COHIBA

CONTROL OF HAZARDOUS SUBSTANCES
IN THE BALTIC SEA REGION

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WP3 INNOVATIVE APPROACHES TO CHEMICAL CONTROLS OF HAZARDOUS SUBSTANCES

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Summary

COHIBA project was one of the first to estimate the discharges to and the concentrations in the Estonian environment of MCCP, SCCP, PFOS, PFOA, HBCDD, NP, NPE, OP, OPE. Most of these substances are very poorly researched and analysed in Estonia (Loos et al. 2009), with the exception of dioxins (Tallinn University 2005; Roose, Roots 2005; Schleicher et al. 2005; Roots 2004) and heavy metals (Tallinn University of Technology 1994, 2010), which have already been monitored by the government for years.

Actual measurements of 11 substances of specific concern to the Baltic Sea in the Estonian anthropogenic sources were made. The sampling points were five wastewater treatment plants (WWTPs), one landfill and an urban storm water runoff.

Samples were taken from the WWTPs every two months from May 2009 to August 2010. Along with the effluents, sludge samples were also taken from two WWTPs. The samples of landfill leachate and the WWTP sludge were taken twice – in the winter and the summer. Storm water samples were first taken of water from melting snow, and afterwards of the first heavier rain thereafter. This was done to illustrate the effects of melting snow that contains the air deposits during a longer period of time, and the actual rain effects after all the snow has melted.

The parameters and HS of all the wastewater, sludge and water samples were identified. Simultaneously, chemical analyses for acute toxicity and chronic toxicity tests were also conducted on the water samples.

In the following paragraphs, the substances are listed. The environmental quality standards (European Parliament and Council 2008a) that are established in the field of water policy in the European Union (European Parliament and Council 2000) are given for the surface waters, not the effluents, therefore, the comparison with AA-EQS is made only to give a rough idea about the order of magnitude of pollution by hazardous substances. The comparison is made to show the effect of hazardous substances that move from effluents to the environment. A constant flow of hazardous substances, even in small concentrations, is an environmental risk that can cause problems to biota.

Mercury

In COHIBA samples from the WWTP effluents, mercury was measured on the LOQ (0,05 µg/l) twice (out of 24 samples), all the rest of the analyses showed the results to be under the LOQ. In sludge, however, mercury was found over the LOQ (0,02 mg/kg) from all three samples – 0,23 to 0,50 mg/kg. Mercury was found once from the landfill (0,10 µg/l) and not found from the storm water samples.

Cadmium

The LOQ of Cd was changed in March 2010, when a new method was introduced to the EERC. Before that, the LOQ was 0,1 µg/l, and after March 2010 it was 0,02 µg/l. Generally speaking, the results from the effluents were not found when the LOQ was higher, but gave numerical results when the LOQ was lowered. The highest detected concentration for cadmium was 0,15 µg/l from effluents. Cadmium was also found from both samples of the storm waters (0,05 and 0,16 µg/l), but not found from the landfill samples or the sludge samples from the WWTPs.

Organotin

In COHIBA, TPhT was not found from any samples. TBT was found twice from the WWTP effluents and in both cases the EQS was exceeded (WWTP1 2,9 and WWTP2 2,2 ng/l – EQS 0,2 ng/L). TBT was not found from landfill leachate samples or storm waters. It must be noted that the LOQ for TBTs was 1 ng/l which is lower than the EQS; therefore no adequate conclusions on the levels of TBTs can be made. By March 2011, EERC has the result of only one sludge sample, and the result is 4,1 µg/kg. There is no limit value for organotins in sludge. Other organotin compounds were also found in many cases form different sites.

Phenolic compounds

In COHIBA, all named phenolic substances were found from the WWTP effluents, however, it must be noted that the results from the WWTP3 stood out from the results of other WWTPs as significantly higher showing a possible big industrial input. It should also be noted that the EQS of the NP and OP-s is lower than the LOQ and therefore the comparison on how many times the EQS was exceeded was not possible to make.

The phenolic substances were analysed one from the sludge of WWTP1 and twice from the WWTP3. Similarly to the results from the effluents, the only substance to be found over the LOQ from both WWTPs was NP. For other phenolic substances, the results were below the LOQ for WWTP1 and over the LOQ for WWTP3. Phenolic substances were not found from the storm water samples. NP was found from both landfill samples and Nonylphenol diethoxylates were found from one sample. OP or OPEs were not found from the landfill leachate.

Pesticides

In COHIBA, endosulfan was not found from any of the effluents nor the storm waters. However, β-endosulfan was found once from the sludge of WWTP3 (1,3 mg/kg) and endosulfan sulphate was found once from the landfill (38,4 ng/l) and it is over the EQS (5 ng/l).

Dioxins and furans

Dioxins were measured from the effluents in the COHIBA project. The proposed EQSs are higher than the concentrations detected in effluents.The results were shown as a range of all the results. Dioxins were not measured from the sludge of WWTPs. However, there are environmental quality standards only for sediments and sludge. When analysing the dioxins, the LOQ is dependent on the particular sample. In the summary tables only the results that exceeded the LOQs have been shown. The results clearly showed the presents of dioxins and furans in effluent waters. Among the non-ortho PCBs, i.e. co-planar PCBs, the most dominant was clearly Co-PCB 77.

SCCP and MCCP

In COHIBA, both SCCP and MCCP were found from all the effluents in concentrations over the LOQ. Out of 24 samples, 22 exceeded the EQS of 0,4 µg/l, with the median concentration being 1,01 µg/l . Both SCCPs and MCCPs were also found in concentrations over the LOQ from the sludge samples of WWTPs.

SCCPs were measured in concentrations exceeding the EQS in both landfill leachate and storm waters. MCCP was found in concentrations over the LOQ in storm waters. In landfills, it was measured only once and the result was below the LOQ.

Brominated flame retardants

In COHIBA, pentaBDEs were considered to be congeners 28, 47, 99, 100, 153 and 154; octaBDEs were considered to be congeners 183 and 203; and decaBDE was considered to be congener 209.

PentaBDEs were detected from all WWTPs, however, the results of all congeners were below LOQ in WWTP4a. Out of 24 samples, pentaBDEs were found from 10 (41,6%), with the maximum of all results being 0,47 ng/l and median <LOQ. In landfills, the concentration of pentaBDEs was 5,94 and 10,67 ng/l and in storm waters, the concentrations were <LOQ and 1,3 ng/l. In sludge samples, the concentrations of pentaBDEs were 26,58 to 29,86 µg/kg.

However, the EQS of 0,5 ng/l has been prescribed for single congeners. There were no concentrations detected over the EQS for any congeners in the WWTP effluents. Congeners 47, 66 and 99 were measured at concentrations over the LOQ at times, the most common congener being BDE-99 that was detected over the LOQ in 9 out of 24 samples. Congeners BDE-100 and BDE-153 were also detected at some samples, however, the concentrations were under the LOQ.

In landfills, congeners BDE-47 and BDE-99 were measured over the LOQ (0,15 ng/l) and EQS (0,5 ng/l) both times, and congeners BDE-153 and BDE-154 were measured over the LOQ and EQS once. In storm waters, BDE-47, BDE-99, BDE-100, and BDE-153 were measured in concentrations over the LOQ in one sample, with BDE-99 being over the EQS of 0,5 ng/l.

OctaBDEs were not found in concentrations over the LOQ from WWTP effluents or storm-waters, but were found once from the landfill (1,36 ng/l, BDE-183). However, the octaBDEs were found from the sludge sample in concentrations 1,92 to 2,25 µg/kg.

BDE-209 (or decaBDE) was found in 23 out of 24 measurements of WWTP effluents, it was also found from the sludge samples in concentrations from 303,6 to 1183,0 µg/kg. In land-fills, the concentrations were 3,28 and 3,73 ng/l, and 3,73 and 10,40 ng/l in storm waters.

In COHIBA, HBCDs were found from all of the WWTPs. Out of 23 samples, HBCDs were found from 21 samples, with the median of 1,23 ng/l. The proposed EQS (under revision until 07.2011) is 1,6 ng/l. The EQS from effluents was exceeded in 8 samples. HBCDs were also measured once from two WWTP sludge samples in concentrations 12,8 – 93,4 µg/kg. However, there is no EQS for sludge.

HBCDs were measured twice from the landfill and storm waters. In landfill leachate the concentration was over the LOQ once, not exceeding the EQS. In storm waters, the HBCDs were over the EQS both times. The proposed marine water EQS (0,8ng/l, under revision until 07.2011) was exceeded eight-fold (6,48 ng/l) and five-fold (3,94 ng/l). The marine or salt water EQS was used because the water is taken directly to the sea.

Perfluorinated compounds

There are no environmental quality standards for perfluorinated substances, however, a concentration of 0,65 ng/l has been proposed as a limit for PFOS (under revision until 07.2011). PFOS and PFOA were found from all the WWTPs. Out of 24 samples, the concentration of PFOS exceeded the proposed EQS in 17 times. PFOA was found over the LOQ in all the samples in concentrations 1,03 – 13,6 ng/l. Both substances were also found in concentrations over the LOQ in the sludge samples (PFOS 2,21 – 2,96 and 0,38 – 0,73 µg/kg).

The landfill leachate and storm water samples were taken twice. In both storm water samples, both PFOS and PFOA were found in concentrations over the LOQ and over the proposed EQS for PFOS (1,27 – 1,51 ng/l PFOS and 0,54 – 1,86 ng/l PFOA). However, in both landfill samples, the concentrations were significantly high and exceeded proposed EQS for PFOS by hundreds of times (11 -108 ng/l PFOS and 533 -590 ng/l PFOA).

Biotests

One third of 30 samples showed some toxicity according at least one obligatory biotest. Both samples from landfill leachate were very toxic for all three test organisms, the highest EC50=23%. Storm water samples were not toxic. Algae growth inhibition test showed toxicity of effluents more often than *Daphnia magna* acute toxicity test and luminescent bacteria test. Only the samples from landfill were toxic according the luminescent bacteria test.

Optional bio-tests were performed only for two samples and showed various results. Samples were not toxic according *Lemna minor* and umu-test, but toxic according fish hepatocyte vitellogenin induction and EROD activity test. According egg-larvae test only one sample was toxic.

1 Introduction

Control of Hazardous Substances in the Baltic Sea or COHIBA–project includes all Baltic Sea countries except Russia. The objective of COHIBA is to support the implementation of the HELCOM Baltic Sea Action Plan (BSAP) (HELCOM 2007) with regard to hazardous substances by developing joint actions to reach the goal of "Baltic Sea with life undisturbed by hazardous substances". The 11 substances/substance groups identified in the BSAP as being of special concern to the Baltic Sea are also the focus of this project. The COHIBA project lasted for three years (2009-2012).

The COHIBA project aims to identify the most important sources of 11 hazardous substances of special concern. The project analyses flow patterns of these substances and quantifies their releases and inputs to the Baltic Sea. The project will also develop innovative and cost-effective evaluation practices of effluent ecotoxicity, based on the Whole Effluent Assessment (WEA) approach. The target is also to define toxicity-based discharge limits, a threshold toxicity, to effluents discharged into receiving waters in the Baltic Sea region. In addition, the aim is to share knowledge about best practices within the participating countries and to assist authorities and industries to control hazardous substances. The project will enhance the capability of the Baltic Sea countries to implement their international obligations under the forthcoming European Marine Strategy (European Parliament and Council 2008b) and the Water Framework Directive (European Parliament and Council 2000). It also contributes to national implementation programmes to reach the cessation targets for HELCOM/EU priority hazardous substances by 2020 (HELCOM 1998).

The COHIBA project consists of following work packages (WP-s):

WP1. Project management and administration (lead by Finnish Environment Institute SYKE)
WP2. Communication and Information (lead by HELCOM Secretariat)
WP3. Innovative approaches to chemical controls of hazardous substances (lead by SYKE)
WP4. Identification of sources and estimation of inputs/impacts on the Baltic Sea (lead by IVL Swedish Environmental Research Institute)
WP5. Cost effective management options to reduce discharges, emissions and losses of hazardous substances (lead by Federal Environment Agency of Germany)
WP6. Capacity building and knowledge transfer (lead by Baltic Environmental Forum)

The target of WP3 is to contribute to the identification of sources for the 11 hazardous substances in BSAP by performing screening in municipal and industrial wastewaters, landfill effluents and storm waters, in all participating countries. WP3 also aims for developing joint evaluation of ecotoxicity of the effluents and for recommending PBT (persistent, bioaccumulating, toxic)-based discharge limit values based on the WEA approach for the Baltic Sea region. Currently most of the restrictions concerning discharges and emissions are based on the determination of chemical concentrations. However, the majority of effluents comprise a mixture of chemicals. It is impossible to identify all these substances and their transformation products or to determine the effects of all individual substances or their synergistic interactions in the environment. Thus there is a need to regulate discharges on the basis of direct assessments of their biological effects, to complement the chemical analyses. Another important aim of WP3 is to harmonise the chemical and ecotoxicological assessment methods in the Baltic Sea region serving also EU WFD and REACH requirements (European Parliament and Council 2006). The results will be used as input to the integrated HELCOM assessment of hazardous substances and of the sources for the substances of concern to the Baltic Sea.

2 Monitoring programme

2.1 Case studies and monitoring points

The following objects were analysed under the COHIBA WP3 study: four waste water treatment plants, one landfill, and one runoff of an urban area (storm water).

Two of our wastewater treatment plants (WWTPs) were located in North-Eastern Estonia (WWTP1 and WWTP2) and two were located in Northern Estonia (WWTP3 and WWTP4a). As the WWTP4a went under reconstruction and discontinued working, it was replaced to WWTP4b in April 2010, also located in Northern Estonia. All treated effluents are discharged into the Gulf of Finland. Besides the WWTPs, the storm water runoff of an urban area (Tallinn, **Figure 1**) and the leachate of a landfill were analysed (**Table 1**). All the case studies and locations to be screened were defined based on an initial evaluation of potential sources and main uses.

