltic Environmental Forum, and Centre of Environmental Protection Policy. The main objective of the project was to investigate the occurrence of selected priority substances and some other pollutants in the receiving environment (surface water and sediments), and also in wastewater and sewage sludge. All together the project covered 44 sites, where 9 hazardous substance groups (covering 102 substances: metals, phenols and their ethoxylates, PAHs, chlorinated pesticides, VOCs, organotin compounds, phthalates, polybrominated diphenylethers, and other substances (SCCP, pentachlorophenol, chlorpyrifos, cyanides, AOH)) were analyzed, and ecotoxicity tests were performed for 37 sites. Samples were taken in 2006.



“Screening study on occurrence of hazardous substances in the eastern Baltic sea” was performed in the eastern Baltic Sea environment (fish and Sea water) on the occurrence of 8 substance groups (TBT and TPhT, polybrominated diphenylethers, HBCDD, perfluorinated substances, nonylphenols and their ethoxylates, octylphenols and their ethoxylates, chlorinated paraffins (short and medium chain), endosulfane) identified as hazardous under the Baltic Sea Action Plan. The sampling was carried out by institutions in various countries (Center of Marine Research in Lithuania), and analysis performed by IVL and NILU. Samples were taken in 2008. Two of the sampling sites were in Lithuania: coastal area north from Klaipėda (5 samples of biota and 2 samples of water), and in open sea north-east from Klaipėda (2 samples of biota and 2 samples of water).

The survey carried out during BaltActHaz project in 2011 focused on 9 groups of substances (nonylphenols and their ethoxylates, octylphenols and their ethoxylates, organotins, polybrominated diphenylethers, HBCDD, perfluorinated substances, phthalates, chlorinated paraffins (short and medium chain), chloroform), and covered different types of sites, which could potentially emit the hazardous substances: wastewater from various industries (discharged to combined sewage system or directly to the environment), wastewater from other commercial facilities (e.g. laundries, supermarkets), from households, run-off from specific areas, and filtrate from landfills (not treated at site but discharged to combined sewage system).

In the frame of Cohiba project, analyses of selected substances - organotin compounds, phenols, brominated diphenyl ethers, chloroalkanes, perfluorotensides were performed in wastewater, sludge, landfill leachate and storm water samples.

## E. PROPOSALS FOR IMPROVEMENT OF THE MONITORING PROGRAMME BASED ON BALTAZHAZ FINDINGS

### 1. SUMMARY OF THE MAIN FINDINGS ON HAZARDOUS SUBSTANCES OCCURRENCE IN BALTAZHAZ PROJECT AND OTHER HS SCREENING ACTIVITIES IN THE COUNTRY

#### Organotin compounds

Source tracking results are available for several cations of organotin compounds thanks to investigations of BaltActHaz project: TBT, DBT, MBT, DOT, MOT, TPhT, DPhT, MPhT, and tricyclohexyltin.

#### Tributyltin

Tributyltin compounds (cations) are priority substances under the WFD. They have the established EQS under the Dir. 2008/105/EC and Wastewater Regulation of Lithuanian MoE. EQS, and also ELV according to Wastewater Regulation of Lithuanian MoE are presented in Table 4 for a comparison against the measured concentrations.

In surface waters, TBT was investigated just in a few places below the bigger towns. Its concentrations in Nemunas below Kaunas and in Nevėžis below Panevėžys were 0,004 µg/l, what exceeds the environmental quality standards (see Table 4).

The characteristic feature of TBT is its accumulation in sediments. TBT concentrations in riverine sediments were found to be 1,6 – 585 µg/kg. Especially high concentrations were detected in sediments of Klaipėda channel and in the port territory (12,8 – 2400 µg/kg).

TBT was found in the range of 3,1 – 6,4 ng/g f.w in biota samples (in 3 out of 8 herring samples) during the screening in Eastern Baltic marine environment.

According to source tracking results, shipyards are the most obvious source of TBT. It was detected in all 10 analysed samples in the range of 0,0037 – 9,8 µg/l. The other 2 industries from which TBT was discharged were metal processing and galvanics, and leather industries. However, TBT was not found in emissions from any other sources. TBT is known to be dealkylated to DBT and MBT, or to adsorb to sediment particles. Thus, TBT were found in 22 out of 25 samples of sewage sludge during the Screening of dangerous substances in the aquatic environment of Lithuania in 2006.

Table 4. Summary of the main findings on tributyltin (cation) occurrence in various environmental media and its source tracking results (data from BaltActHaz, Screening in 2006, Screening in 2008, and Cohiba projects).

| Type of matrix                  | Concentrations  | EQS, µg/l             |                      |                       |                      |
|---------------------------------|---|-----------------------|----------------------|-----------------------|----------------------|
|                                 |   | AA-EQS                |                      | MAC-EQS               |                      |
|                                 |   | Inland surface waters | Other surface waters | Inland surface waters | Other surface waters |
| Water                           | Up to 0,004 µg/l  | 0,0002                | 0,0002               | 0,0015                | 0,0015               |
| Sediments                       | Up to 2400 µg/kg in the port territory, elsewhere – up to 585 µg/kg | n.a.                  |                      |                       |                      |
| Biota                           | 3,1 – 6,4 ng/g f.w.   |                       |                      |                       |                      |
| Emission sources                | Concentrations  | ELV, µg/l             |                      |                       |                      |
|                                 |   | To sewage system      |                      | To the environment    |                      |
| Industrial emissions            | Up to 9,8 µg/l  | 0,4                   |                      | 0,02                  |                      |
| Wastewater from municipal WWTPs | < 0,001 µg/l  |                       |                      |                       |                      |

|  |                  |  |  |
|--|------------------|--|--|
| Other emissions (surface run-off, storm water, leakage from landfills) | < 0,005 µg/l     |  |  |
| Sewage sludge  | 1,5 – 53,2 µg/kg |  |  |

### Dibutyltin

In surface waters, DBT was investigated just in a few places: below Kaunas (0,01 µg/l), Panevėžys (0,006 µg/l), and Sovetsk (0,004 µg/l).

As it was a case for TBT, the other organotin compounds also accumulate in sediments. The measured DBT concentrations in riverine sediments were in the range of 1,9 – 100 µg/kg. The highest DBT concentrations in sediments were found in sediments of Klaipėda channel and in the port territory (1,7 – 164 µg/kg).

DBT was also found in one biota sample during the screening in Eastern Baltic marine environment. Flounder from coastal area contained 2,1 ng/g f.w. of DBT.

The very obvious source for DBT emissions was found to be shipyards: 9 out of 10 investigated samples contained DBT (0,0013 – 4,5 µg/l). Apart of shipyards, a variety of other industries (at least 8 industries) emit DBT. DBT was also found to be discharged from municipal WWTPs, landfills, with surface run-off. Substantial amounts of DBT accumulate in sewage sludge.

Table 5. Summary of the main findings on dibutyltin (cation) occurrence in various environmental media and its source tracking results (data from BaltActHaz, Screening in 2006, Screening in 2008, and Cohiba projects].

| Type of matrix  | Concentrations   |
|---|--|
| Water   | 0,004 – 0,01 µg/l  |
| Sediments   | Up to 164 µg/kg in the port territory, elsewhere – up to 100 µg/kg |
| Biota   | 2,1 ng/g f.w.  |
| Emission sources  | Concentrations   |
| Industrial emissions                                      | Up to 4,5 µg/l   |
| Wastewater from municipal WWTPs                           | Up to 19,6 µg/l  |
| Other emissions (surface run-off, leakage from landfills) | Up to 0,084 µg/l   |
| Sewage sludge   | 5,9 – 382 µg/kg  |

### Monobutyltin

MBT in surface waters was measured and found in concentration of 0,08 µg/l both below Panevėžys and Sovetsk.

It was more extensively investigated in sediments than in surface waters. Again, as it was a case for TBT and DBT, also MBT was widely present in riverine sediments (1,4 – 150 µg/kg). Its concentrations in sediments of Klaipėda channel and in the port territory were 1,5 – 56,8 µg/kg.

MBT was not found in biota.

MBT was found in discharges from at least 10 different industries. It is also discharged from municipal WWTPs, landfills, surface run-off. MBT concentrations in sewage sludge are in the range of 37,8 – 886 µg/kg.