Figure 1. Storm water urban runoff sampling point in the COHIBA project.

The factors taken into account when selecting the case studies for the COHIBA project in Estonia were:

- Located on the coastline or close to the Baltic Sea (< 50 km from the coast);
- Likely to discharge selected hazardous substances;
- Big enough to get representative results for the whole country.

Table 1. Information about the sampling points.

WWTP	Year of establishment	Type of treatment	Capacity (m3/d)	Appr. population equivalents	receiving water
WWTP1	2009	Mechanical + Biological + Biol. N and P + Chemical P	54 240	223 333	Deep-sea outlet, Gulf of Finland
WWTP2	2005	Mechanical + Biological + Biol. N and P + Chemical P	45 500	140 000	River, 12 km from shoreline, Gulf of Finland
WWTP3	2000	Mechanical + Biological + Biol. N and P	5 100	15 217	River, 18 km from shoreline, Gulf of Finland
WWTP4a	1981	Mechanical + Biological	2 000	10 000	Gulf of Finland
WWTP4b	1980's	Mechanical + Biological	3 000	15 000	Deep-sea outlet, Gulf of Finland
Landfill	2000	Biological + Biol. N			River, 50 km from the shoreline, Gulf of Riga
Storm water	n/a	none			20 m from the shoreline, Gulf of Finland

The samples for WWTPs were taken every two months from May 2009 to August 2010 (**Table 2**). The samples for landfill leachate and WWTP sludge were taken twice – winter and summer. In Estonia, the storm water samples were taken as a snow melting water sample first and a sample from the first heavier rain after that. It was done to illustrate the effect of the melting snow that contains the air deposit during the longer period of time, and the actual rain effects after all the snow has melted.

For all wastewaters, sludge and water samples base parameters and the hazardous substances listed in the Baltic Sea Action Plan (BSAP) by HELCOM were identified. Parallel to these analyses biological tests were conducted. The first two analysis rounds were performed concerning toxicity only, next four both for toxicity and selected substances. The last two samplings were for chemical analyses only. Because the WWTP 4a was exchanged to WWTP4b so late, it was decided to take additional samples to get representative toxicity results.

The sludge samples were taken twice from WWTP3 (January and June 2010) and once from WWTP1. The samples were analysed for selected hazardous substances of the BSAP.

Table 2. COHIBA sampling schedule.

Object	May 2009	July 2009	Sept 2009	Oct 2009	Nov 2009	Jan 2010	March 2010	April 2010	May 2010	June 2010	Aug 2010
WWTP1	x	x	x		x	x*		x		x	x
WWTP2	x	x	x		x	x		x		x	x
WWTP3	x	x	x		x	x*		x		x*	x
WWTP4a	x	x	x		x	x					
WWTP4b								x		x**	x**
Storm Water							x		x		
Landfill				x						x	

* - the sludge samples;
** - biotests were also performed from WWTP4b to elongate the time series for the results.

The basic parameters for the single objects were analysed either in situ (such as temperature, pH, conductivity) or in the Estonian Environmental Research Centre (EERC) laboratory (TOC, SS, nutrients) respectively. The results are shown in Annexes C-G.

The biological tests were performed by Estonian Marine Institute, University of Tartu (EMI) and Finnish Environment Institute (SYKE).

Analyses of hazardous substances according to BSAP were performed by laboratories of EERC (Endosulfan, Cadmium, and Mercury), SYKE (PBDE, HBCD, PFC, NP), the Swedish Environmental Research Institute – IVL (Organotin compounds) in Stockholm, the Institute for Ecology of Industrial Areas – IETU (Chlorinated Paraffins), and the National Institute for Health and Welfare – THL (Dioxins). The results are shown in Annexes C-G.

2.2 Waste water and landfill sampling

All waste water samples were taken according to ISO 5667 - 10. The personnel performing sampling is accredited according to Estonian Environmental Ministry Regulations on sampling (RTL 2002, 56, 833).

The samples were taken into HPDE canisters. In WWTPs canisters were placed in a refrigerator (+4°C) (WWTP1, WWTP2) or cooled down with the freezer elements (the rest). The canisters were kept in cold during the sampling. All samples were taken as 24 h mixed samples adjusted to the flow (WWTP2, WWTP3) or time (the rest). The samples of WWTPs were taken from the outflow. The landfill leachate was taken from the outlet of lagoons after it was treated.

Right after the samples were collected they were brought into the laboratory within the same day. The samples were then mixed properly and separated for different tests and analyses. For chemical analyses samples were bottled according to the instructions of the analysing laboratories. For laboratories out of Estonia samples were packed, again according to the instructions of the laboratories and sent via air transport.

For biotests samples were bottled into plastic bottles and frozen immediately after bottling.

All samples were handled similarly.

2.3 Storm water sampling

The samples were taken into HPDE canisters. Samples were taken as grab samples. Sampling was started about half an hour after the start of the rain except for snow melting water.

All storm water samples were taken according to ISO 5667 – 10. The personnel performing sampling is accredited according to Estonian Environmental Ministry Regulations on sampling (RTL 2002, 56, 833).

2.4 Sludge sampling

The WWTP sludge was taken before its further treatment, i.e. sludge is centrifuged before it is taken to digestion. Samples were taken into plastic or glass jars which were washed and rinsed according to the instructions given by analysing laboratories.

All sewage sludge samples were taken according to ISO 5667 - 13. The personnel performing sampling is accredited according to Estonian Environmental Ministry Regulations on sampling (RTL 2002, 56, 833).

3 Parameters and methods

3.1 Basic parameters

The flow rate, temperature, pH, and conductivity were measured in situ.

3.1.1 pH and temperature

For determination of pH ISO 10523 method was used. The determination of the pH value is based on measuring the potential difference of an electrochemical cell using a pH meter. The pH of a sample also depends on the temperature because of dissociation equilibrium. Therefore, the temperature of the sample was always stated together with the pH measurement.

3.1.2 BOD_7

For analysis of BOD_7 ISO 5815-1 method was used. The sample of water to be analysed was pre-treated and diluted with varying amounts of dilution water rich in dissolved oxygen and containing a seed of aerobic microorganisms, with suppression of nitrification. The sample was incubated at 20 ^oC for 7 days in the dark, in a completely filled and stoppered bottle. The dissolved oxygen concentration was determined before and after incubation, and the mass of oxygen consumed per litre of sample was calculated.

3.1.3 COD

For analysis of COD ISO 6060 method was used. Reflux in the presence of mercury(II) sulphate of a test portion with a known amount of potassium dichromate and silver catalyst in strong sulphuric acid for a fixed period of time, during which part of the dichromate is reduced by the oxidable material present. Titration of the remainder of the dichromate with ammonium iron(II) sulphate. Calculation of the COD value from the amount of dichromate reduced. 1 mole of dichromate ($Cr_2O_7^{2-}$) is equivalent to 1,5 moles of oxygen (O_2).

3.1.4 Suspended solids

For analysis of suspended solids EVS-EN 872:2005 method was used. Using vacuum filtration apparatus the sample was filtered through a glass fibre filter. The filter was then dried at 105 ^oC ± 2 ^oC and the mass of the residue retained on the filter was determined by weighing. Instead of 2 μm filter as required by the standard the 0,45 μm filter was used as required by Estonian legislation and the Council Directive 91/271/EEC concerning urban waste water treatment. Due to that the results may be greater than other results using the same method.

3.1.5 P_{tot} and $P\text{-}PO_4^{3-}$

For analyses of P_{tot} and $P\text{-}PO_4^{3-}$ EVS-EN ISO 6878:2004 method was used.

The basis for this method are the reaction of ortophosphate ions with an acid solution containing molybdate and antimony ions to form an antimony phosphomolybdate complex, and the reduction of the complex with ascorbic acid to form a strongly coloured molybdenum blue complex. Measurement of the absorbance of this complex is used to determine the concentration of ortophosphate present. Polyphosphate and some organophosphorus compounds were determined if converted to molybdate reactive ortophosphate formed by sulphuric acid hydrolysis. Many organophosphorus compounds were converted to ortophosphate by mineralization with peroxidisulfate. Nitric acid-sulphuric acid mineralization was used if a more vigorous treatment was required.

3.1.6 Nitrogen (N_{tot})

For analysis of nitrogen (N_{tot}) EVS-EN ISO 11905-1 method was used. Ammonia, nitrite and many organic nitrogen-containing compounds in the test sample were oxidised to nitrate using peroxidisulfate in a buffered alkaline system by boiling at elevated pressure in a closed container. Subsequent reduction of nitrate to nitrite was carried out by passage of the digest through a mixing coil containing copperized cadmium. The resulting nitrite was reacted with 4-aminobenzene sulfonamide and N-(1-naphtyl)-1,2-diaminoethane dihydrochloride to produce a pink colour. Photometric measurement was carried out at 540 nm.

3.1.7 $N\text{-}NH_4$

For analysis of $N\text{-}NH_4$ ISO 7150-1 method was used. Spectrometric measurement at about 655 nm of the blue compound formed by reaction of ammonium with salicylate and hypochlorite ions in the presence of sodium nitrosopentacyanoferrate(III) (sodium nutroprusside). Hypochlorite ions are generated *in situ* by the alkaline hydrolysis of N, N'-dichloro-1,3,5-triazine-2,4,6 (1H, 3H, 5H)-trione, sodium salt (sodium dichloroisocyanurate). Reaction of the chloramine with sodium nitroprusside. Any chloramines present in the sample are quantitatively determined as a consequence. Sodium citrate is incorporated in the reagent to mask interference from cations, notably calcium and magnesium.

3.1.8 Alkalinity

For analysis of alkalinity EVS-EN ISO 9963-1:1999 method was used. The sample was titrated with standard acid solution to fixed pH endpoint values of 8,3 and 4,5. These endpoints, which were determined potentiometrically, are the selected equivalence points for the determinations of the three principal components: hydrogen carbonate, carbonate and hydroxide. The pH 8,3 endpoint approximates to the equivalent concentrations of carbonate and carbon dioxide and represents the titration of approximately all the hydroxide and half of the carbonate present. The pH 4,5 endpoint approximates the equivalence point for hydrogen ion and hydrogen carbonate and allows for the determination of the total alkalinity of the sample. For alkalinity determinations in accordance to this method, bromocresol green-methyl red indicator solution was used.

3.1.9 Fe

For the analyses of Iron in the effluents SFS 3028 method was used. Iron in the sample was brought into reactive state by oxidation with peroxydisulfate in acidic media. Oxidation was carried out in a closed vessel under pressure. Iron (III) was reduced by hydroxylammonium chloride to iron (II), which forms with 2,4,6-tri(2'-pyridyle)-1,3,5-triazine (TPTZ) a violet coloured complex compound Fe(TPTZ)22+ (pH range 3,4 …5,8). The absorbance of the coloured compound was measured at wavelength 593 nm.

3.1.10 S (dissolved)

For the analyses of dissolved sulphur in the effluents STJ V15 method was used. 20 ml of sample or its dilution was taken into 50 ml volumetric flask for analysis and 2,0 ml HCl and 1 ml gelatine containing reagent was added. As a comparison sample 20 ml of deionised water + HCl + gelatine containing reagent was taken. The absorbance was measured after 30 minutes by spectrophotometer at wavelengths 440 nm in the 20 mm cell. If water sample was turbid or yellowish an additional blank test was used. As a blank test 0 ml of sample or its dilution into 50 ml volumetric flask was taken and 2,0 ml HCl and 1 ml deionised water was added. The absorbance of blank test was measured after 30 minutes by spectrophotometer at wavelengths 440 nm in the 20 mm cell. Sample result was corrected by subtracting the blank test value from the sample value.

3.1.11 TOC

For analysis of total organic carbon (TOC) EVS-EN 1484 method was used. The determinations were carried out as instructed by the manufacturer of the instrument manual liquiTOCII. This method is based on the oxidation of organic carbon (org. C) in water to carbon dioxide (CO2) by combustion with high temp (800 C). Inorganic carbon (TIC) was removed by acidification (pH<10) and purification. The final determination of CO_2 was carried out by IR-detector.

3.2 Hazardous substances

All hazardous substances or groups of substances listed in the BSAP were analysed. The methods of analysis used for the hazardous substances are listed in **Table 3**.

Table 3. Methods of analysis of involved laboratories.

Substance/substance group	LOQ	Laboratory
Dioxin, furans and dioxin-like PCBs		THL
Tributyltin compounds	1 ng/l	IVL
pBDEs	0,15 ng/l	SYKE
Perfluorinated substances	0,5 ng/l	SYKE
Hexabromocyclododecane	0,1 ng/l	SYKE
Nonylphenols, Octylphenols	0,7/ 0,17/ 0,35 µg/l	SYKE
Short-chain and medium chain chlorinated paraffins	0,12 µg/l	IETU
Endosulfan	5 ng/l	EERC

Substance/substance group	LOQ	Laboratory
Mercury	0,05 µg/l	EERC
Cadmium	0,1 µg/l; 0,02 µg/l since March 2010	EERC

3.2.1 Metals

The heavy metals were analysed by the laboratory of Estonian Environmental Research Centre.

3.2.1.1 Cadmium

For analysis of cadmium three different methods were used: EVS-EN ISO 15586:2004 (Water quality - Determination of trace elements using atomic absorption spectrometry with graphite furnace), EVS-EN ISO 11885:2009 (Water quality - Determination of selected elements by inductively plasma optical emission spectrometry (ICP-OES)) and EVS-EN ISO 17294-2:2004 (Water quality – Application of inductively coupled plasma mass spectrometry (ICP–MS) – Part 2: Determination of 62 elements). EVS-EN ISO 15586:2004 was used until 25.03.2010, after EVS-EN ISO 17294-2:2004 was used. Due to that the limit of determination was lower since then.

Pre-treatment of water samples for Cd
Water sample was filtered and then nitric acid was added until pH of the solution was 1 or lower.

Pre-treatment of solid samples for Cd
For metal analyses 0,5 g of sample was weighed in microwave vessel and then 5 ml of nitric acid was added. After that the sample was mineralized in microwave oven by heating and cooled down afterwards. This was followed by filtration of the sample and filling the sample volume to 25 ml.

Instrumental method for Cd
Determination of cadmium by atomic absorption spectrometry with graphite furnace (GFAAS) is based on EVS-EN ISO 15586:2004. A small sub-sample of sample solution was injected into a graphite furnace of an atomic absorption spectrometer. By increasing the temperature stepwise, the sample was dried, pyrolized and atomized. A light source emits light specific for a certain element(s) and the atoms absorb that light. The decrease in light intensity was measured with a detector at a specific wavelength (Cd was measured at the wavelength of 228,8 nm). The concentration of an element in a sample was determined by comparing the absorbance of the sample with the absorbance of calibration solutions. If necessary, interferences were overcome by adding a matrix modifier to the samples.

Determination of cadmium by inductively coupled plasma optical emission spectrometry (ICP-OES) is based on EVS-EN ISO 11885:2009. A sample solution was introduced into the core of inductively coupled argon plasma (ICP), which generates temperature of approximately 8000°C. At this temperature all elements become thermally excited and emit light at their characteristic wavelengths. The spectra are dispersed by a grating spectrometer and the intensities of the lines are monitored by a detector. The signals from the detector(s) are processed and controlled by a computer system.

According to EVS-EN ISO 17294-2:2004 the determination of cadmium by inductively coupled plasma mass spectrometry (ICP-MS) consists of the following steps: 1) a measuring solution is transferred into radiofrequency plasma where energy transfer processes from the plasma cause dissolution, atomisation and ionisation of elements; 2) in the mass spectrometer, the ions are separated and the elements identified according to their mass-to-charge ratio (m/z), while the concentration of the element is proportional to the number of ions; 3) transmission of the ions through the mass separation unit and detection is analysed by data handling system.

3.2.1.2 Mercury

For analysis of mercury (Hg), EVS EN 1483 method was used.

Pre-treatment of water samples for Hg
Nitric acid was added immediately to the test sample until pH of the solution was one or lower. After that 10 ml of sulfuric acid, 2,5 of ml nitric acid and 10 of ml potassium permanganate were added to 100 ml of sample. The solution should permanently be coloured purple. If necessary, more potassium permanganate was added. The solution was heated in a water bath at 70 ± 5 °C for five hours and cooled down afterwards until room temperature. After that hydroxyl amine hydrocloride solution was added until purple colour disappeared.

Pre-treatment of solid samples for Hg
0,5 g of sample was weighed in a flask and 10 ml of sulfuric acid and 2.5 ml of nitric acid were added. The solution was heated in a water bath at 70 ± 5 °C for five hours. After that the solution was allowed to cool down until room temperature and 10 ml of potassium permanganate was added. The solution should permanently be coloured purple. If necessary, more potassium permanganate was added. The sample was then filled until volume of 130 ml and hydroxyl amine hydrocloride solution was added until purple colour disappeared.

Instrumental method for Hg
Mercury was reduced to the elemental form by tin(II) chloride in an acid medium and then mercury atoms were transported into an analytical cell by an air flow (the “cold vapour” technique). Absorbances were measured at a wavelength of 253,7 nm in the radiation beam of an atomic absorption spectrometer. Concentrations were calculated using a calibration curve.

3.2.2 Organotin compounds

Monobutyltin and monooctyltin are used as PVC heat stabilizers. Diphenyltins are used in polymer manufacturing, in the manufacturing of polyurethane and silicone curing. Tributyltins are used as industrial biocides, e.g. as antifungal agents in textiles and paper, wood pulp and paper mill systems. Tributyltins are used in marine anti-fouling agent, but concern over their toxicity has led to a worldwide ban by the International Maritime Organization. Triphenyltins are used as active components of antifungal paints and agricultural fungicides.

The analyses of organotin compounds were performed by IVL Swedish Environmental Research Institute.

Method of analysis for organotin compounds in water
Simultaneous ethylation and extraction followed by analysis using GC-MS-MS. (SS-EN ISO 17353:2005 modified).

Method of analysis for organotin compounds in sludge
Acidic extraction of freeze dried sludge followed by ethylation and analysis using GC-MS-MS. (ISO 23161:2009 modified).

3.2.3 Phenolic substances

4-Nonylphenols are a number of isomeric phenol compounds with normal or branched hydrocarbon chain. 4-Nonylphenol (4-NP) is used in e.g. paint, plastic industry and in the production of washing agents and nonylphenol ethoxylates. Nonylphenol ethoxylates (NPE) are mixtures of nonionic surfactants used as detergents, emulsifiers, wetting agents, defoaming agents, etc. Nonylphenol and nonylphenol ethoxylates have been restricted in the European Union as a hazard to human and environmental safety.

Octylphenols (OP) are mainly used for the production of phenol resins, which are used in rubber production as a tackifier for tyres. Octylphenol ethoxylates have many uses, mainly the production of cleaning products such as detergents, but also in lesser quantities in many other applications, such as pesticides, paints and varnishes. Octylphenol is toxic for fishes and shows endocrine effects.

Nonylphenol ethoxylates and bisphenol A (BPA) are known as endocrine disruptors, which can mimic the body's own hormones and thus lead to negative health effects. BPA especially, can affect growth, reproduction and development in aquatic organisms.

The analyses of phenolic compounds were performed by Finnish Environment Institute (SYKE).

Method of analysis for phenolic substances in water:
For analysis of phenolic compounds, the surrogate standard (12C-heptylphenol) as well as the quantification standards ($^{13}C_6$-ring 4-NP, $^{13}C_6$-ring 4-NP1EO, $^{13}C_6$-ring NP2EO, $^{13}C_6$-ring OP, $^{13}C_6$-ring OP1EO, $^{13}C_6$-ring OP2EO and d_{16}-BPa) were added to acidified (pH <3) samples before extraction. The 100 ml of whole water sample was extracted and purified with conditioned solid phase extraction disks using vacuum. The compounds were eluted from the cartridges with acetone. Elute was evaporated near to dryness (30°C) with stream of nitrogen. Methanol/water was used to re-dissolve the sample to the final volume and the injection standard (12C-pentylphenol) was added.

Method of analysis for phenolic substances in sludge:
Surrogate standard (^{12}C-heptylphenol) was added to the sample (2-3 g dw) before shaking with acetone-pentane (2 h). Acetone was removed by shaking with water. Separated pentane layer was evaporated just to the dryness and the sample was re-dissolved to methanol. Water (pH 2-3) was added so that the methanol volume is less than 40%. The quantification standards ($^{13}C_6$-ring 4-NP, $^{13}C_6$-ring 4-NP1EO, $^{13}C_6$-ring NP2EO, $^{13}C_6$-ring OP, $^{13}C_6$-ring OP1EO, $^{13}C_6$-ring OP2EO and d_{16}-BPa) were added. The conditioned solid phase extraction cartridge (styrene-divinylbenzene polymer, SDB) was used for sample purification. The acetone extract was evaporated to the dryness (30°C) with nitrogen, re-dissolved with methanol/water and the injection standard (^{12}C-pentylphenol) was added.

Instrumental analysis was performed with liquid chromatography (LC) ion trap mass spectrometry (IT-MS) with electrospray ionization. The blank and control samples were determined in the all sample series.

3.2.4 Endosulfans

Endosulfan is an organochlorine compound that is used as an insecticide. Endosulfan consists of two isomers that differ in the configuration. These isomers are known as alpha-endosulfan and beta-endosulfan. The ratio of alpha-endosulfan and beta-endosulfan is approximately 2:1 in technical products. Endosulfan is acutely toxic, potential for bioaccumulation, and has role as an endocrine disruptor. Endosulfan is banned in the European Union. Because of its threats to the environment, a global ban on the use and manufacture of endosulfan is being considered under the Stockholm Convention. Endosulfan transforms into endosulfan sulfate and endosulfan diol. Endosulfan is subject to long range atmospheric transport.

Endosulfan analyses were performed by the laboratory of Estonian Environmental Research Centre. Preparation and analyse method for endosulfans is based on ISO 6468:1996.

Pre-treatment for endosulfans in water
Sample preparation was performed by liquid-liquid extraction with organic solvent (iso-octane + internal standard PCB189). After the concentration of the extract and after clean up procedure in the florisil column, sample extracts were analysed by gas chromatography, using electron capture detector. Analyse technique: GC-ECD, column: CP SIL 8CB DF 0.25um, gas chromatographic conditions: carrier N2 1ml/min, makeup N2 30 ml/min, detector 350OC, injector 270OC. Quality control was carried out by analysing blancs and control samples. Certified reference materials were used in preparation of calibration solutions and control samples.

Pre-treatment for endosulfans in sludge
The fresh sludge was air dried in dark room. Air dry and grinded sludge was mixed thoroughly with 1 ml of internal standard PCB189 and 15 ml of n-hexane. The samples were extracted by sonication and concentrated using rotary evaporation. Concentrated extracts were treated with copper powder for removing sulfur and cleaned in acidic silica column.

Solvent excess in the samples were evaporated and n-hexane were replaced with isooctane.

Analyse technique: GC-ECD, column: CP SIL 8CB DF 0.25um, gas chromatographic conditions: carrier N2 1ml/min, makeup N2 30 ml/min, detector 350OC, injector 270OC. Quality control was carried out by analyzing blanks and samples with a known concentration. Certified reference materials were used in preparation of calibration solutions and control samples.

3.2.5 Dioxins, furans and PCBs

Polychlorinated dibenzodioxins (PCDDs, dioxins) are a group of polyhalogenated compounds. There are 75 different types of PCDD congeners.

Dioxins have been shown to bioaccumulate in humans and wildlife due to their lipophilic properties, and are known teratogens, mutagens, and suspected human carcinogens. Dioxins occur as by-products in the manufacture of organochlorides, in the incineration of chlorine-containing substances such as PVC (polyvinyl chloride), in the bleaching of paper, and from natural sources such as volcanoes and forest fires.

Polychlorinated dibenzofurans (PCDFs, furans) are very toxic chemicals with properties and chemical structures similar to dioxins. Furan occurs at low levels in commercial coal tars. It also is a by-product of smoking.

The analyses of Polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs), biphenyls (PCBs) and co-planar biphenyls (co-PCBs) were performed by National Institute for Health and Welfare (THL) in Finland.

Pre-treatment for dioxins, furans and PCBs in water and sludge

For water samples, analytes were liquid-liquid extracted from water samples with toluene, about 200 ml of toluene/ liter of water. From sludge samples analytes were soxhlet extracted with 30% ethanol-toluene. After extraction solvent was exchanged to hexane, and sulfur-containing compounds were precipitated with activated copper. Sample in hexane was transferred to a large silica gel column (20 mm*250 mm) containing from top to bottom $AgNO_3$-silica, Na_2SO_4, neutral silica, 15% H_2SO_4-silica, and 44% H_2SO_4-silica. PCDD/Fs and PCBs were eluted from silica gel column with 200 ml of hexane that was concentrated to about 1 ml. Hexane was transferred to a 2 cm column of aluminum oxide in a Pasteur pipette with the aid of a small additional amount of hexane. First 2 ml of hexane eluted out of the column was discarded. Analytes were then eluted from aluminum oxide with 5 ml of 20% dichloromethane-hexane to 5 mm*50 mm carbon column. Mono- and di-*ortho*-PCBs were eluted out from the carbon column in the forward direction with the same 5 ml of 20% dichloromethane-hexane and concentrated to 500 µl in hexane for GC-MS analysis. PCDD/Fs and non-*ortho*-PCBs were eluted from the carbon column in the reverse direction with 15 ml of toluene and concentrated to 15 µl in nonane for separate GC-MS analysis.

Instrumental method for dioxins, furans and PCBs
Carbon-13 (^{13}C) labelled internal standards added to the samples in the start of the analysis were used to quantitate the analytes. The final quantification was performed by gas chromatography - high resolution mass spectrometry (GC-HRMS). Two µl splitless injections to GC were made, and mass spectrometer was operated in selective ion recording mode. A gas chromatograph was connected high resolution mass spectrometer (resolution 10000).

3.2.6 Chlorinated paraffins (SCCP and MCCP)

Chloroparaffins are complex mixtures of n-alkanes homologues with variable chain lengths and chlorine contents consisting of several thousands of congeners, homologues, isomers and enantiomers, their properties depend on the length of the carbon chain of the paraffin molecules used and on the proportion of chlorine added.

Short chain chlorinated paraffins SCCPs (C_{10}-C_{13}) and medium chain chlorinated paraffins MCCPs (C_{14}-C_{17}) are liquids. SCCPs are allowed to be used only in mining conveyor belts but medium chain chlorinated paraffins are used as flame retardants in rubber, flexible plastics, certain textiles and other specific applications.

3.2.6.1 SCCP

The analyses of short chain chlorinated paraffins SCCPs (C_{10}-C_{13}) were performed by Institute for Ecology of Industrial Areas (IETU) in Poland.

Pre-treatment for SCCPs in water
An aliquot (1 l) of unfiltered effluent was passed through Bakerbond C-18 cartridge. Before using the cartridges were washed using consecutively 6 ml of methanol and 6 ml of distilled water. The sample of effluent was passed through the cartridge at a flow rate about 5 ml/min. After that, all cartridges were air dried using vacuum for 30 min. SCCPs were eluted using 10 ml of hexane. The solvent in the eluate was evaporated to approximately 0.5 ml under the nitrogen stream. Due to strong matrix all samples were cleaned-up in the next SPE procedure with cartridges filled with 1 g of Bakerbond Amino (NH_2) and 1 g of Bakerbond Cyan (CN) phases. Before using the cartridges were washed with 10 ml of hexane. The concentrated eluate from the previous cleaning stage was quantitatively transferred on the top of the cartridge. SCCPs were eluted from the bed

by passing through the cartridge 10 ml of hexane. The solvent was evaporated to approximately 0.3 ml under the nitrogen stream and the final volume was set to 0.5 ml with hexane.