Table 6. Summary of the main findings on monobutyltin (cation) occurrence in various environmental media and its source tracking results (data from BaltActHaz, Screening in 2006, Screening in 2008, and Cohiba projects].

| Type of matrix  | Concentrations   |
|---|--|
| Water   | 0,008 µg/l   |
| Sediments   | Up to 150 µg/kg,<br>in the port territory - up to 56,8 µg/kg |
| Biota   | Not found  |
| Emission sources  | Concentrations   |
| Industrial emissions                                      | Up to 0,78 µg/l  |
| Wastewater from municipal WWTPs                           | Up to 18,5 µg/l  |
| Other emissions (surface run-off, leakage from landfills) | Up to 0,059 µg/l   |
| Sewage sludge   | 37,8 – 886 µg/kg   |

### Diocetyltn

Octyltin compounds are somewhat less investigated than butyltin compounds. However, from the data available, they seem to be less widespread in different environmental matrixes and in emissions from various sources.

There is no data about DOT in surface waters. It was not found in biota. DOT concentration in sediments reaches up to 7,2 µg/kg in some places.

DOT was found to be present in emissions from 3 different industries. It was once detected in effluents from municipal WWTP, also once in landfill leachate. However, it was always present in sewage sludge (in total 24 samples analysed).

Table 7. Summary of the main findings on dioctyltin (cation) occurrence in various environmental media and its source tracking results (data from BaltActHaz, Screening in 2006, Screening in 2008, and Cohiba projects].

| Type of matrix  | Concentrations   |
|---|------------------|
| Water   | No data          |
| Sediments   | 7,2 µg/kg        |
| Biota   | Not found        |
| Emission sources  | Concentrations   |
| Industrial emissions                                      | Up to 0,13 µg/l  |
| Wastewater from municipal WWTPs                           | Up to 0,01 µg/l  |
| Other emissions (surface run-off, leakage from landfills) | Up to 0,043 µg/l |
| Sewage sludge   | 2,5 – 81,8 µg/kg |

### Monooctyltin

MOT, as it was for DOT, was found in riverine sediments in some places (in concentration up to 34,1 µg/kg). There is no data about its presence in waters. In biota MOT was not found.

MOT was detected in discharges from 5 different industries. In discharges from municipal WWTPs it was found just once. Also, it was once detected in landfill leachate. However, it was always present in sewage sludge (in total 24 samples analysed).

Table 8. Summary of the main findings on monoctyltin (cation) occurrence in various environmental media and its source tracking results (data from BaltActHaz, Screening in 2006, Screening in 2008, and Cohiba projects].

| Type of matrix  | Concentrations   |
|---|------------------|
| Water   | No data          |
| Sediments   | Up to 34,1 µg/kg |
| Biota   | Not found        |
| Emission sources  | Concentrations   |
| Industrial emissions                                      | Up to 0,32 µg/l  |
| Wastewater from municipal WWTPs                           | Up to 0,013 µg/l |
| Other emissions (surface run-off, leakage from landfills) | Up to 0,038 µg/l |
| Sewage sludge   | 6,8 – 165 µg/kg  |

### Triphenyltin

There is no data on TPhT in surface waters. In sediments it was found in concentrations up to 16,3 µg/kg in some places. TPhT in biota was not detected.

Source tracking for TPhT did not result in finding of this compound either in industrial emissions, either in emissions from other sources. TPhT was just once detected in sewage sludge in concentration 2,8 µg/kg.

Table 9. Summary of the main findings on dibutyltin (cation) occurrence in various environmental media and its source tracking results (data from BaltActHaz, Screening in 2006, Screening in 2008, and Cohiba projects].

| Type of matrix  | Concentrations   |
|---|------------------|
| Water   | No data          |
| Sediments   | Up to 16,3 µg/kg |
| Biota   | Not found        |
| Emission sources  | Concentrations   |
| Industrial emissions                                      | Not found        |
| Wastewater from municipal WWTPs                           | Not found        |
| Other emissions (surface run-off, leakage from landfills) | Not found        |
| Sewage sludge   | Up to 2,8 µg/kg  |

### Diphenyltin

There is no data on DPhT concentrations in surface waters. It was not found in sediments. However, DPhT was detected in 6 out of 8 biota (flounder and herring) samples during the screening in Eastern Baltic marine environment: DPhT concentration reached 4,6 ng/g f.w.

Source tracking didn't reveal any DPhT sources: it was not found neither in industrial emissions, neither in emissions from other sources.

Table 10. Summary of the main findings on dibutyltin (cation) occurrence in various environmental media and its source tracking results (data from BaltActHaz, Screening in 2006, Screening in 2008, and Cohiba projects].

| Type of matrix   | Concentrations        |
|------------------|-----------------------|
| Water            | No data               |
| Sediments        | Not found             |
| Biota            | < 0,9 – 4,6 ng/g f.w. |
| Emission sources | Concentrations        |

|   |           |
|---|-----------|
| Industrial emissions                                      | Not found |
| Wastewater from municipal WWTPs                           | Not found |
| Other emissions (surface run-off, leakage from landfills) | Not found |
| Sewage sludge   | Not found |

### Monophenyltin

MPhT was found in concentrations 3,3 – 5 µg/kg in the port territory. There is no data on MPhT concentrations in surface waters. In biota it was not detected.

Again, source tracking did not reveal any sources for MPhT: it was not found neither in industrial emissions, neither in emissions from other sources

Table 11. Summary of the main findings on dibutyltin (cation) occurrence in various environmental media and its source tracking results (data from BaltActHaz, Screening in 2006, Screening in 2008, and Cohiba projects].

| <b>Type of matrix</b>                                     | <b>Concentrations</b> |
|---|-----------------------|
| Water   | No data               |
| Sediments   | Up to 5 µg/kg         |
| Biota   | Not found             |
| <b>Emission sources</b>                                   | <b>Concentrations</b> |
| Industrial emissions                                      | Not found             |
| Wastewater from municipal WWTPs                           | Not found             |
| Other emissions (surface run-off, leakage from landfills) | Not found             |
| Sewage sludge   | Not found             |

### Tricyclohexyltin

Source tracking was carried out for tricyclohexyltin. However, no sources of this compound were revealed. Data on environmental occurrence of this compound are not available.

### **Nonylphenols and their ethoxylates**

Source tracking results are available for the following nonylphenols and their ethoxylates:

- 4-n-NP (CAS 104-40-5) and 4-NP (CAS 84852-15-3);
- NP1EO (CAS 27986-36-3), NP2EO (CAS 20427-84-3), and NP3EO.

It is considered that releases of nonylphenols from production processes are low. Rather, the primary source of NP in the environment is considered to be NPEs, which can break down into NP after being released into the environment during their production, formulation into various other products, and the use of such products.

#### 4-n-NP

During BaltActHaz, 4-n-NP was not found in any of the investigated samples (from industries, WWTPs, leakage from landfill, household or supermarket effluents, run-off).

It was also investigated during the Screening of dangerous substances in the aquatic environment of Lithuania, but not found in any media.

Namely 4-n-NP is a priority hazardous substances according to Wastewater regulation; it also has the established EQS (Dir. 2008/105/EC and Wastewater Regulation of Lithuanian MoE).

## 4-NP

4-NP was found in emissions from 15 different industries (up to 1100 µg/L from paint industry, up to about 40 µg/L from pharmaceutical and textile industries, up to 23,9 µg/L from household and industrial cleaning chemicals), also in discharge from WWTPs, in surface run-off from industrial areas, in supermarket and household effluents, and in leakage from landfills during BaltActHaz.

During the screening in Eastern Baltic marine environment, 4-NP was found in coastal waters (0,029 and 0,050 µg/L), and in one (out of eight) sample of biota (12 ng/l f.w.). However, CAS number was not indicated in the description of the study, thus it is not exactly certain that namely 4-NP with CAS 84852-15-3, and not 4-n-NP with CAS 104-40-5, which is also sometimes referred to as 4-NP, was investigated.

Data on 4-NP environmental concentrations are not available.