Pre-treatment for SCCPs in sludge
The fresh sludge was air dried in dark room and after grinding was passed through 0.25 mm sieve. An aliquot of air dried sludge (2 g) was mixed thoroughly with 2 g of diatomaceous earth and placed in an extraction cell and mounted in the tray of pressurized liquid extraction (10 Mpa, 100ºC, hexane/acetone 1:1 v/v). Obtained extract was evaporated to the volume of 1 ml and quantitatively transferred on the top of the cartridge filled with 1 g of Amino (NH_2) and 1 g of Cyan (CN) phases. Before use the cartridges were washed with 10 ml of hexane. SCCPs were eluted using 10 ml of hexane. The solvent was evaporated to approximately 0.3 ml under the nitrogen stream and the final volume was set to 0.5 ml with hexane.

Instrumental method for SCCPs
SCCPs were determined chromatographically by using gas chromatography equipped with μ-electron capture detector (ECD).

3.2.6.2 MCCP

The analyses of medium chain chlorinated paraffins MCCPs (C_{14}-C_{17}) were analysed by Institute of Non-Ferrous Metals in Gliwice.

Pre-treatment for MCCPs in water
Water samples of 1 l were filtrated. Before use, Discovery DSC-18 (C-18) cartridges were washed using 2 ml of methanol and 2 ml of distilled water. Volumes of 1l of water were passed through the cartridges at flow rate about 5 ml/min. After that, cartridges were dried under vacuum for 15 min. Chlorinated paraffins were eluted using 6 ml of hexane. The solvent in the eluant were evaporated just to dryness and reconstituted in 1 ml of hexane.

Pre-treatment for MCCPs in sludge
10 g sludge sample is extracted in the ultrasonic bath in 75 ml of dichloromethane for 1 hour. After the extraction, extract is filtrated and evaporated just to the dryness on the vacuum evaporator. Before the chromatographic analysis, extract is reconstructed in 1 ml of hexane and sulfur was removed by adding copper. The recovery of this method was estimated at 93.4%.

Instrumental method for MCCPs
The samples were determined chromatographically with gas chromatograph equipped with ECD.

3.2.7 Brominated flame retardants

The analyses of all brominated flame retardants were performed by Finnish Environment Institute (SYKE).

3.2.7.1 PBDEs

Polybrominated diphenylethers are a group of substances with varying degrees of bromination. There are altogether 209 possible congeners with varying chemical properties and biological activities. PBDEs are used as flame retardants in a wide array of products. The use of penta- and octaBDE is banned in EU but inflow to EU market is occurring via importing e.g. electronic circuits, textiles and plastics.

Pentabromodiphenyl ether (pentaBDE), octabromodiphenyl ether (octaBDE), and decabromodiphenylether (decaBDE) are mentioned in BSAP as substances of specific concern to the Baltic Sea. Commercially available polybrominated diphenylethers are mixtures of different congeners. In pentaBDE, the main congeners are 28, 47, 99, 100, 153, and 154 which were all included in screening. In octaBDE, the main congeners are 183, 196, 197, 203, 206, and 207 but only two congeners (183 and 203) were included in screening. DecaBDE contains mainly congener 209 which was included in screening. In addition congeners 17, 66 and 85 were analysed.

Pre-treatment for PBDEs in water
For analysis of PBDEs surrogate standard ($_{13}C_{12}$-BDE 77) was added to the samples before water samples (approx. 3200 ml) were extracted as whole samples. The liquid-liquid extraction with dichloromethane (DCM) was performed two times to attain good recoveries (over 70%).

Pre-treatment for PBDEs in sludge
Freeze-dried sample (1 g) was extracted with DCM at pressurized liquid extraction. Surrogate standard ($_{13}C_{12}$-BDE 77) was added to the samples before extraction.

Instrumental method for PBDEs
The extracts were cleaned with multilayer silica column and basic alumina column (according to standard ISO 22032). The samples were concentrated and solvent was changed to nonane before instrumental analysis. Low pressure gas chromatography tandem mass spectrometry (LP-GC-TQ MS) was used for instrumental analysis of PBDE compounds. Prior to injection, $_{13}C_{12}$-BDEs (28, 47, 99, 153, 183, 209) were added as quantification standards. The final results are recovery corrected and the blank samples were determined in the all sample series.

3.2.7.2 HBCDD

Technical hexabromocyclododecane is used as flame retardant in extruded and expanded polystyrene foam that is used as thermal insulation in the building industry. HBCDDs are brominated cycloalkanes with 16 possible stereoisomers. The isomers have different chemical properties and biological activities. HBCDDs are thermolabile compounds and thermal rearrangement of isomers occurs at temperatures above 160 °C leading to changes of isomer ratios. Therefore, in instrumental analysis it is important not to affect isomer ratios.

Currently HBCDDs are under review of Stockholm Convention. HBCDD is mentioned in BSAP as substances of specific concern to the Baltic Sea. Typically technical HBCDD contains mainly γ-isomer, but α- and β-isomers are also present. The α-isomer is the main isomer found in aquatic organisms and sediments, although γ -isomer is predominant in products.

Pre-treatment for HBCDDs in water
Surrogate standards ($^{13}C_{12}$- α-, β- and γ-HBCDD) were added to the samples before water samples (approx. 1600 ml) were extracted as whole samples. The liquid-liquid extraction with dichloromethane was performed twice to assure good recoveries (over 70%).

Pre-treatment for HBCDDs in sludge
Freeze-dried sample (1 g) was extracted with dichloromethane at pressurized liquid extraction. Surrogate standards ($^{13}C_{12}$- α-, β- and γ-HBCDD) were added to the samples before extraction.

Purification and instrumental method for HBCDDs

The extracts were cleaned with acidified silica and basic alumina columns. The samples were concentrated and solvent was changed to methanol before instrumental analysis. Ultra performance liquid chromatography tandem mass spectrometry was used for instrumental analysis of three HBCDD diastereomers (α-, β- and γ-HBCDD). Prior to injection, d_{18} α-, β- and γ-HBCDD were added as quantification standards. The final results were recovery corrected and the blank samples were determined in the all sample series.

3.2.8 Perfluorinated compounds

Perfluorinated compounds comprise a large number of fully fluorinated alkanes with different functional groups (*e.g.* acid, sulfonate).

Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are mentioned in BSAP as substances of specific concern to the Baltic Sea. In addition, perfluorohexanoic acid (PFHxA) and perfluorodecanoic acid (PFDA) were analysed.

Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate are chemically and biologically inert and very stable. PFOS binds to blood proteins and accumulates to liver. PFCs are used widespread *e.g.* in electric and electronic parts, fire fighting foam, photo imaging, hydraulic fluids and textiles. Perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride are included in the list of Stockholm Convention on persistent organic pollutants. Their production and use shall be restricted. The marketing and use of perfluorooctane sulfonates is restricted in Europe.

The analyses of all perfluorinated compounds were performed by Finnish Environment Institute (SYKE).

Pre-treatment for PFCs in water

Surrogate standards ($^{13}C_2$-PFHxA, $^{13}C_4$-PFOS and $^{13}C_2$-PFDA) were added to the samples before centrifugation. The solid phase extraction (copolymer cartridges) was used for sample purification and concentration. A portion of the extract was analysed without concentration. Prior to injection, $^{13}C_4$-PFOA was added as a quantification standard.

Pre-treatment for PFCs in sludge

Freeze-dried sediment sample (1 g) was placed in a polypropene tube and surrogate standards ($^{13}C_2$-PFHxA, $^{13}C_4$-PFOS and $^{13}C_2$-PFDA) were added. 200 mmol/l NaOH in methanol was added for digestion. After 30 min, 2 mol HCl in methanol was added for neutralisation. Analytes were extracted in wrist-action shaker twice with methanol. The extracts were concentrated, and then purified with activated carbon and glacial acetic acid. Purified extract was diluted with deionized water and $^{13}C_4$-PFOA was added as a quantification standard.

Instrumental method for PFCs

Analyses were performed with ultra performance liquid chromatography connected to tandem mass spectrometer. The liquid chromatography eluents were water and methanol buffered with ammonium acetate. Calibration was done using linear-only standards and the results were reported as a sum of both linear and branched isomers. The final results were recovery corrected and the blank samples were determined in the all sample series.

3.3 Obligatory biotests

3.3.1 *Vibrio fischeri* luminescent bacteria test

Vibrio fisheri tests were performed by project partner Finnish Environment Institute (SYKE). Tests were performed according to the ISO 11348-3 standard. Standard describes a method for determining the inhibition of the luminescence emitted by the marine bacterium *Vibrio fischeri* (NRRL B-11177). Method is using freeze-dried bacteria.

This method is applicable to waste water, aqueous extracts and leachates, fresh water (surface and ground water), sea and brackish water, eluates of sediment (freshwater, brackish and sea water), pore water and single substances, diluted in water.

Test time for all samples was 30 minutes.

3.3.2 Daphnia magna acute toxicity

Tests were performed by EMI according to ISO 6341 standard. This standard describes a method for the determination of the acute 24-h and 48-h toxicity to *Daphnia magna Straus (Cladocera, Crustacea)* of chemical substances which are soluble under the conditions of the test, or can be maintained as a stable suspension or dispersion under the conditions of the test; industrial or sewage effluents, treated or untreated, after recantation, filtration or centrifugation if necessary; surface or ground waters.

Daphthoxkit^{TM} test-kits were provided by Microbiotests Inc. This kit-test makes use of the dormant *Daphnia* eggs (ephippia). Hatching of the ephippia was initiated 3 days prior to the start of the toxicity test at 21 ± 1^{o} C, under continuous illumination of at least 6000 lux. At the start of the tests the neonates were not older than 24 hours. Neonates were fed 2 hours before the tests with microalgae. Animals were not fed during the test. Testing was per-formed in darkness. Standard freshwater was used for *Daphnia* hatching and effluent dilutions.

The standard procedure for effluent tests recommends the concentrations 100%, 50%, 25%, 12,5% and 6,25%, but since the first two rounds of samples were nontoxic, the lowest concentration (6,25%) was replaced with 75% to obtain more effect. The effluent samples collected after September 2009 were tested with such modification.

Effluent effect on *Daphnia* was registered after 24h and 48h. The EC50 values were calculated using online calculator BioDataFit 1.02 (http://www.changbioscience.com/stat/ec50.html).

3.3.3 Algae growth inhibition test

Algae tests were performed by EMI according to the standard ISO 8692 using the Algaltoxkit F^{TM} provided by Microbiotests Inc. This standard specifies a method for the determination of the growth inhibition of unicellular green algae by substances and mixtures contained in water or by wastewater.

A 72h algal growth inhibition test was performed in long cell test vials, with *Pseudokirchneriella subcapitata* de-immobilized from algal beads. Algae were incubated at 22±1°C at constant sideway illumination of 10000 lux. The measurement of algal growth in the long cells was carried out after 24h, 48h and 72h incubation with spectrophotometer LIBRA S32 BIOCHROM.

The calculation of ErC50 values was performed with Algaltoxkit Data Treatment Software by MicroBioTests Inc.

3.4 Optional biotests

It was recommended in the application that for the detection of hazardous effects of effluents participants would also perform optional tests. For the detection of chronic effects of effluents we used egg-larvae test of zebrafish, long-term *Daphnia magna* test and *Lemna minor* test. Genotoxicity of the samples were detected by using umu-test. We also used biomarkers describing xenobiotic metabolism (EROD analyse) and hormonal effects (vitellogenin test).

The waters tested for chronic toxicity were taken from WWTP3 and WWTP4b in January 2010. All optional tests were performed by Finnish Environment Institute (SYKE).

3.4.1 Egg-larvae test of zebrafish *(Danio rerio)*

Fish are particularly susceptible to the influence of substances, for example chemicals, during the reproductive stage (gametogenesis) and early developmental stages (embryo and larval stages). Determination of the toxicity to fish in early developmental stages is thus a more sensitive index of tolerance than that obtained by determination of acute toxicity to adult fish. However, only tests incorporating all stages of the life cycle of fish are expected to give an accurate estimate of the chronic toxicity of chemicals to fish. A reduced exposure with respect to life stages may reduce the sensitivity and, thus, underestimate the chronic toxicity. However, experience has shown that for many chemicals the sensitivity obtained in embryo-larval tests correlates with that obtained in full life cycle tests. Most experience with embryo-larval tests in Europe has been obtained with the freshwater fish *Danio rerio* (Hamilton-Buchanan), commonly called zebrafish.

Egg-larvae-tests were performed as semi-static according the ISO 12890 standard (ISO 12890: 1999).

We deviated here from the standard in that the untreated water from lake Päijänne (raw water for Helsinki city tap water) was used both as a control and as a dilution water, and also in that the test waters were changed only every second day. Päijänne water was also used to breed the fish. In all other respects water quality and test conditions followed the ISO 12890 standard.

The test concentrations were selected after the acute toxicity tests of *Daphnia magna*. The used test concentrations were 100 %, 50 %, 25 % and 0 %.

Mixed sex population of adult zebrafish was grown as described in the standard. Fish were brought to the laboratory conditions four weeks before the tests. Males and females were separated to different tanks. Fish were let to spawn as described in the standard. During the acclimatization period fish were fed with clean *Daphnia*, frozen larvae of chironomids and Tetra Min flakes (Tetra GmbH, Germany).

3.4.2 *Lemna minor* test (Duckweeds)

Duckweeds are fast growing higher plants, spreading from the tropic to the arctic zone. As primary producers they are a food source for waterfowl, fish and small animals and serve as physical support for a variety of small invertebrates. Duckweed can be damaged by water constituents and effluents. The subsequent inhibition of growth is calculated from the observation parameters (frond number, frond area, chlorophyll, dry weight) by a number of defined calculation methods.