Table 12. Summary of the main findings on 4-NP occurrence in various environmental media and its source tracking results (data from BaltActHaz, Screening in 2006, Screening in 2008, and Cohiba projects).

| Type of matrix  | Concentrations   |
|---|------------------|
| Water   | No data          |
| Sediments   | No data          |
| Biota   | Up to 12 ng f.w. |
| Emission sources  | Concentrations   |
| Industrial emissions                                      | Up to 1100 µg/l  |
| Wastewater from municipal WWTPs                           | Up to 0,42 µg/l  |
| Other emissions (surface run-off, leakage from landfills) | Up to 8,52 µg/l  |
| Sewage sludge   | No data          |

## NPE (NP1EO, NP2EO, NP3EO)

All three nonylphenol ethoxylates were found in emissions from different industries: NP1EO – from 13, NP2EO – from 6, and NP3EO – from 5 industries. The highest measured concentrations were from:

- Textile industry: 230 µg/l of NP1EO, 15,2 µg/l of NP2EO;
- Laundries: 58,2 µg/l of NP1EO, 18,8 µg/l of NP2EO, and 15,3 µg/l of NP3EO;
- Leather industry: 38, 5 µg/l of NP1EO, 17,9 µg/l of NP2EO, and 94,4 µg/l of NP3EO;
- Household and industrial cleaning chemicals: 21,5 µg/l of NP1EO;
- Rubber industry: 19 µg/l of NP1EO, 15,3 µg/l of NP2EO;
- Car washing: 10,6 µg/l of NP1EO.

NP1EO was twice found in discharge from WWTPs during the screening of hazardous substances in 2006 (0,41 µg/l and 2,2 µg/l). Nonylphenol ethoxylates were much more often present in sewage sludge than in WWTP discharge, and varied in the following ranges: 400 – 94900 µg/kg for NP1EO, 199 – 38500 µg/kg for NP2EO, and 111 – 8410 µg/kg for NP3EO.

However, during the Screening of dangerous substances in 2006, nonylphenol ethoxylates were not detected neither in water, neither in sediments. Also, they were not detected in coastal waters or in biota during the screening in Eastern Baltic marine environment.

Table 13. Summary of the main findings on NP1EO occurrence in various environmental media and its source tracking results (data from BaltActHaz, Screening in 2006, Screening in 2008, and Cohiba projects).

| Type of matrix | Concentrations |
|----------------|----------------|
| Water          | Not found      |
| Sediments      | Not found      |

|   |                       |
|---|-----------------------|
| Biota   | Not found             |
| <b>Emission sources</b>                                   | <b>Concentrations</b> |
| Industrial emissions                                      | Up to 58,2 µg/l       |
| Wastewater from municipal WWTPs                           | Up to 2,2 µg/l        |
| Other emissions (surface run-off, leakage from landfills) | Up to 3,71 µg/l       |
| Sewage sludge   | Up to 94900 µg/kg     |

Table 14. Summary of the main findings on NP2EO occurrence in various environmental media and its source tracking results (data from BaltActHaz, Screening in 2006, Screening in 2008, and Cohiba projects).

|   |                       |
|---|-----------------------|
| <b>Type of matrix</b>                                     | <b>Concentrations</b> |
| Water   | Not found             |
| Sediments   | Not found             |
| Biota   | Not found             |
| <b>Emission sources</b>                                   | <b>Concentrations</b> |
| Industrial emissions                                      | Up to 18,8 µg/l       |
| Wastewater from municipal WWTPs                           | Not found             |
| Other emissions (surface run-off, leakage from landfills) | Up to 1,34 µg/l       |
| Sewage sludge   | Up to 38500 µg/kg     |

Table 15. Summary of the main findings on NP3EO occurrence in various environmental media and its source tracking results (data from BaltActHaz, Screening in 2006, Screening in 2008, and Cohiba projects).

|   |                       |
|---|-----------------------|
| <b>Type of matrix</b>                                     | <b>Concentrations</b> |
| Water   | Not found             |
| Sediments   | Not found             |
| Biota   | No data               |
| <b>Emission sources</b>                                   | <b>Concentrations</b> |
| Industrial emissions                                      | Up to 94,4 µg/l       |
| Wastewater from municipal WWTPs                           | Not found             |
| Other emissions (surface run-off, leakage from landfills) | Not found             |
| Sewage sludge   | Up to 8410 µg/kg      |

## Octylphenols and their ethoxylates

Source tracking results are available for the following octylphenols and their ethoxylates:

- 4-tert-OP (CAS 140-66-9);
- OP1EO (CAS 9036-19-5), OP2EO, and OP3EO.

### 4-tert-OP

4-t-OP was found to be present in surface waters (7 samples, 0,02 – 0,03 µg/l) during the screening in 2006. It was also found in coastal water (0,0012 µg/l) during the screening in Eastern Baltic marine environment. However, in biota it was not detected. It was also not found in riverine sediments.

Source tracking showed that 4-t-OP is released from various industries, at least from 15 different branches (0,011 – 7,39 µg/l). The measured concentrations in household effluents reached 8,19 µg/l. It is also found in discharges from WWTPs (up to 1,014 µg/l), in sewage sludge (up to 1100 µg/kg), and in discharges from other emissions sources, such as in surface runoff (up to 0,021 µg/l) and in landfill leachate (up to 0,824 µg/l).



Table 16. Summary of the main findings on 4-tert-OP occurrence in various environmental media and its source tracking results (data from BaltActHaz, Screening in 2006, Screening in 2008, and Cohiba projects).

| Type of matrix   | Concentrations   | EQS, µg/l             |                      |                       |                      |
|--|------------------|-----------------------|----------------------|-----------------------|----------------------|
|  |                  | AA-EQS                |                      | MAC-EQS               |                      |
|  |                  | Inland surface waters | Other surface waters | Inland surface waters | Other surface waters |
| Water  | 0,02 – 0,03 µg/l | 0,1                   | 0,01                 | -                     | -                    |
| Sediments  | Not found        | n.a.                  |                      |                       |                      |
| Biota  | Not found        |                       |                      |                       |                      |
| Emission sources   | Concentrations   | ELV, µg/l             |                      |                       |                      |
|  |                  | To sewage system      |                      | To the environment    |                      |
| Industrial emissions   | Up to 7,39 µg/l  | 400                   |                      | 20                    |                      |
| Wastewater from municipal WWTPs  | Up to 1,014 µg/l |                       |                      |                       |                      |
| Other emissions (surface run-off, storm water, leakage from landfills) | Up to 0,75 µg/l  |                       |                      |                       |                      |
| Sewage sludge  | 30 – 1100 µg/kg  |                       |                      |                       |                      |

### OPE (OP1EO, OP2EO, OP3EO)

OPE were not found in surface waters or sediments during the screening in 2006. Also, they were not found in biota during the screening of dangerous substances in Eastern Baltic marine environment.

Source tracking results showed the presence of octylphenol ethoxylates of various degree of ethoxylation to be present in emissions from various industries: OP1EO – from 11, OP2EO – from 10, and OP3EO – from 4 industry branches. The highest measured concentrations were from:

- Household and industrial cleaning chemical production: 130 µg/l of OP1EO, 4,27 µg/l of OP2EO;
- Leather industry: 10 µg/l of OP1EO, 44,2 µg/l of OP2EO, and 120 µg/l of OP3EO;
- Laundries: 3,7 µg/l of OP1EO, 1,54 µg/l of OP2EO;
- Printing houses: 7,32 µg/l of OP1EO;

Table 17. Summary of the main findings on OP1EO occurrence in various environmental media and its source tracking results (data from BaltActHaz, Screening in 2006, Screening in 2008, and Cohiba projects).

| Type of matrix  | Concentrations   |
|---|------------------|
| Water   | Not found        |
| Sediments   | Not found        |
| Biota   | Not found        |
| Emission sources  | Concentrations   |
| Industrial emissions                                      | Up to 130 µg/l   |
| Wastewater from municipal WWTPs                           | Up to 0,023 µg/l |
| Other emissions (surface run-off, leakage from landfills) | Up to 0,315 µg/l |
| Sewage sludge   | Up to 128 µg/kg  |

Table 18. Summary of the main findings on OP2EO occurrence in various environmental media and its source tracking results (data from BaltActHaz, Screening in 2006, Screening in 2008, and Cohiba projects).

| Type of matrix | Concentrations |
|----------------|----------------|
| Water          | Not found      |
| Sediments      | Not found      |
| Biota          | Not found      |

| Emission sources  | Concentrations   |
|---|------------------|
| Industrial emissions                                      | Up to 44,2 µg/l  |
| Wastewater from municipal WWTPs                           | Up to 0,069 µg/l |
| Other emissions (surface run-off, leakage from landfills) | Up to 0,081 µg/l |
| Sewage sludge   | Up to 88 µg/kg   |

Table 19. Summary of the main findings on OP3EO occurrence in various environmental media and its source tracking results (data from BaltActHaz, Screening in 2006, Screening in 2008, and Cohiba projects).

| Type of matrix  | Concentrations   |
|---|------------------|
| Water   | Not found        |
| Sediments   | Not found        |
| Biota   | No data          |
| Emission sources  | Concentrations   |
| Industrial emissions                                      | Up to 120 µg/l   |
| Wastewater from municipal WWTPs                           | Up to 0,083 µg/l |
| Other emissions (surface run-off, leakage from landfills) | Up to 0,032 µg/l |
| Sewage sludge   | No data          |

## Phthalates

Source tracking results are available for the following phthalates and their ethoxylates:

- di-(2-ethylhexyl)-phthalate (DEHO, CAS 117-81-7), dibutyl-n-phthalate (DBP, CAS 84-74-2), diethylphthalate (DEP, CAS 84-66-2), di-iso-butylphthalate (DIBP, CAS 84-69-5), butylbenzylphthalate (CAS 85-68-7);
- dimethylphthalate (CAS 131-11-3), di-n-propylphthalate (CAS 131-16-8), di-pentylphthalate (CAS 131-18-0), di-cyclohexylphthalate (CAS 84-61-7), di-n-octylphthalate (CAS 117-84-0).