EC values are determined to allow for an assessment of toxic effects of water constituents (e.g. chemicals, plant protection products). The evaluation for at least two observation parameters is based on the average specific growth-rates.

The used method for the determination of growth-inhibiting response of duckweed (*Lemna minor*) to test effluents was a validated in-house method of SYKE's laboratory.

3.4.3 Fish hepatocyte vitellogenin induction

Among the best understood of the environmental endocrine disrupters are those that mimic the action of estrogens. Both in vivo and in vitro methods have been developed and used for the detection of estrogenic properties of chemicals and waste waters.

Vitellogenin is a precursor for egg yolk, normally only in adult female fish. Estrogens are the primary stimulus for its synthesis and secretion in the liver of females. Male fish have also the vitellogenin gene, but it is inactive in them. However, if males are exposed to estrogens or substances mimicking estrogens the gene activates, and also male liver starts to synthesise vitellogenin. Male fish primary hepatocytes have been used successfully for the detection of the estrogenic potency of waste waters and chemicals in vitro.

Freshly isolated hepatocytes from hatchery-reared males of brown trout (*Salmo trutta m. Lacustris*) were used for the in vitro screening of the vitellogenin-inducing effects of effluents and the possible changes in detoxification metabolism of the fish liver cells. Hepatocytes were isolated according to a slightly modified method of Moon et al. (1985). Medium 199 (Sigma), with added L-glutamine (Sigma), $NaHCO_3$, Na_2HPO_4 (Merck) and an antibiotic-antimycotic solution (Sigma), was used for the washing, dilution and incubation medium. The viability of freshly isolated hepatocytes was assessed by the Trypan Blue exclusion method (Moon et al., 1985). Only preparations with over 90% viability were accepted for the tests.

Hepatocytes were diluted to yield the concentration of 1 x 106 cells mL-1 and then distributed into disposable Petri dishes in a final volume of 8 ml. Cells were incubated in duplicate for 72 hours. The exposure temperature was 12o C ± 1o C. A series of dilutions, 0 %, 6,3 %, 12,5 %, 25 % and 50 %, were used to ensure that a maximum vitellogenic response was obtained with minimum suppression from any toxic effects of the effluents. Vitellogenin in the culture medium was the measured endpoint of the estrogenic activity of effluents. Estradiol-17β was run alongside each test as a positive control with concentrations of 0 µg/mL, 6,3 µg/mL, 12,5 µg/mL, 25 µg/mL and 50 µg/mL.

The vitellogenin was assayed with ELISA according to the method of Nielsen et al. (1998). The monoclonal anti-salmon vitellogenin, BN-5 (Biosense Laboratories AS, Bergen, Norway) was used as an antibody and purified rainbow trout vitellogenin (Biosense Laboratories AS, Bergen, Norway) was used as a standard.

3.4.4 Determination of fish hepatocyte ethoxyresorufin-O-deethylase (EROD) activity

The measurement of pollution biomarkers in fish, such as the measurement of biotransformation enzyme activities, is likely to provide information about exposure levels, bioavailability and the early biological effects of substances present in aquatic ecosystems. The measurement of the EROD enzyme activity allows the diagnosis of the exposure of fish to inducers of the P450 1A cytochrome, such as certain polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and dioxins. A large amount of research work bears witness to the extent of the studies conducted. An induction of EROD activity reflects the presence of inducers such as those mentioned above. On the other hand, the absence of induction does not necessarily reflect the absence of exposure of the fish to organic contaminants, account being taken of the inhibition phenomena of the EROD induction of possible modification of the bioavailability of the inducers or of low exposure concentrations.

Hepatocyte EROD activity was used as the indicators of toxicity. Cell EROD activity was measured according to a kinetic in-house method of SYKE's laboratory, modified from methods of Klotz et al. (1984), Hodson et al. (1991) and van den Heuvel et al. (1995). Tests were performed on white multiplates. The activity was recorded with a Fluoroskan Ascent FL (Labsystem) multiplate reader (excitation 530 nm, emission 584 nm). Reduced enzyme activities in the liver cells were considered as an indication of cytotoxicity.

The cell protein concentration was assayed by Bio-Rad protein assay (Bio-Rad Laboratories, Canada) using bovine serum albumin as a standard.

3.4.5 umu-test

Genotoxicity of the effluents were tested by using umu-test.

Tests were performed by using ISO 13829 standard (ISO 13829:2000). This standard specifies a procedure which can be used to determine the genotoxicity1) of water and waste water using the umu-test. This assay is based on the detection of genotoxicity of a test sample which increases the expression of the SOS repair system associated with the umuC-gene. SOS repair occurs when cells are overwhelmed by genotoxins allowing the cell to survive at the cost of mutagenesis. umuC-gene is the acronym for UV mutagenesis gene C. The induction of the umuC-gene is part of the specific response of the bacterial cell to DNA-damage.

The genetically engineered bacterium *Salmonella typhimurium* TA1535/pSK1002 serves as a test organism. The bacteria are exposed under controlled conditions to different concentrations of the samples to be tested. The test is based on the capability of genotoxic agents to induce the umuC-gene in the Salmonella strain in response to genotoxic lesions in the DNA. Due to its capability to respond to different types of genotoxic lesions, only one single strain is necessary to detect different kinds of genotoxic substances. The induction of the umuC-gene is thus a measure for the genotoxic potential of the sample. Since the umuC-gene is fused with the lacZ-gene for β-galactosidase, the induction of the umuC-gene can be easily assessed by determination of the β-galactosidase activity.

4 Results from chemical analysis of effluents, sludge, landfill leachate and storm waters

4.1 Basic parameters

The basic parameters were measured according to Estonian legislation (RTL 2002, 56, 833) that regulates the methods to be used for seawater, surface water, groundwater, wastewater, effluent and sewage sludge sampling. This legislation also stipulates the parameters that have to be determined during sampling, including temperature, colour, conductivity, and pH of water, and concentration of dissolved gases (such as oxygen) in water. The results of the basic parameters are shown in **Table 4** and **Table 5**.

Table 4. Basic parameters from the monitoring points. Minimum and maximum values are shown. In brackets, median values are shown for WWTP effluents.

Site	T (°C)	pH	conductivity (µS/m)	TOC (mg/l)
WWTP1	10,0 – 24,2 (19,8)	6,33 – 8,13 (6,99)	1460 – 2090 (2010)	16 – 38 (24)
WWTP2	8,0 – 20,0 (13,7)	6,38 – 8,16 (7,26)	699 – 1200 (809)	7,9 – 14 (12)
WWTP3	8,8 – 20,1 (15,9)	6,99 – 7,69 (7,51)	309 – 2990 (2275)	8,6 – 130 (11)
WWTP4a	6,2 – 17,3 (13,4)	7,20 – 7,82 (7,60)	671 – 758 (708)	10 – 115 (11)
WWTP4b	9,5 – 18,5 (17,1)	7,40 – 7,58 (7,56)	1573 – 1724 (1659)	11 – 16 (13)
Landfill	6,1 – 17,2	8,22	4840 - 6650	263 - 366
Storm waters	6,4 – 7,4	7,41 – 7,88	322 - 2510	5,6 – 5,9

The pH value of the effluents didn’t exceed the limits in any cases.

Table 5. Basic parameters from sampling points.

Site	**PE**	**BOD7 (mg/l)**	**BOD7 limit value**	**COD_{Cr} (mg/l)**	**COD_{Cr} limit value**	**Suspended solids (mg/l)**	**SS limit value**	**Tot-P (mg P/l)**	**Tot-P limit value**	**PO4-P (mg P/l)**	**Tot-N (mg N/l) (Kjeldahl)**	**Tot-N limit value**	**NH4-N (mg N/l)**	**Alkalinity (mmol/l)**
WWTP1	92 000	<3 – 6,1	15	58 -120	150	2 – 24	15	0,11 – 18	1	0,03 – 14	3,6 – 16	15	<0,1 – 9,3	2,55 – 4,49
WWTP2	84 600	<3 – 9	15	16 – 79	150	<2 – 9	15	0,16 – 0,74	1	0,03 – 0,63	3, 8 – 11	15	3,8 – 11	3,4 – 5,1
WWTP3	12 000	<3 – 31	15	14 – 53	150	<2 – 14	25	0,1 – 1,2	1,5	<0,2 - 1	8,3 – 41	-	0,42 – 40	3,76 – 7, 62
WWTP4a	2000	<3 – 7,8	15	16 – 37	150	< 2 – 10	25	1,5 – 5,2	1,5	1,3 – 4,5	11 – 18	-	0,06 – 8,5	2,58 – 3,48
WWTP4b	2000	<3 – 5,2	15	32 – 56	150	3 – 12	25	1,6 – 3	1,5	0,03 – 2,8	27 – 38	-	20 – 36	5, 25 – 6,1
Landfill	100 000*	55 -130	15	900 – 1300	150	100 – 300	25	5 – 5,1	2	1,6 – 3,4	244 -301	75	118 – 244	28, 22 – 54,34
Storm waters		5 – 5,6	-	49 – 105	150	52 – 140	40	0,16 – 0,7	-	0,02 – 0,06	4,6 – 6,1	-	0,19 – 0,35	1,46 – 3,94

* the landfill serves for 100 000 persons. The average amount of leachate is 4300 m3 a year.
The limit values are given in Estonian legislation (RTL 2002, 56, 833)

BOD_7 was usually in limits, but exceeded the environmental quality standards twice in WWTP3. In landfills, the BOD_7 was over the limits in all samples, exceeding the standards 3- to 8-fold. COD_{Cr} was over the limits only in the landfill.

The concentration of SS was over the limits in WWTP1 in half of the samples. In other WWTPs, the SS was in the limits. In the landfill, the SS exceeded the limits 4- to 12-fold.

The SS was also over the limits in storm waters. It must be noted that there are no treatment facilities for polluted storm waters even though the Estonian legislation states that the waters must be treated before being lead to the receiving water.

Tot-P exceeded the limits 3 times in WWTP1 and was over the limits in all samples in WWTP3, WWTP4a, and WWTP4b. Tot-P was also over the limits both times in landfill samples. Tot-N was over the limits once in WWTP1, but didn’t exceed the limits in other samples.

$P\text{-}PO_4$, $N\text{-}NH_4$, Fe, alkalinity, and dissolved Sulphur were also measured. There are no limits for these parameters in Estonian legislation.

The flow rates of the WWTPs are given in **Figure 2**. The figure illustrates the differences between the sizes of the WWTPs. No significant seasonal changes were detected during our sampling rounds, except in April. However, according to the WWTPs’ own data, clear seasonal changes in flow rates do exist in Estonia – the flow rates being higher during the spring and autumn when the evaporation is low, precipitation higher, or the snow is melting. In **Figure 3**, the examples of flow rates of WWTP1 and WWTP2 are shown. In WWTP2, varying inputs from industries also affect the changes in flow rates. Other three WWTPs showed similar dynamics.

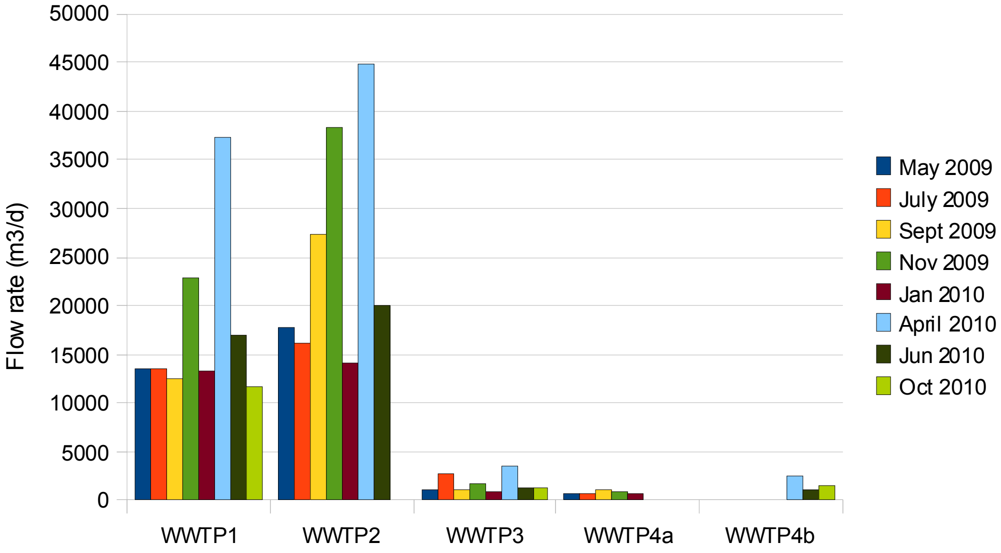

Figure 2. Flow rates of WWTPs.

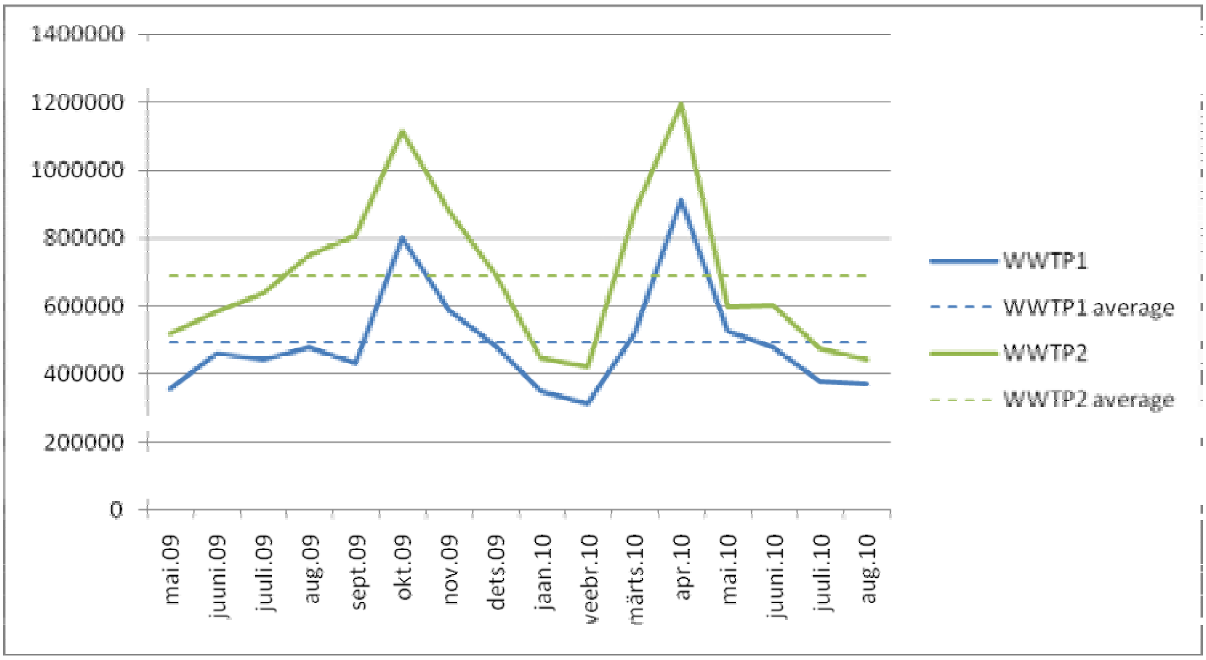

Figure 3. The dynamic in the monthly changes of flow rates in Estonia, with the example of WWTP1 and WWTP2.

The differences in monthly average flow rates can be more than two-fold. High flow rates mean that the concentrations of the hazardous substances are diluted and may not be detected even if present.

4.2 Metals

Both mercury and cadmium are listed as hazardous substances in the Baltic Sea Action Plan, and their entry into the Baltic Sea has to be minimized. Both of these substances are also listed as priority substances under the EU Water Framework Directive (WFD) and environmental quality standards are given for both of the heavy metals in Directive 2008/105/EU. According to the Directive, the annual average concentration of mercury must not exceed 0,05 µg/l. Its maximum allowed concentration is 0,07 µg/l, which is valid for the inland surface waters, transitional waters and coastal waters. The environmental quality standard for cadmium for the inland surface waters is subdivided into five different classes of water hardness, whereas there is a standard of 0,2 µg/l for the average concentration of cadmium per year for both transitional and coastal waters. Directive 86/278/EEC regulates the sewage sludge for use on land. The limits for mercury and cadmium in the sewage sludge allowed to use on land are 16-25 and 20-40 mg/kg, respectively.

In COHIBA samples from the WWTP effluents, mercury was measured on the LOQ (0,05 µg/l) twice (out of 24 samples), all the rest of the analyses showed the results to be under the LOQ. In sludge samples, however, mercury was found over the LOQ (0,02 mg/kg) from all three samples – 0,23 to 0,50 mg/kg. Mercury was found once from the landfill (0,10 µg/l, also exceeding the EQS) and not found from the storm water samples.

The LOQ of Cd was changed in March 2010, when a new method was introduced to the EERC. Before that, the LOQ was 0,1 µg/l, and after March 2010 it was 0,02 µg/l. Generally speaking, the results from the effluents were not found when the LOQ was higher, but gave numerical results when the LOQ was lowered. The highest detected concentration for cadmium was 0,15 µg/l from effluents. Cadmium was also found from both samples of the storm waters (0,05 and

0,16 µg/l), but not found from the landfill samples or the sludge samples from the WWTPs. The summary of the results is shown in **Table 6**, **Table 7**, and **Table 8**.

Table 6. Hg and Cd concentrations in COHIBA WWTP effluent samples.

				WWTPs			
	unit	LOQ	EQS	MIN	MAX	MEDIAN	% >LOQ
Cd	µg/l	0,1 and 0,02	0,08-0,25	<0,02	0,15	n/a	n/a
Hg	µg/l	0,05	0,05	<0,05	0,05	<0,05	12%

Table 7. Hg and Cd concentrations in COHIBA sludge samples.

				Sludge	
	unit	LOQ	EQS	MIN	MAX
Cd	mg/kg	1	20-40* (10**)	<1	<1
Hg	mg/kg	0,02	16-25* (10**)	0,23	0,50

*Directive 86/278/EEC

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Table 8. Hg and Cd concentrations in COHIBA landfill and storm water samples.

				landfill		storm water	
	unit	LOQ	EQS	MIN	MAX	MIN	MAX
Cd	µg/l	0,1 and 0,02	0,08-0,25	<0,02	<0,02	0,05	0,16
Hg	µg/l	0,05	0,05	<0,05	0,10	<0,05	<0,05

4.3 Organotin compounds

The Directive 2008/105/EC prescribes environmental quality standards for tributyltin cation. According to these standards an annual average concentration of 0,2 ng/l and a maximum permissible concentration of 1,5 ng/l have to be observed. These standards are effective for the inland surface waters as well as for transitional waters and coastal waters. HELCOM BSAP lists both TBT and TPhT as substances of specific concern to the Baltic Sea.

In COHIBA, TPhT was not found from any samples. TBT was found twice from the WWTP effluents, not found from landfill leachate samples or storm waters. By March 2011, EERC has the result of only one sludge sample, and the result is 4,1 µg/kg.

The summary of the results is shown in **Table 9**, **Table 10**, and **Table 11**.

Table 9. TBT and TPhT concentrations in COHIBA WWTP effluent samples.

	WWTPs						
	unit	**LOQ**	**EQS**	**MIN**	**MAX**	**MEDIAN**	**% >LOQ**
TBT	ng/l	1	0,2	<1	2,90	<1	8%
TPhT	ng/l	1		<1	<1	<1	0%

Table 10. TBT and TPhT concentrations in COHIBA sludge samples.

	WWTP sludge		
	unit	**MIN**	**MAX**
TBT	µg/kg	4,10	-
TPhT	µg/kg	<5	-

Table 11. and TPhT concentrations in landfill and storm water samples.

				landfill		storm waters	
	unit	**LOQ**	**EQS**	**MIN**	**MAX**	**MIN**	**MAX**
TBT	ng/l	1	0,2	<1	<5	<1	<1
TPhT	ng/l	1		<1	<6	<1	<1

Besides TBT and TPhT, Monobutyltin cation (MBT), Dibutyltin cation (DBT), Tetrabutyltin (TTBT), Monooctyltin cation (MOT), Dioctyltin cation (DOT), and Tricyclohexyltin cation (TCyT) were also analysed. Generally speaking, smaller molecules, such as MBT, DBT and MOT were found over the LOQ uniformly from all the WWTPs at times from both effluents and sludge. Of these substances, MBT was found most frequently, with the highest concentration of 10 ng/l from WWTP3. MBT was also high in landfill leachate, with the highest concentration of 58 ng/l. In contrast with the aforementioned results, MBT was not detected from storm waters, however, DBT was, with the highest concentration of 5,4 ng/l. The findings of smaller molecules from the effluents could indicate an historical pollution with TBT.

4.4 Phenolic substances

The Directive 2008/105/EC prescribes environmental quality standards for Nonylphenol (NP) and Octylphenol (OP). According to these standards an annual average concentration of 0,3 µg/l (NP) and 0,1 µg/l (OP) and a maximum permissible concentration of 2,0 µg/l for Nonylphenol have to be observed. There is no maximum permissible concentration for OP. HELCOM BSAP also lists the Nonylphenol ethoxylates (NPE) and Octylphenol ethoxylates (OPE) as substances of specific concern to the Baltic Sea.

In COHIBA, all named phenolic substances were found from the WWTP effluents, however, it must be noted that the results from the WWTP3 stood out from the results of other WWTPs as significantly higher (**Figure 4**), somewhat distorting the general results. It should also be noted that the EQS of the NP and OP-s is lower than the LOQ, therefore all the results over the LOQ are also over the EQS.

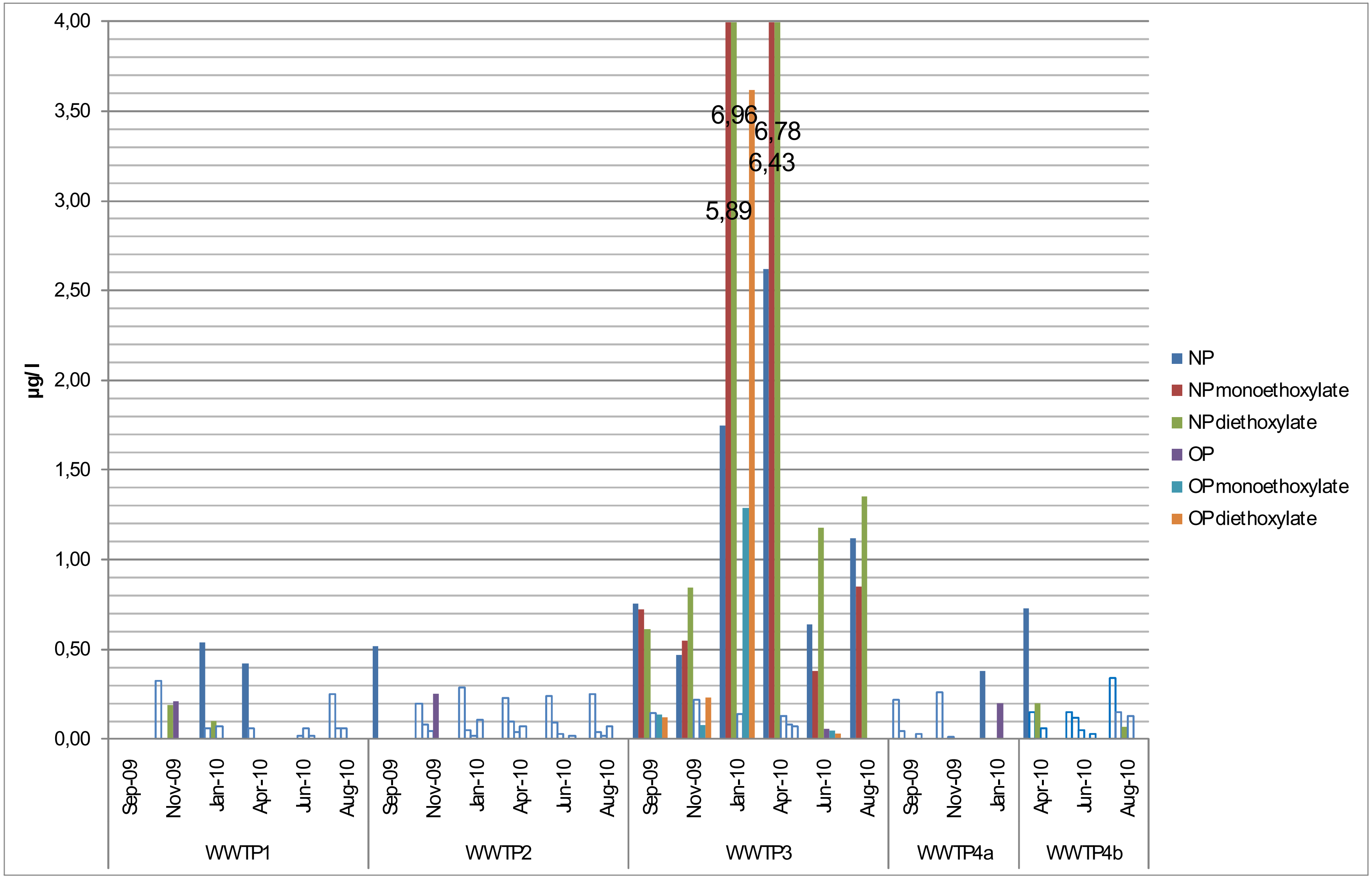


Figure 4. Results of phenolic substances in the WWTPs. The results below the LOQ are shown as blank columns.

Out of 24 samples, NP was found from 50% of the effluents and was also the only substance to be detected over the LOQ from all WWTPs at least once. Other substances were less common. NP monoethoxylates, and both OPE-s were found to be over the LOQ only in WWTP3 (**Table 12**).

Table 12. concentrations of phenolic substances in COHIBA WWTP effluent samples.

				WWTPs			
	unit	**LOQ**	**EQS**	**MIN**	**MAX**	**MEDIAN**	**% >LOQ**
NP	µg/l	0,35	0,3	<0,35	2,62	<0,35	50%
NPE (mono)	µg/l	0,17		<0,17	6,43	<0,17	25%
NPE(di)	µg/l	0,07		<0,07	6,96	<0,07	42%
OP	µg/l	0,17	0,1	<0,17	0,26	<0,17	17%
OP(mono)	µg/l	0,07		<0,07	1,29	<0,07	17%
OP(di)	µg/l	0,07		<0,07	3,62	<0,07	17%

The phenolic substances were analysed one from the sludge of WWTP1 and twice from the WWTP3. Similarly to the results from the effluents, the only substance to be found over the LOQ from both WWTPs was NP. For other phenolic substances, the results were below the LOQ for WWTP1 and over the LOQ for WWTP3 **Table 13**.

Table 13. TBT and TPhT concentrations in COHIBA sludge samples.

	WWTP sludge			
	unit	**LOQ**	**MIN**	**MAX**
NP	mg/kg	1	2,01	24,20
NPE (mono)	mg/kg	0,6	<0,6	31,10
NPE(di)	mg/kg	0,4	<0,4	26,40
OP	mg/kg	0,6	<0,6	0,77
OP(mono)	mg/kg	0,2	<0,2	5,08
OP(di)	mg/kg	0,3	<0,3	9,64

Phenolic substances were not found from the storm water samples. NP was found from both landfill samples and Nonylphenol diethoxylates were found from one sample. OP or OPE-s were not found from the landfill leachate (**Table 14**).