The latter ones were not found in any discharges during BaltiActHaz investigations.

During the screening in 2006, phthalates were found in 22 wastewater samples out of 25 investigated, and in all 25 samples of sewage sludge. The following phthalates were found the most often: DEHP, DBP, DIBP, and diiso-nonylphthalate. The highest concentration was for DEHP (0,42 – 53,2 µg/l in wastewater), with 4 cases of exceeded ELV.

### Di-(2-ethylhexyl)-phthalate (DEHP)

During BaltActHaz, DEHP was found in emissions from 6 different industries (up to 26 µg/L from paint production, up to about 14 µg/L from plastic industry, up to 2,5 µg/L from shipyards, 1,1 µg/L from production of building materials, up to 71 µg/L from car washing, and up to 16 µg/L from regeneration of used oil), also up to 36 µg/L in supermarket effluents, up to 12 µg/L in household effluents, and up to 59 µg/L in leakage from landfills.

Table 20. Summary of the main findings on DEHP occurrence in various environmental media and its source tracking results (data from BaltActHaz, Screening in 2006, Screening in 2008, and Cohiba projects).

| Type of matrix | Concentrations  | EQS, µg/l             |                      |                       |                      |
|----------------|-----------------|-----------------------|----------------------|-----------------------|----------------------|
|                |                 | AA-EQS                |                      | MAC-EQS               |                      |
|                |                 | Inland surface waters | Other surface waters | Inland surface waters | Other surface waters |
| Water          | Up to 3,85 µg/l | 1,3                   | 1,3                  | -                     | -                    |
| Sediments      | 22000 µg/kg     | n.a.                  |                      |                       |                      |

| Biota  | No data        |                  |                    |
|--|----------------|------------------|--------------------|
| Emission sources   | Concentrations | ELV, µg/l        |                    |
|  |                | To sewage system | To the environment |
| Industrial emissions   | Up to 71, µg/l | 8                | 0,4                |
| Wastewater from municipal WWTPs  | Up to 53,2µg/l |                  |                    |
| Other emissions (surface run-off, storm water, leakage from landfills) | 59 µg/l        |                  |                    |
| Sewage sludge  | 438000 µg/kg   |                  |                    |

### Dibutyl phthalate (DBP)

During BaltActHaz, DBP was found in emissions from 3 different industries (up to 1,2 µg/l from shipyards, up to 1,8 µg/l from car washing, and up to 4 µg/L from regeneration of used oil), also up to 1,4 µg/l in supermarket effluents, and up to 1,8 µg/l in leakage from landfills.

Table 21. Summary of the main findings on DBP occurrence in various environmental media and its source tracking results (data from BaltActHaz, Screening in 2006, Screening in 2008, and Cohiba projects).

| Type of matrix   | Concentrations  |
|--|-----------------|
| Water  | Up to 1,25 µg/l |
| Sediments  | 356 µg/kg       |
| Biota  | No data         |
| Emission sources   | Concentrations  |
| Industrial emissions   | Up to 4 µg/l    |
| Wastewater from municipal WWTPs  | Up to 6,53µg/l  |
| Other emissions (surface run-off, storm water, leakage from landfills) | 1,8 µg/l        |
| Sewage sludge  | 19600 µg/kg     |

### Diethylphthalate (DEP)

During BaltActHaz, DEP was found in emissions from 3 different industries (up to 1,3 µg/l from shipyards, up to 7,9 µg/l from car washing, and up to 1,9 µg/l from paint production), also up to 26 µg/l in supermarket, up to 1,3 µg/l in leakage from landfills and up to 4,8 µg/l from household effluents.

Table 22. Summary of the main findings on DEP occurrence in various environmental media and its source tracking results (data from BaltActHaz, Screening in 2006, Screening in 2008, and Cohiba projects).

| Type of matrix   | Concentrations  |
|--|-----------------|
| Water  | Up to 0,07 µg/l |
| Sediments  | No data         |
| Biota  | No data         |
| Emission sources   | Concentrations  |
| Industrial emissions   | Up to 7,9 µg/l  |
| Wastewater from municipal WWTPs  | Up to 1,56µg/l  |
| Other emissions (surface run-off, storm water, leakage from landfills) | 0,06 µg/l       |
| Sewage sludge  | 62 µg/kg        |

## Di-iso-butylphthalate (DIBP)

During BaltActHaz, DBP was found to be up to 4,6 µg/l in paint production industry discharges, up to 3,1 µg/l in shipyard discharges, up to 68 µg/l in car washing discharges, up to 2,9 in leakage from landfills, and up to 4 µg/L from supermarkets.

During screening in 2006, DBP was found in WWTP up to 2,89 µg/l, in surface water 5,6 µg/l, and in sediments 1700 µg/kg.

Table 23. Summary of the main findings on Di-iso-butylphthalate occurrence in various environmental media and its source tracking results (data from BaltActHaz, Screening in 2006, Screening in 2008, and Cohiba projects).

| Type of matrix   | Concentrations  |
|--|-----------------|
| Water  | Up to 5,6 µg/l  |
| Sediments  | 1700 µg/kg      |
| Biota  | No data         |
| Emission sources   | Concentrations  |
| Industrial emissions   | Up to 68 µg/l   |
| Wastewater from municipal WWTPs  | Up to 2,89 µg/l |
| Other emissions (surface run-off, storm water, leakage from landfills) | 1,32 µg/l       |
| Sewage sludge  | 2460 µg/kg      |

## Butylbenzylphthalate

Butylbenzylphthalate was found just in two samples. One of them was a discharge from paint production industry (1,3 µg/l). The other sample, which contained butylbenzylphthalate, was effluents from a supermarket (2,1 µg/l).

## **Polybrominated diphenylethers**

Various brominated compounds were detected in sediments of the Nemunas river below Rusnė during the Screening of dangerous substances in 2006.

Polybrominated diphenyl ethers were present in nearly all biota samples (0,014 – 0,18 ng/g f.w. of individual BDEs) investigated during the screening in the eastern Baltic marine environment. BDE47, BDE99, BDE100 and BDE154 were also found in coastal area and in open sea near Klaipėda.

According to source tracking results during the survey by BaltActHaz project, some PBDE are present in effluents from wood pulp and paper production, printing houses, textile industry, leather industry, plastic industry, shipyards, production of building materials, laundries, car washing, leachate from landfills, etc. The most often were found the following PBDE: PBDE47, PBDE99, PBDE100; in plastic industry, shipyards and laundries – also PBDE196, PBDE197, PBDE203, NBDE, PBDE209, and HCBDD. Of the industries, laundries seem to be the most relevant due to rather widespread presence of various PBDE in their emissions, and also plastic industry, where concentration of PBDE209 was recorded 34 µg/l in one sample (no ELV is established for comparison). PBDE47 and PBDE99 were present in all analyzed samples from landfills.

Screening of dangerous substances in 2006 also showed that various brominated diphenylethers were present in WWTPs. They were found in sewage sludge of several WWTPs in the range of 5,1 – 3410 µg/kg for different congeners. However, the limit of detection of the method applied for pentabromdiphenylether was too high to make certain judgements.