Table 14. Concentrations of phenolic substances in landfill and storm water samples.

				landfill		Storm waters	
	unit	LOQ	EQS	MIN	MAX	MIN	MAX
NP	µg/l	0,35	0,3	0,39	0,99	<0,35	<0,35
NPE (mono)	µg/l	0,17		<0,17	<0,17	<0,17	<0,17
NPE(di)	µg/l	0,07		<0,07	0,09	<0,07	0,09
OP	µg/l	0,17	0,1	<0,17	<0,17	<0,17	<0,17
OP(mono)	µg/l	0,07		<0,07	<0,07	<0,07	<0,07
OP(di)	µg/l	0,07		<0,07	<0,07	<0,07	<0,07

Besides those substances, bisphenol-A (BPA) was also analysed. BPA was detected uniformly from all the WWTPs, landfill and storm waters at several times, the highest concentration being 5,79 µg/l from WWTP2. BPA was not detected from the sludge samples.

4.5 Endosulfan

The Directive 2008/105/EC prescribes environmental quality standards for endosulfan. According to these standards, the sum of α- and β-endosulfan and endosulfan sulphate should not exceed 0,005 µg/l (5 ng/l) as an annual average and a maximum permissible concentration of 0,01 µg/l (10 ng/l) has to be observed.

In COHIBA, endosulfan was not found from any of the effluents nor the storm waters. However, β-endosulfan was found once from the sludge of WWTP3 (1,3 mg/kg) and endosulfan sulphate was found once from the landfill (38,4 ng/l). The summary of the results is shown in **Table 15**, **Table 16**, and **Table 17**

Table 15. Endosulfan concentrations in WWTP effluents.

				WWTPs			
	unit	LOQ	EQS	MIN	MAX	MEDIAN	% >LOQ
Endosulfan	ng/l	5	5*	<5	<5	<5	0%

* for sum of α- and β-isomers and endosulfan sulphate

Table 16. Endosulfan concentrations in WWTP sludge samples.

	WWTP sludge			
	unit	LOQ	MIN	MAX
α–Endosulfan	mg/kg	1	<1	<1
β–Endosulfan	mg/kg	1	<1	1,30
Endosulfan sulphate	mg/kg	1	<1	<1

Table 17. Endosulfan concentrations in landfill and storm water samples.

				landfill		storm waters	
	unit	**LOQ**	**EQS**	**MIN**	**MAX**	**MIN**	**MAX**
α–Endosulfan	ng/l	5	5*	<5	<5	<5	<5
β–Endosulfan	ng/l	5	5*	<5	<5	<5	<5
Endosulfan sulphate	ng/l	5	5*	<5	38,40	<5	<5

* for sum of α- and β-isomers and endosulfan sulphate

4.6 Dioxins, furans and PCBs

The dioxins are summarised somewhat less than other substances, the main reasons being varying LOQ and too small number of samples. The results can be used as comparisons for next studies but are definitely not good for generalising.

The dioxins were measured only from the effluents, landfill leachate and storm waters but not from the sludge of WWTPs. There are proposed EQSs for dioxins in sediments and sludge. The proposed EQSs for dioxins in waters are: 4,0 ng WHO98-TE/kg ww for sum of PCDD+PCDF in fresh water; 8.0 ng WHO98-TE/kg ww for sum of PCDDs+PCDFs+DL-PCBs in sea water. The concentrations of substances in effluents, storm waters and leachate did not exceed those proposed EQSs.

The results here are given as a range of all the results. The LOQ of the measurement depends on the particular sample; hence we haven't shown it separately. In **Table 18**, **Table 19**, and **Table 20**, only the results that exceeded the LOQs are shown.

In WWTPs, only dioxins and furans shown in the table were found over the LOQ. Among non-ortho PCBs, i.e. co-planar PCBs, the most dominant one was Co-PCB 77.

Table 18. Dioxins and furans in WWTP effluents.

Dioxins and furans	**CAS**	**Unit**	**WWTP effluent**
1,2,3,4,6,7,8-HpCDD	35822-46-9	pg/l	0,1339 – 0,3486
1,2,3,4,6,7,8-HpCDF	67562-39-4	pg/l	0,1199 – 0,1318
OCDD	3268-87-9	pg/l	0,5838 – 4,2626
OCDF	39001-02-0	pg/l	0,2611 – 0,7774
WHO-TEQ 2005 pg/g (upperbound)			0,3545 – 1,1120
WHO-TEQ 2005 pg/g (mediumbound)			0,1772 – 0,5563
WHO-TEQ 2005 pg/g (lowerbound)			0 – 0,0062

Table 19. Non-ortho PCBs in WWTP effluents.

Non-ortho PCBs i.e. co-planar PCBs	**Unit**	**WWTP effluent**
CO-PCB-77	pg/l	0,9554 – 5,3337
CO-PCB-81	pg/l	0,0789 – 0,9013
CO-PCB-126	pg/l	0,1117 – 0,4507
WHO-TEQ 2005 pg/l (upperbound)		0,0081 – 0,0304

Table 20. Other PCBs in WWTP effluents.

Other PCBs	**Unit**	**WWTP effluent**
PCB-18	ng/l	0,0378 – 0,3569
PCB-28/31	ng/l	0,0423 – 0,2989
PCB-33	ng/l	0,0094 – 0,0851
PCB-47	ng/l	0,0425 – 0,9360
PCB-49	ng/l	0,0089 – 0,0530
PCB-51	ng/l	0,0124 – 0,1939
PCB-52	ng/l	0,0245 – 0,1090
PCB-60	ng/l	0,0041 – 0,0165
PCB-66	ng/l	0,0110 – 0,0648
PCB-74	ng/l	0,0078 – 0,0451
PCB-99	ng/l	0,0112 – 0,0376
PCB-101	ng/l	0,0249 – 0,0898
PCB-105	ng/l	0,0063 – 0,0311
PCB-110	ng/l	0,0231 – 0,0800
PCB-114	ng/l	0,0014 – 0,0025
PCB-118	ng/l	0,0220 – 0,0841
PCB-128	ng/l	0,0062 – 0,0191
PCB-138	ng/l	0,0305 – 0,1090
PCB-141	ng/l	0,0044 – 0, 0212
PCB-153	ng/l	0,0259 – 0,0741
PCB-156	ng/l	0,0042 – 0,0187
PCB-157	ng/l	0,0007 – 0,0015
PCB-167	ng/l	0,0009 – 0,0038
PCB-170	ng/l	0,0063 – 0,0494
PCB-180	ng/l	0,0084 – 0,0776
PCB-183	ng/l	0,0079 – 0,0172
PCB-187	ng/l	0,0079 – 0,0236
PCB-189	ng/l	0,0006 – 0,0013
PCB-194	ng/l	0,0051 – 0,0124
WHO-TEQ 2005 pg/g (upperbound)		0,0110 – 0,0350
WHO-TEQ 2005 pg/g (mediumbound)		0,0065 – 0,0336
WHO-TEQ 2005 pg/g (lowerbound)		0,0002 – 0,0322

The substances were measured only once from both landfill and storm water. The results are shown in **Table 21**, **Table 22**, and **Table 23**.

Table 21. Dioxins in landfill and storm water.

Dioxins	CAS	Unit	Landfill	Storm
2,3,7,8-TCDD	1746-01-6	pg/l	0,3857	<0.24
2,3,7,8-TCDF	51207-31-9	pg/l	0,4366	0,9281
1,2,3,7,8-PeCDF	57117-41-6	pg/l	<0.21	0,6103
2,3,4,7,8-PeCDF	57117-31-4	pg/l	0,6331	1,3616
1,2,3,6,7,8-HxCDD	57653-85-7	pg/l	0,5355	0,3892
1,2,3,7,8,9-HxCDD	19408-74-3	pg/l	<0.46	0,7216
1,2,3,4,7,8-HxCDF	70648-26-9	pg/l	0,6446	1,3251
1,2,3,6,7,8-HxCDF	57117-44-9	pg/l	0,3582	1,0586
1,2,3,7,8,9-HxCDF	72918-21-9	pg/l	0,7688	<0.57
2,3,4,6,7,8-HxCDF	60851-34-5	pg/l	<0.51	1,2565
1,2,3,4,6,7,8-HpCDD	35822-46-9	pg/l	14,2608	5,2454
1,2,3,4,6,7,8-HpCDF	67562-39-4	pg/l	2,4998	4,4531
1,2,3,4,7,8,9-HpCDF	55673-89-7	pg/l	<0.58	0,9985
OCDD	3268-87-9	pg/l	96,6663	51,1375
OCDF	39001-02-0	pg/l	7,1487	10,5312
WHO-TEQ 2005 pg/g (upperbound)		pg/l	1,5107	1,6362
WHO-TEQ 2005 pg/g (mediumbound)		pg/l	1,2797	1,3782
WHO-TEQ 2005 pg/g (lowerbound)		pg/l	1,0487	1,1202

Table 22. Non-ortho PCBs in landfill and storm water.

Non-ortho PCBs i.e. co-planar PCBs		Landfill	Storm
CO-PCB-77	pg/l	76,1324	264,2970
CO-PCB-81	pg/l	3,8974	13,0018
CO-PCB-126	pg/l	2,3693	4,4809
CO-PCB-169	pg/l	0,2155	0,3203
Sum	pg/l	82,6147	282,1000
WHO-TEQ 2005 pg/l (upperbound)		0,2522	0,4880

Table 23. Other PCBs in landfill and storm water.

Other PCBs		Landfill	Storm
PCB-18	ng/l	1,6213	4,8894
PCB-28/31	ng/l	2,3288	7,7242
PCB-33	ng/l	0,7043	1,8133
PCB-47	ng/l	0,2047	0,8330
PCB-49	ng/l	0,6496	2,1335
PCB-51	ng/l	0,0650	0,1707
PCB-52	ng/l	0,7698	2,2876
PCB-60	ng/l	0,3073	0,7463
PCB-66	ng/l	1,1794	2,4903

Other PCBs		Landfill	Storm
PCB-74	ng/l	0,6560	1,2754
PCB-99	ng/l	0,4817	0,6736
PCB-101	ng/l	0,7052	1,1046
PCB-105	ng/l	0,5105	0,5104
PCB-110	ng/l	1,1019	1,4437
PCB-114	ng/l	0,0281	0,0291
PCB-118	ng/l	1,1342	1,3025
PCB-122	ng/l	0,0102	0,0110
PCB-123	ng/l	<0.0030	0,0170
PCB-128	ng/l	0,1925	0,2053
PCB-138	ng/l	0,9449	0,9382
PCB-141	ng/l	0,1259	0,1516
PCB-153	ng/l	0,6802	0,7880
PCB-156	ng/l	0,0263	0,1064
PCB-157	ng/l	<0.0020	0,0209
PCB-167	ng/l	<0.0060	0,0284
PCB-170	ng/l	0,2864	0,1671
PCB-180	ng/l	0,4276	0,2827
PCB-183	ng/l	0,0799	0,0741
PCB-187	ng/l	0,1407	0,1202
PCB-189	ng/l	0,0035	0,0057
PCB-194	ng/l	0,0671	0,0322
PCB-206	ng/l	<0.0060	0,0072
PCB-209	ng/l	0,0361	0,0092
All PCBs together (ng/l)	ng/l	< 16	32,6748
WHO-TEQ 2005 pg/g (upperbound)		0,3042	0,5510
WHO-TEQ 2005 pg/g (mediumbound)		0,3041	0,5510
WHO-TEQ 2005 pg/g (lowerbound)		0,3040	0,5510

4.7 Chlorinated paraffins (SCCP and MCCP)

The Directive 2008/105/EC prescribes environmental quality standards for SCCP. According to these standards, the concentration of SCCP should not exceed 0,4 µg/l as an annual average and a maximum permissible concentration of 1,4 µg/l has to be observed. HELCOM BSAP also lists MCCP as a substance of specific concern to the Baltic Sea.

In COHIBA, both SCCP and MCCP were found from all the effluents in concentrations over the LOQ. Out of 24 samples, 22 exceeded the EQS of 0,4 µg/l, with the median concentration being 1,01 µg/l (**Table 24**). Both SCCPs and MCCPs were also found in concentrations over the LOQ from the sludge samples of WWTPs (**Table 25**).

Table 24. Concentrations of chlorinated paraffins in WWTP effluents.

				WWTPs			
	unit	LOQ	EQS	MIN	MAX	MEDIAN	% >LOQ
SCCP	µg/l		0,4	0,32	2,94	1,01	100%
MCCP	µg/l	0,02		0,73	8,40	2,26	100%

Table 25. Concentrations of chlorinated paraffins in WWTP sludge samples.

	WWTP sludge			
	unit	**LOQ**	**MIN**	**MAX**
SCCP	mg/kg		5,99	10,50
MCCP	mg/kg		0,03	2,27

SCCPs were measured in concentrations exceeding the EQS in both landfill leachate and storm waters. MCCP was found in concentrations over the LOQ in storm waters. In landfills, it was measured only once and the result was below the LOQ (**Table 26**).

Table 26. Concentrations of chlorinated paraffins in landfill and storm water samples.

				landfill		Storm waters	
	unit	**LOQ**	**EQS**	**MIN**	**MAX**	**MIN**	**MAX**
SCCP	µg/l		0,4	3,57	10,38	0,85	1,84
MCCP	µg/l	0,02		<0,02	-	1,11	2,91

4.8 Brominated flame retardants

Polybromodiphenylethers (pBDEs)

The Directive 2008/105/EC prescribes environmental quality standards for pentabromodiphenylethers (congener numbers 28, 47, 99, 100, 153 and 154). According to these standards, the concentration of 0,5 ng/l should not be exceeded. HELCOM BSAP also lists penta-, octa-, and decaBDEs as substances of specific concern to the Baltic Sea.

In COHIBA, pentaBDEs were considered to be congeners 28, 47, 99, 100, 153 and 154; octaBDEs were considered to be congeners 183 and 203; and decaBDE was considered to be congener 209.