Also during Cohiba project, brominated diphenyl ethers were detected in industrial wastewaters, municipal wastewaters, sludge and landfill leachate.

### SCCP

SCCP were investigated but not found in any sample during the Screening of dangerous substances in the aquatic environment of Lithuania in 2006. However, SCCP were present in all biota samples in the ranges 6,5 – 62 ng/g/f.w. during the screening in Eastern Baltic marine environment.

Source tracking showed that SCCP are emitted to the environment from at least 5 different industries. The highest concentration was found in discharge from one laundry (53 µg/l). SCCP concentrations in other cases was in the range of 0,15 – 75 µg/l.

During BaltActHaz, SCCP was found in surface runoff (0,2 µg/l in surface run-off from industrial areas), but not detected in discharges from municipal WWTPs and landfill leachate. However, it was found in these types of emissions during COHIBA project. SCCP concentrations in discharge from municipal WWTPs varied in the range of 0,14 – 1,95 µg/l. Its concentration in landfill leachate was 0,69 and 0,97 µg/l. High SCCP concentrations, reaching 4950 and 11600 µg/kg, were found in sewage sludge.

Table 24. Summary of the main findings on SCCP occurrence in various environmental media and its source tracking results (data from BaltActHaz, Screening in 2006, Screening in 2008, and Cohiba projects].

| Type of matrix   | Concentrations     | EQS, µg/l             |                      |                       |                      |
|--|--------------------|-----------------------|----------------------|-----------------------|----------------------|
|  |                    | AA-EQS                |                      | MAC-EQS               |                      |
|  |                    | Inland surface waters | Other surface waters | Inland surface waters | Other surface waters |
| Water  | Not found          | 0,4                   | 0,4                  | 1,4                   | 1,4                  |
| Sediments  | Not found          | n.a.                  |                      |                       |                      |
| Biota  | 6,5 – 62 ng/g f.w. |                       |                      |                       |                      |
| Emission sources   | Concentrations     | ELV, µg/l             |                      |                       |                      |
|  |                    | To sewage system      |                      | To the environment    |                      |
| Industrial emissions   | Up to 53 µg/l      | 40                    |                      | 0,2                   |                      |
| Wastewater from municipal WWTPs  | Up to 1,95 µg/l    |                       |                      |                       |                      |
| Other emissions (surface run-off, storm water, leakage from landfills) | Up to 1,14 µg/l    |                       |                      |                       |                      |
| Sewage sludge  | Up to 11600 µg.kg  |                       |                      |                       |                      |

### MCCP

There is nearly no data on environmental MCCP concentrations. MCCP were investigated just during the screening in Eastern Baltic marine environment, but in biota they were not detected.

According to source tracking results, MCCP are emitted from at least 11 different industries in Lithuania. The highest concentration was found to be from a laundry – 170 µg/l. Otherwise concentrations were in the range of 0,32 – 13 µg/l.

Table 25. Summary of the main findings on MCCP occurrence in various environmental media and its source tracking results (data from BaltActHaz, Screening in 2006, Screening in 2008, and Cohiba projects].

| Type of matrix | Concentrations |
|----------------|----------------|
| Water          | No data        |
| Sediments      | No data        |
| Biota          | Not found      |

| <b>Emission sources</b>                                   | <b>Concentrations</b> |
|---|-----------------------|
| Industrial emissions                                      | Up to 170 µg/l        |
| Wastewater from municipal WWTPs                           | 1,22 – 31,50 µg/l     |
| Other emissions (surface run-off, leakage from landfills) | Up to 4,11 µg/l       |
| Sewage sludge   | Up to 123 µg/kg       |

As it was a case for SCCP, MCCP were also not detected in discharges from municipal WWTPs, landfills, or in surface run-off during BaltActHaz investigations. But MCCP were found in these types of emissions during COHIBA project. MCCP concentrations in discharges from municipal WWTPs varied in the range of 1,22 – 31,50 µg/l; its concentration in sewage sludge was 123 µg/kg in one sample. MCCP concentration in storm water was 0,08 - 3,64 µg/l, in landfill leachate 1,54 – 4,11 µg/l.

### PFOS and PFOA

11 different perfluorotensides were investigated during the survey by BaltActHaz. Analysis of emissions from industrial sites does not suggest a widespread use of these compounds in Lithuania. Emissions of PFOS were found only from plastic industry. PFOA was found from two more industries: in addition to plastic industry, they were found in emissions from semiconductors production and laundries. For all these industries, PFOS and PFOA were found just in single cases.

Currently the main emissions pathway of perfluorotensides to the environment is via the landfills. Leakage from landfills contained the biggest variety of compounds in the biggest number of samples: PFOA, PFHpA, and PFBS were present in all 4 samples; PFNA and PFDA were present in 3 samples; PFOS and PFHxS were present in 2 samples.

During Cohiba project, measured concentrations of PFOS were in the range from 0,06 ng/l to 3,90 ng/l. The highest concentration of PFOS (3,90 ng/l) was found in storm water sample, whereas the lowest value (0,06 ng/l) was found at industrial WWTP. PFOS was not detected in landfill leachate samples.

Observed concentrations of PFOA were in the range from 0.48 ng/l to 6.43 ng/l. The highest concentration (6.43 ng/l) was found at industrial WWTP. At municipal WWTP, the mean values of PFOA were similar (about 3.00 ng/l).

Table 26. Summary of the main findings on PFOS occurrence in various environmental media and its source tracking results (data from BaltActHaz, Screening in 2006, Screening in 2008, and Cohiba projects).

| <b>Type of matrix</b>  | <b>Concentrations</b> |
|--|-----------------------|
| Water  | Up to 2,9 µg/l        |
| Sediments  | No data               |
| Biota  | 61 ng/g               |
| <b>Emission sources</b>  | <b>Concentrations</b> |
| Industrial emissions   | Up to 6,43 ng/l       |
| Wastewater from municipal WWTPs  | Up to 1,3 ng/l        |
| Other emissions (surface run-off, storm water, leakage from landfills) | 3,9 µg/l              |
| Sewage sludge  | 3,5 µg/kg             |

Table 27. Summary of the main findings on PFOA occurrence in various environmental media and its source tracking results (data from BaltActHaz, Screening in 2006, Screening in 2008, and Cohiba projects).

| <b>Type of matrix</b>   | <b>Concentrations</b> |
|-------------------------|-----------------------|
| Water                   | No data               |
| Sediments               | No data               |
| Biota (IVL)             | No data               |
| <b>Emission sources</b> | <b>Concentrations</b> |

|  |                 |
|--|-----------------|
| Industrial emissions   | Up to 0,27 µg/l |
| Wastewater from municipal WWTPs  | Up to 3 ng/l    |
| Other emissions (surface run-off, storm water, leakage from landfills) | 1,5 µg/l        |
| Sewage sludge  | No data         |

## 2. PROPOSALS FOR IMPROVEMENT OF THE CURRENT MONITORING PROGRAMME

Based on investigation carried out during the BaltActHaz project, the following priority hazardous and priority substances were identified as being discharged into the aquatic environment of Lithuania, and therefore need to be covered by the State monitoring program:

- Tributyl tin compounds (cations);
- Nonylphenols (mixture);
- PBDE (including pentaBDE);
- SCCP (C10-13 chloralkanes);
- Di-(2-ethylhexyl)-phthalate (DEHP);
- 4-tert-octylphenol.

In addition to these, the following substance from the List of other controlled substances in the Wastewater Regulations of Lithuanian MoE were identified as being discharged to the environment:

- Dibutylphthalate.

Based on knowledge from literature sources, and complemented according to the existing information on emissions and environmental occurrence, the following matrixes can be named as relevant for these identified substances:

Table 28. Relevant matrixes for the analysed priority substances.

| Substance | TBT                          | NP (mixture) | 4-t-OP                          | DEHP | DBP | PBDE | SCCP                            |
|-----------|------------------------------|--------------|---------------------------------|------|-----|------|---------------------------------|
| Water     | Yes, but less than sediments | Yes          | Yes                             | Yes  | Yes | Yes  | Yes (practically not found yet) |
| Sediments | Yes                          | Yes          | Yes (practically not found yet) | Yes  | Yes | Yes  | Yes (practically not found yet) |

Source tracking of hazardous substances has revealed a broader spectrum of substances that are of possible concern in Lithuania although they are not included into the lists of priority or priority hazardous substances. Those substances are:

- Diethylphthalate (DEP);
- Dibutyltin (DBT);
- Monobutyltin (MBT);
- C14-17 chloralkanes (MCCP).

In the substance group of phenols and their ethoxylates, source tracking results showed the relevance of 4-NP (CAS 84852-15-3), which was found in emissions from 15 different industries, in some cases – in apparently high concentrations. However, this substance is covered by the analysing of mixture of nonylphenols, thus its separate inclusion into the monitoring programme is not a necessity.

Also, emissions of nonylphenol ethoxylates and octylphenol ethoxylates of various degree of ethoxylation were detected during the source tracking. However, the available data on environmental occurrence of

phenol ethoxylates does not show their presence in environmental media: phenol ethoxylates are known to break down into phenols in the environment.

PFOS is a substance, which is subject to review for possible identification as a priority substance, or priority hazardous substance. During the source tracking, emissions of PFOS were detected just in one sample from plastic industry. Plastic industry and also laundries were found to discharge more different perfluorinated compounds, e.f. PFOA. In addition, PFOA was found in emissions from production of semiconductors.

Summarizing information on the analysed priority substances (coverage, relevance of matrixes, emissions, environmental occurrence), the proposal for monitoring programme is presented in Table 29.

Currently the applied analysis methods for organic substances in EPA laboratory do not include some of substances/ substance groups included into the proposal for monitoring programme (see Table 2 p.10).

These substances are:

- the priority substances brominated diphenylethers (in water) and C10 – C13 chloroalkanes (in water and sediments);
- diethylphthalate, dibutyltin, monobutyltin, and C14-17 chloralkanes.

Comments regarding assimilation of the missing methods and development of laboratory capacities see presented in chapter 2.





|                         |                    |                       |    |    |    |    |    |    |    |    |    |    |    |   |  |  |   |   |   |   |   |   |   |   |
|-------------------------|--------------------|-----------------------|----|----|----|----|----|----|----|----|----|----|----|---|--|--|---|---|---|---|---|---|---|---|
|                         |                    | Kuktiškiai            |    |    |    |    |    |    |    |    |    |    |    |   |  |  |   |   |   |   |   |   |   |   |
| R82                     | Venta              | Below<br>Mažeikiai    |    |    |    |    |    | 12 | 12 | 12 |    |    |    |   |  |  |   |   |   |   |   |   |   |   |
| R430                    | Varduva            | Near Griežė           |    |    |    |    |    | 12 | 12 | 12 |    |    |    |   |  |  |   |   |   |   |   |   |   |   |
| R498                    | Kulpė              | Near Kryžių<br>kalnas | 12 | 12 | 12 | 12 | 12 | 12 | 12 | 12 | 12 | 12 | 12 |   |  |  | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
|                         |                    |                       |    |    |    |    |    |    |    |    |    |    |    |   |  |  |   |   |   |   |   |   |   |   |
| 2; 3b;<br>10; 12;<br>14 | Curonian<br>lagoon |                       | 12 | 12 | 12 | 12 | 12 | 12 | 12 |    | 12 | 12 |    | 1 |  |  | 1 | 1 | 1 | 1 |   | 1 |   |   |

## F. SCREENING OF SUBSTANCES OF POSSIBLE CONCERN

### 1. LISTS OF SUBSTANCES OF POSSIBLE CONCERN

Some chemical substances still emerge as being of concern due to their undesired toxicological and ecotoxicological properties and effects. Various legal frameworks (e.g. WFD) present lists of hazardous substances requiring priority actions, and such substances fall under the requirement for their monitoring. There are also some frameworks and databases that present lists of substances of possible concern. E.g. Article 16(4) of WFD requires review of the PS list at least every four years.

Some of these lists of substances of possible concern are introduced further in the text. In most cases it is still unknown whether these substances are of relevance for Lithuania as well. Since there is no monitoring of such substances, their real relevance to Lithuania could be revealed by carrying out the screening surveys.

Annex III of Dir. 2008/105/EC presents a list of substances subject to review for possible identification as priority substances or priority hazardous substances:

- AMPA;
- Bentazon;
- Bisphenol-A;
- Dicofol;
- EDTA;
- Free cyanide;
- Glyphosate;
- Mecoprop (MCP);
- Musk xylene;
- Perfluorooctane sulphonic acid (PFOS);
- Quinoxifen (5,7-dichloro-4-(p-fluorophenoxy)quinoline).

Substances proposed for EQS derivation, the so called new candidate priority substances, are presented on Circa website. Draft substance impact report of March 2011 included the following substances:

- Bifenox;
- Terbutryn;
- Cybutryne (Irgarol);
- Cypermethrin;
- Dichlorvos;
- Heptachlor epoxide;
- PFOS and perfluorooctane sulfonic fluoride;
- HBCDD;
- Quinoxifen;
- Dicofol;
- Aclonifen;
- Diclofenac;
- 17 alpha-ethibylestradiol;
- Ibuprofen;
- 17 beta-estradiol.

NORMAN (Network of reference laboratories for monitoring of emerging environmental pollutants) presents its list of emerging substances. Its latest update approved on March 2011 includes the following groups substances:

- Algal toxins;
- Anticorrosives;

- Antifoaming agents ;
- Antifouling compounds;
- Antioxidants;
- Biocides;
- Bio-terrorism / sabotage agents;
- Complexing agents ;
- Detergents ;
- Disinfection by-products (drinking water);
- Drugs of abuse;
- Flame retardants ;
- Food additives;
- Fragrances;
- Gasoline additives;
- Industrial chemicals;
- Nanoparticles;
- Perfluoroalkylated substances and their transformation products;
- Personal care products;
- Pesticides;
- Pharmaceuticals;
- Plasticisers;
- Trace metals and their compound;
- Wood preservatives.

The full list can be found on:

[http://www.norman-network.net/index\\_php.php?interface=1024&module=public/about\\_us/emerging&lang=en](http://www.norman-network.net/index_php.php?interface=1024&module=public/about_us/emerging&lang=en)

### List of plant protection product active substances and their methabolites

Based on knowledge from Lithuanian Plant Protection Service, there are a number of plant protection product (PPP) active substances and their metabolites that based on their properties are of possible concern. These substances are candidate substances to be included into the monitoring program. At first their screening survey in agricultural areas shall be carried out.

Table 30. Candidate list of plant protection product (PPP) active substances and their metabolites to be included into the monitoring program

| Substance   | Product name  | Absorption coefficient in soil Koc, 1/kg | Half life period in soil, DT50, days |
|---|---|--|--------------------------------------|
| Bentazone   | Basagran 480  | 52                                       | 45                                   |
| Ethofumezate  | Betanal Expert, Ethofol SC, Ethosat 500 SC, Nortron, Powertwin 400 SC, Goltix Super | 132                                      | 97                                   |
| Fluazifop-P (RS-2-[4-(5-trifluoromethyl-2-pyridiloxi)propionic acid Compound 10 (5-trifluormethyl-2-(1H)pyridine) | Fusilade forte 150EC  | 49                                       | 9                                    |
| Fluroxipiric meptil metabolite<br>Fluroxipiric acid   | Starane XL, Starane 180, Tomigan 180, Ariane S                                      | 68                                       | 39,6                                 |
| Clopiralide   | Galera, Lontrel 300, Ariane S   | 2,9                                      | 23                                   |
| Clomazone   | Nimbus SE, Metric, Brasan 540 EC  | 286                                      | 167                                  |
| Metamitrone + metabolite<br>desamin metamitrone   | Torero 500 SC, Goltix 700 SC, Goltix Super  | 86<br>102                                | 21,5<br>31                           |

|  |  |                                 |                                    |
|--|--|---------------------------------|------------------------------------|
| Metrybuzine and its metabolites diketo-metrybuzine and desamino-diketo-metrybuzine       | Metric, Mistral 700 WG, Sencor 70 WG               | 37<br>98,6<br>32,2              | 9,6<br>42,3<br>14,3                |
| Metsulfuronmethyl and its metabolites  | Accurate 200 WG, Ergon, Mezo WG                    | 39,5                            | 24                                 |
| Nicosulfurone  | Milagro 40 SC                                      | 20,7                            | 21                                 |
| Piridate metabolite CL 9673  | Lentagran WP                                       | 20-188                          | 18                                 |
| Sulfosulfurone   | Monitor  | 5-80                            | 50                                 |
| Tiphensulfuronmethyl and its metabolite tiphensulfuronic acid                            | Calibre 50 SX                                      | 28<br>11                        | 10<br>74                           |
| Triasulfuron and its metabolites   | Lintur 70 WG, Logran 20 WG                         | 7-25                            | 38                                 |
| Tribenuronmethyl and its metabolites<br>IN-L5296;<br>IN-A4098;<br>IN-00581               | Calibre 50 SX, Granstar Premia 50 SX, Trimer 50 SG | 30<br>89<br>98<br>15            | 14<br>165<br>30<br>131             |
| Trisulfuronmethyl and its metabolites<br>IN-W3725;<br>IN-D8526;<br>IN-E7710;<br>IN-M7222 | Caribou 50WG, Harmony 50SX, Ergon                  | 40<br><br>6<br>172<br>115<br>62 | 6,5<br><br>89<br>152<br>109<br>254 |
| Trisulfuronmethyl  | Arrat, Tooler                                      | 7                               | 11-21                              |

### Pharmaceutical substances

Pharmaceutical substances are considered as substances of possible concern. No measurement data are available for pharmaceuticals in Lithuanian environment yet. The accurate statistics about the use of individual compounds is not readily available because of privacy and industry competition issues. One of the information sources on pharmaceuticals is JSC IMS Health, which collects information on pharmaceutical sales profiles. According to their data, total consumption of pharmaceuticals for human use in Lithuania in 2005 included 517 pharmaceutical substances. This variety is still small compared to the other developed European countries. However, the number has a tendency to increase over the recent years. The majority of pharmaceutical substances (48.2 %) were consumed in amounts between 1 kg and 100 kg. 5 % of substances were consumed in negligible amounts below 1 g. 4.4 % were consumed between 1 and 10 tonnes, and only 0.9 % were consumed in more than 10 tonnes. Among these are aspirin, paracetamol, amoxicillin, and metformin. The risk assessment carried out for pharmaceuticals in Lithuania showed that risk cannot be excluded for amoxicillin, ciprofloxacin and spiramycin. Even more – PEC for spiramycin could be overestimated due to its veterinary use.

### Availability of standard methods for emerging substances

Sensitivity of methods of analysis, i.e. limit of determination, in many cases is much higher than PNEC or proposed EQS. This is related to further problems for selection and for future monitoring.

## 2. SCREENING SURVEY AS A TOOL TO IDENTIFY EMERGING SUBSTANCES AND AN INPUT TO THE MONITORING PROGRAMME

Many of the chemical substances found in society end up in sewers and treatment plants. The amounts of some substances are regularly monitored within the obligatory inspection programmes. However the numerous organic contaminants, on the other hand, are not analysed regularly because doing so would be both difficult and costly. In addition, new chemical substances are appearing all the time. Therefore a special programme with campaign-type sampling and analysis of new environmental pollutants and pharmaceutical residues, in particular, could be applied. This 'screening programme' makes it possible to carry out spot checks to see how far these substances occur in the environment, what are their sources, and whether ecosystems, biota, human beings are at risk of exposure to them. In many countries screening programme is a central part of environmental monitoring programme for toxic pollutants. The number of samples is limited in both space and time, while the results may be regarded as a first investigation of the release and environmental occurrence of a certain pollutant. Sludge, sediments and wastewater from industry and WWTPs are usually sampled, since they collect pollutants from many sources, but also water, air or fish could be analysed.

Objectives of the screening:

- Identify EU/WFD prioritized and nationally selected organic pollutants in aquatic environments near sources of discharge,
- Provide information to source identification – but not single pollution sources (impact monitoring, compliance checking => enterprises),
- To develop best practices, analytical methods and cooperation between laboratories,
- To identify substances which should enter the regular national monitoring networks.

### Setting the screening survey

A proper screening study consists of 4 major closely related parts: substance selection, preliminary theoretical research, measurement study and survey follow-up.

#### 1. Substance selection

- As early as the selection stage, consideration should be given to the question of **for what purpose the results will be used.**
  - o Usually it is not primarily intended to support research on new environmental pollutants, but, rather, constitutes compliance with the requirements to report certain substances laid down in a number of EU directives and international conventions.
  - o Many of such substances are of no relevance to country and screening in these cases might be a useful instrument in demonstrating this, so to avoid investing major resources into measuring them.
  - o Another purpose is to follow up work in order to achieve a pollutant-free environment. Substances found in high concentrations can be followed up over a lengthy period of time.
  - o Another one of the reasons for selecting a certain substance might be to use the results in order to plug data holes for the purposes of risk assessment or justifying a risk-reducing measure.
- Chemicals/ products registers can be also used for selection of substances, i.e. from among chemicals used in large volumes.

#### 2. Preliminary theoretical research

- o Certain information about the **properties, use and dispersal** of a substance is required in order to set up sampling and analysis.
- o Theoretical research should also collect data on the **different types of impacts** the substance produces. That way, when performing the risk assessment, it can be decided whether the concentrations being measured necessitate action or not.
- o On the basis of substance properties, it can also be possible, for example, to compare

concentrations to those of other known substances or groups of substances, such as PCB, in order to obtain an “estimated screening reference value”, against which to make a comparison when a concentration is high.

### 3. Measurement study

- On the basis of what is known about the properties of substances and the information available on their dispersal conditions and routes, a type of matrix (i.e. the medium being analysed, such as water, sludge, air or fish), as well as a sampling strategy should be chosen. The objective of the survey and the reason why we have selected one substance in particular are relevant to the choice of location and matrix.
- When selecting samples, balance of choice between mapping as many different matrices as possible, disseminating measurement data across the country or detecting statistical differences should be considered. In this respect, too, the choice of substance informs the decision as to which substance should be given priority in a given study.
- There are many challenges in analytical development during screening studies. It is better to try to select substances for which analytical methods exist. Screening is not intended for the purpose of developing analytical methods, but since measurement studies often require new substances to be analysed, it can be more or less necessary to develop the analytical method partly (e.g. pre-treatment part different matrix, complex samples).
- Evaluation stage is very important in the measurement study step. What do the results actually tell? Are values high or low, based on the available knowledge of impacts? How accurate are values arrived at through analyses conducted in other countries and other measurements? Evaluation is performed on the basis of literature review and the rationale for the choice of substance to be submitted for screening. It is also important that all the information on samples, matrices, localities and methods considered relevant for future use is well-documented in the report.

### 4. Survey follow-up

- Evaluation is an important part of the screening survey. Can the screening be considered final or further data is needed to be able to draw conclusions and answer questions raised when selecting the substance? Whether obtained results are of a sufficient quantity and good quality.
- Drawing the ideas for actions, measures is an important follow-up step. There are a variety of measures, e.g. influence the choice of substance by companies (voluntary agreements), to include substance for a new screening e.g. in 5 years in order to delineate a trend, to include substance into regular monitoring programme etc.
- Disseminating the results is also important to draw up some proposals for further actions, therefore it should be decided to whom should the proposals put forward be addressed.
- The data should be easily available for all interested parties. For example in Sweden having long tradition of screening studies, the data host for screening is IVL, Swedish Environmental Research Institute Ltd. Data and reports can be downloaded from the following website of the screening data host: [www.ivl.se](http://www.ivl.se)

## G. DERIVATION OF ENVIRONMENTAL QUALITY STANDARDS

Article 16 of the Water Framework Directive (WFD; 2000/60/EC) sets out the strategy against chemical pollution of surface waterbodies. The chemical status assessment is used alongside the ecological status assessment to determine the overall quality of a waterbody. Environmental Quality Standards (EQSs) are tools used for assessing the chemical status of waterbodies. The EQS Directive 2008/105/EC establishes the maximum acceptable concentration and/or annual average concentration for 33 priority substances and 8 other pollutants which, if met, allows the chemical status of the water body to be described as 'good'. EQSs for the 33 substances identified by the EU as Priority Substances (PSs) and Priority Hazardous Substances (PHSs) are derived at a European level and apply to all Member States. They are also referred to as Annex X substances of the WFD. In addition, the WFD (Annex V, section 1.2.6) establishes the principles to be applied by the Member States to develop EQSs for Specific Pollutants that are 'discharged in significant quantities'.

At the current stage EQS are set only for surface water, however also only for the substances prioritised on EU level. In case substance is prioritised on national or river basin level, EQS should be derived on national level. The general rule applied is: **EQS = Lowest NOEC \* 0,1**

### Deriving EQS for sediments and biota

Not all substances require an assessment for a sediment standard. The criteria for triggering an assessment are consistent with those under REACH Regulation (EC) No 1907/2006 (ECHA, 2008). In general, substances with an organic carbon adsorption coefficient ( $K_{oc}$ ) of  $<500 \text{ l}\cdot\text{kg}^{-1}$  are not likely to be sorbed to sediment. Consequently, a  $\log K_{oc}$  or  $\log K_{ow}$  of  $\geq 3$  is used as a trigger value for sediment effects assessment. Some substances can occur in sediments even though they do not meet these criteria so, in addition, evidence of high toxicity to sediment dwelling organisms or evidence of accumulation in sediments from monitoring, would also trigger derivation of a sediment EQS.

The criteria determining whether or not a biota standard is needed are more complex. A Standard would be required if there was a risk of secondary poisoning of predators (e.g. mammals or birds) from eating contaminated prey (QS<sub>biota, sec pois</sub>), or a risk to humans from eating fishery products (QS<sub>biota, hh</sub>). The triggers are based on those used to determine whether a secondary poisoning assessment is necessary for a substance under REACH Regulation (EC) No 1907/2006 (ECHA, 2008). The triggers for derivation of a QS<sub>biota, hh</sub> are dominated by hazard properties whereas a QS<sub>biota, sec pois</sub> is triggered by the possibility of accumulation in the food chain in conjunction with hazard properties.

More information on derivation of EQS could be found in "Technical guidance for deriving environmental quality standards, 2010" (Guidance Document No 27)

( [http://www.oekotoxzentrum.ch/expertenservice/qualitaetskriterien/doc/TGD-EQS\\_finaldraft.pdf](http://www.oekotoxzentrum.ch/expertenservice/qualitaetskriterien/doc/TGD-EQS_finaldraft.pdf)).



## H. LIST OF ABBREVIATIONS

AA-EQS – annual average environmental quality standard;  
BAF – bioaccumulation factor;  
BBP – benzyl butyl phthalate;  
BDE – brominated diphenylether;  
BSAP – Baltic Sea Action Plan;  
CLRTAP – Convention on Long-range Transboundary Pollution;  
DBP – dibutylphthalate;  
DBT – dibutyltin;  
DEHP – di-(2-ethylhexyl) phthalate;  
DEP – diethylphthalate;  
DIBP – diisobutylphthalate;  
DIN ISO – German edition of ISO standards;  
DOC – dissolved organic carbon;  
DOT – dioctyltin;  
ELV – emission limit value;  
EMP – environmental monitoring programme;  
EPA – Environmental Protection Agency;  
EQS – environmental quality standard;  
HBCDD – hexabromocyclododecane;  
HCB – hexachlorobenzene;  
HS – hazardous substance(s);  
IPPC – Integrated Pollution Prevention and Control;  
ISO – International Organization of Standardization;  
LOD – limit of detection;  
LOQ – limit of quantification;  
LST ISO – Lithuanian edition of ISO standards;  
MAC-EQS – Maximum allowed concentration environmental quality standard;  
MBT – monobutyltin;  
MCCP – medium chain chlorinated paraffins;  
MoE – Ministry of Environment;  
MOT – mono-octyltin;  
NF – nanofiltration;  
NOEC – No Observed Effect Concentration;  
NP – nonylphenol;  
NPE – nonylphenol ethoxylate;  
NP(E) – nonylphenols and their ethoxylates  
NP1EO - nonylphenolmonoethoxylate;  
NP2EO - nonylphenoldiethoxylate;  
NP3EO - nonylphenoltriethoxylate;  
OP – octylphenol;  
OPE – octylphenol ethoxylate;  
OP(E) – octylphenols and their ethoxylates  
OP1EO – octylphenolmonoethoxylate;  
OP2EO - octylphenoldiethoxylate;  
OP3EO - octylphenoltriethoxylate;  
PAH – polyaromatic hydrocarbons;  
PBDE – polybrominated diphenylethers;  
PBT – persistent, bioaccumulative and toxic;  
PFOS – perfluorooctane sulfonate;  
PFOA – perfluorooctanoic acid;  
PPP – plant protection product;  
PS – priority substance;

PVC – polyvinylchloride;  
RO – reverse osmosis;  
SCCP – short chain chlorinated paraffins;  
SOP – standard operating procedure;  
SPM – solid particulate matter;  
TBT – tributyltin;  
TPhT – triphenyltin;  
UNEP – United Nations Environmental Programme;  
WFD – Water Framework Directive;  
WWTP – waste water treatment plant;

## J. REFERENCES

BaltActHaz. Project “Baltic actions for reduction of Pollution of the Baltic Sea from Priority Hazardous substances”. Background study. 2009, 82 p.

BaltActHaz. Investigation of sources of hazardous substances in Lithuania, Latvia and Estonia. Report, 2011, 32 p.

BEF group, Okopo. Proposals for Measures and Actions for the Reduction of Pollution from Hazardous Substances for the Baltic Sea Action Plan. 2007, 160 p.

Dudutyte Z., Manusadžianas L., Ščeponavičiūtė R. COHIBA. Report on dangerous substances in the aquatic environment of Lithuania. Prepared within the project “Screening of dangerous substances in the aquatic environment of Lithuania”, 2007, 82 p.

European Commission. Common implementation strategy for the Water Framework Directive (2000/60/EC). Guidance Document No. 19 - Guidance on surface water chemical monitoring, EC, Environment, 2009, 154 p.

European Commission. Monitoring under the Water Framework Directive, Guidance document no. 7. 2003, 160 p.

HELCOM. Baltic Sea Environment Proceedings No. 120B. Hazardous substances in the Baltic Sea. 2010, 117 p.

HELCOM. Towards a Baltic Sea unaffected by hazardous substances. 2007, 48 p.

Karl Lilja at all. Screening of Selected Hazardous Substances in the Eastern Baltic Marine Environment. IVL, 2009, 57p.

Nordic Council of Ministries. Information sheets on the hazardous substances identified in the HELCOM Baltic Sea Action Plan – Occurrence in the Baltic Sea. Norden, 2010, 52 p.

Regulation on wastewater management approved by Order D1-515 of the Minister of Environment dated 8 October 2007 (Official Gazette, No. 110-4522, 2007) and changed on May 18, 2010, No. D1-416;

State environmental monitoring programme for 2011-2017. Act of the Government of the Republic of Lithuania, 2011-03-02 No.315.

Kruopiene J., Dvarioniene J. Management of Environmental risks in the life cycle of human pharmaceuticals in Lithuania. Environmental research, engineering and management. 2010, No2(52), 41-47 p.



## ANNEX 1. LIST OF LABORATORIES

| Laboratory                                    | Address  |
|---|--|
| GALAB Laboratories; Analytical services       | Max-Planck-Strasse 1<br>D-21502 Geesthacht<br>Germany<br><a href="http://www.galab.de">www.galab.de</a>            |
| Norwegian Institute for Air Research (NILU)   | Instituttveien 18,<br>P.O. Box 100<br>2027 Kjeller<br>Norway<br><a href="http://www.nilu.no">www.nilu.no</a>       |
| Nab Labs Ympäristöanalytiikka Ltd / Rovaniemi | Raidetie 1<br>96910 Rovaniemi<br>Finland<br><a href="http://www.nablabs.fi/">http://www.nablabs.fi/</a>            |
| ALS Scandinavia AB                            | Box 511,<br>SE-183 25 Täby (letters),<br>Sweden<br><a href="http://www.alsglobal.se/">http://www.alsglobal.se/</a> |

### Analysis available at the laboratories

| No. | CAS No.    | Name                             | GALAB | NILU | NAB LABS | ALS |
|-----|------------|----------------------------------|-------|------|----------|-----|
| 1.  | 78763-54-9 | Monobutyltin                     | X     | X    | X        | X   |
| 2.  | 1002-53-5  | Dibutyltin                       | X     |      |          | X   |
| 3.  | 688-73-3   | Tributyltin                      | X     |      |          | X   |
| 4.  | 85535-84-8 | C10-13 chloralkanes              | X     | X    | X        | X   |
| 5.  | 32534-81-9 | Pentabromdiphenylether           | X     |      | X        | X   |
| 6.  | 1736-23-1  | Perfluorooctane sulfonate (PFOS) | X     |      |          | X   |
| 7.  | 335-67-1   | Perfluorooctanoic acid (PFOA)    | X     |      |          | X   |