According to the Commission Directive 2009/90/EC (European Commission 2009), if the amounts of physico-chemical or chemical measurands in a given sample are below the limit of quantification, the measurement results shall be set to half of the value of the limit of quantification concerned for the calculation of mean values. But if the measurands are total sums of a given group, the results below the limit of quantification of the individual substances shall be set to zero. Hence, when discussing the results of pentaBDEs and octaBDEs, the same pattern is followed.

PentaBDEs were detected from all WWTPs, however, the results of all congeners were below LOW in WWTP4a. Out of 24 samples, pentaBDEs were found from 10 (41,6%), with the maximum of all results being 0,47 ng/l and median <LOQ. In landfills, the concentration of pentaBDEs was 5,94 and 10,67 ng/l and in storm waters, the concentrations were <LOQ and 1,3 ng/l. In sludge samples, the concentrations of pentaBDEs were 26,58 to 29,86 µg/kg (**Table 27**)

Table 27. Concentrations of BDE-s in WWTP sludge samples.

	WWTP sludge		
	unit	MIN	MAX
BDE-17	µg/kg	<LOQ	0,35
BDE-28	µg/kg	<LOQ	0,66
BDE-47	µg/kg	8,65	10,80
BDE-66	µg/kg	<LOQ	0,87
BDE-85	µg/kg	<LOQ	<LOQ
BDE-99	µg/kg	12,00	12,95
BDE-100	µg/kg	1,90	2,74
BDE-153	µg/kg	2,30	3,11
BDE-154	µg/kg	<LOQ	<LOQ
BDE-183	µg/kg	0,92	1,07
BDE-203	µg/kg	1,00	1,18
BDE-209	µg/kg	303,60	1183,00

However, the EQS of 0,5 ng/l has been prescribed for single congeners. There were no concentrations detected over the EQS for any congeners in the WWTP effluents. Congeners 47, 66 and 99 were measured at concentrations over the LOQ at times, the most common congener being BDE-99 that was detected over the LOQ in 9 out of 24 samples. Congeners BDE-100 and BDE-153 were also detected at some samples, however, the concentrations were under the LOQ (**Table 28**).

Table 28. Concentrations of BDE-s in WWTP effluents.

				WWTPs			
	unit	LOQ	EQS	MIN	MAX	MEDIAN	% >LOQ
BDE-17	ng/l	0,15		<0,15	<0,15	<0,15	0%
BDE-28	ng/l	0,15	0,5	<0,15	<0,15	<0,15	0%
BDE-47	ng/l	0,15	0,5	<0,15	0,23	<0,15	8%
BDE-66	ng/l	0,15		<0,15	0,18	<0,15	8%
BDE-85	ng/l	0,15		<0,15	<0,15	<0,15	0%
BDE-99	ng/l	0,15	0,5	<0,15	0,32	<0,15	38%
BDE-100	ng/l	0,15	0,5	<0,15	<0,15	<0,15	0%
BDE-153	ng/l	0,15	0,5	<0,15	<0,15	<0,15	0%
BDE-154	ng/l	0,15	0,5	<0,15	<0,15	<0,15	0%
BDE-183	ng/l	0,15		<0,15	<0,15	<0,15	0%
BDE-203	ng/l	0,15		<0,15	<0,15	<0,15	0%
BDE-209	ng/l	0,15		<0,15	2,76	0,41	4%

In landfills, congeners BDE-47 and BDE-99 were measured over the LOQ (0,15 ng/l) and EQS (0,5 ng/l) both times, and congeners BDE-153 and BDE-154 were measured over the LOQ and EQS once. In storm waters, BDE-47, BDE-99, BDE-100, and BDE-153 were measured in concentrations over the LOQ in one sample, with BDE-99 being over the EQS of 0,5 ng/l (**Table 29**).

Table 29. Concentrations of BDEs in landfill leachate and storm waters.

				landfill		storm waters	
	unit	**LOQ**	**EQS**	**MIN**	**MAX**	**MIN**	**MAX**
BDE-17	ng/l	0,15		<0,15	<0,15	<0,15	<0,15
BDE-28	ng/l	0,15	0,5	<0,15	<0,15	<0,15	<0,15
BDE-47	ng/l	0,15	0,5	2,14	2,53	<0,15	0,40
BDE-66	ng/l	0,15		<0,15	<0,15	<0,15	<0,15
BDE-85	ng/l	0,15		<0,15	<0,15	<0,15	<0,15
BDE-99	ng/l	0,15	0,5	3,41	4,46	<0,15	0,51
BDE-100	ng/l	0,15	0,5	<0,15	<0,15	<0,15	0,18
BDE-153	ng/l	0,15	0,5	<0,15	1,44	<0,15	0,21
BDE-154	ng/l	0,15	0,5	<0,15	2,63	<0,15	<0,15
BDE-183	ng/l	0,15		<0,15	1,36	<0,15	<0,15
BDE-203	ng/l	0,15		<0,15	<0,15	<0,15	<0,15
BDE-209	ng/l	0,15		3,28	3,73	3,73	10,40

OctaBDEs were not found in concentrations over the LOQ from WWTP effluents or storm waters, but were found once from the landfill (1,36 ng/l, BDE-183). However, the octaBDEs were found from the sludge samples in concentrations 1,92 to 2,25 µg/kg.

BDE-209 (or decaBDE) was found in 23 out of 24 measurements of WWTP effluents, it was also found from the sludge samples in concentrations from 303,6 to 1183,0 µg/kg. In landfills, the concentrations were 3,28 and 3,73 ng/l, and 3,73 and 10,40 ng/l in storm waters.

Hexabromocyclododecane (HBCD)

There are no environmental quality standards for HBCDs yet, but a concentration of 1,6 ng/l has been proposed as an EQS. HELCOM BSAP also lists HBCDs as substances of specific concern to the Baltic Sea.

Finnish Environment Institute SYKE that analysed Estonian samples, measured HBCDs as α-, β-, and γ- isomers. The differences between the ratio of isomers indicates the source and age of HBCD pollution. However, as analysing the differences between ratios is out of the scope of this study, the other laboratories in COHIBA measured HBCDs as the sum of isomers, and the EQSs are also given as sum of isomers, we have discussed the results from that point of view.

In COHIBA, HBCDs were found from all of the WWTPs. Out of 23 samples, HBCD isomers were found from 21 samples, with the median of 1,23 ng/l (**Table 30**). Out of 23 samples, the proposed EQS of 1,6 ng/l for the sum of HBCD isomers was exceeded in 9 samples. HBCDs were also measured once from WWTP1 sludge and once from WWTP3 sludge (**Table 31**).

Table 30. Concentrations of HBCDs in WWTP effluents.

				WWTPs			
	unit	**LOQ**	**EQS**	**MIN**	**MAX**	**MEDIAN**	**% >LOQ**
HBCDs sum	ng/l	0,10	1,6*	<0,10	3,50	1,23	93%

*since June 2011

Table 31. Concentrations of HBCDs in WWTP sludge samples.

	WWTP sludge			
	unit	**LOQ**	**MIN**	**MAX**
HBCDs sum	µg/kg		12,80	93,40

HBCDs were measured twice from the landfill and storm waters. In landfill leachate the concentration was over the LOQ once, not exceeding the EQS. In storm waters, the HBCDs were over the EQS both times (**Table 32**).

Table 32. Concentrations of HBCDs in landfill and storm water samples.

				landfill		Storm waters	
	unit	**LOQ**	**EQS**	**MIN**	**MAX**	**MIN**	**MAX**
HBCDs sum	ng/l	0,10	1,6*	<0,10	1,07	3,94	6,48

*since June 2011

4.9 Perfluorinated compounds

In COHIBA project, perfluoro-n-hexanoic acid (PFHxA), perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA), and perfluoro-n-decanoic acid (PFDA) were measured. HELCOM BSAP lists PFOS and PFOA as two substances of specific concern to the Baltic Sea; hence we have concentrated our attention on those two substances.

There are no environmental quality standards for perfluorinated substances, however, a concentration of 0,65 ng/l has been proposed as an EQS for PFOS. There are no environmental quality standards or any proposals for the standards, but it must be noted that high levels of PFOA still indicate a high environmental risk. PFOS and PFOA are also of specific concern to the Baltic Sea, listed in HELCOM BSAP.

PFOS and PFOA were found from all the WWTPs. Out of 24 samples, the concentration of PFOS exceeded the proposed EQS in 17 times (**Table 33**). Both substances were also found in concentrations over the LOQ in the sludge samples (**Table 34**).

Table 33. Concentrations of PFOS and PFOA in WWTP effluents.

				WWTPs			
	unit	**LOQ**	**EQS**	**MIN**	**MAX**	**MEDIAN**	**% >LOQ**
PFOS	ng/l	0,5	0,65*	<0,5	2,31	0,71	83%
PFOA	ng/l	0,5		1,03	13,60	3,77	100%

*since June 2011

Table 34. Concentrations of PFOS and PFOA in WWTP sludge samples.

	WWTP sludge			
	unit	**LOQ**	**MIN**	**MAX**
PFOS	µg/kg	0,1	2,21	2,96
PFOA	µg/kg	0,1	0,38	0,73

The landfill leachate and storm water samples were taken twice. In both cases, both PFOS and PFOA were found in concentrations over the LOQ. However, in both landfill samples, the concentrations were significantly high (**Table 35**) The proposed EQS for PFOS (0,65 ng/l) was exceeded 11-fold and 107-fold.

Table 35. Concentrations of PFOS and PFOA in landfill and storm water samples.

				landfill		**storm waters**	
	unit	**LOQ**	**EQS**	**MIN**	**MAX**	**MIN**	**MAX**
PFOS	ng/l	0,5	0,65*	11,39	108,00	1,27	1,51
PFOA	ng/l	0,5		533,00	590,36	0,54	1,86

*since June 2011

Besides PFOS and PFOA, perfluoro-n-hexanoic acid (PFHxA) and perfluoro-n-decanoic acid (PFDA) were also analysed. Both of these substances were detected uniformly from all the WWTPs, from both the effluents and sludge. The highest concentration of PFHxA was 3,1 ng/l from WWTP1s, the highest concentration of PFDA was 4,2 ng/l, found from WWTP2. PFDA was not detected from storm water, but PFHxA was found once – 0,8 ng/l. In landfill leachate, the concentrations of both PFHxA and PFDA were significant, reflecting the situation with PFOS and PFOA that also showed significant concentrations in leachates. The highest concentration of PFHxA was 597 ng/l and the highest concentration of PFDA was 20,7 ng/l.

5 Results from biotests

5.1 Obligatory acute tests

In COHIBA project, three ecotoxicological tests were chosen as obligatory: *Vibrio fischeri*, *Daphnia magna* acute toxicity, and algae (*Pseudokirchneriella subcapitata*) tests.

The most toxic samples according the obligatory toxicological test results were the samples from landfill. All three tests showed rather high toxicity for both samples. EC_{50} was in range 23-50 %. The results of waste water samples were not so plain, but the results were somewhat more toxic for WWTP1 than for other plants.

Vibrio fischeri test showed some effect only in for three samples, two of those from WWTP1 (**Table 36**) More often than others showed samples from WWTP1 effect also according *Daphnia* test. The only real toxic waste water sample according *Daphnia* test was from WWTP1(April 2010, **Table 37**). Besides this one very toxic sample, there was only one waste water sample with high effect according *Daphnia* test (April 2010, WWTP2), the rest of samples showed less than 20% effect. 20% effect at maximal test concentration was chosen to be the limit value for *Daphnia* test in the recommendations of whole effluent assessment (WEA) for HELCOM prepared by COHIBA project.

In addition to two landfill samples algae growth test showed very toxic results for 4 more waste water samples and some effect at maximum concentration in 6 cases (**Table 38**).. The toxic results were gained twice from WWTP1, but not from same sample as with *Daphnia* test. Totally half of six samples from WWTP1 proved to be very toxic at least according one test. Samples from WWTP3 were the most harmless.

In WEA recommendations >30% effect at maximum test concentrations was the toxicity limit for luminescent bacteria and algae tests. According to that none of waste water samples were toxic according *Vibrio fischeri* test and all treatment plants except WWTP4a provided a sample, which was toxic for algae, at least once during the project.

Table 36. Results of *Vibrio fischeri* tests. The effect at maximal concentration of effluent (80%). EC50 values are given in parenthesis where applicable/computable. “na”- not available (not sampled).

Vibrio fischeri Sample	WWTP1	WWTP2	WWTP3	WWTP4	Landfill	Storm water
2009-5	0	0	0	0	na	na
2009-7	5	0	0	1.5	na	na
2009-9 (Landfill 2009-10)	14.3	0	0	0	100 (46.13)	na
2009-11	0	0	0	0	na	na
2010-1(Storm water 2010-3)	0	0	0	0	na	0
2010-4	0	0	0	0	na	0
2010-6	na	na	na	0	100 (39.6)	na
2010-8	na	na	na	0	na	na

Table 37. Results of *Daphnia magna* tests. The effect of undiluted effluent after 48 hours. EC5024h values are given in parenthesis where applicable/computable. "na"- not available (not sampled).

Daphnia magna **Sample**	**WWTP1**	**WWTP2**	**WWTP3**	**WWTP4**	**Landfill**	**Storm water**
2009-5	5	0	0	0	na	na
2009-7	0	0	0	5	na	na
2009-9 (Landfill 2009-10)	10	0	5	5	na	na
2009-11	5	0	0	0	100 (49.05)	na
2010-1(Storm water 2010-3)	5	5	na	na	na	5
2010-4	100 (49.5)	60	0	0	na	5
2010-6	na	na	na	10	100 (24.41)	na
2010-8	na	na	na	15	na	na

Table 38. Results of algae (Pseudokirchneriella subcapitata) tests. Growth inhibition of undiluted effluent after 72h. EC50 values are given in parenthesis where applicable/ computable. "na"- not available (not sampled).

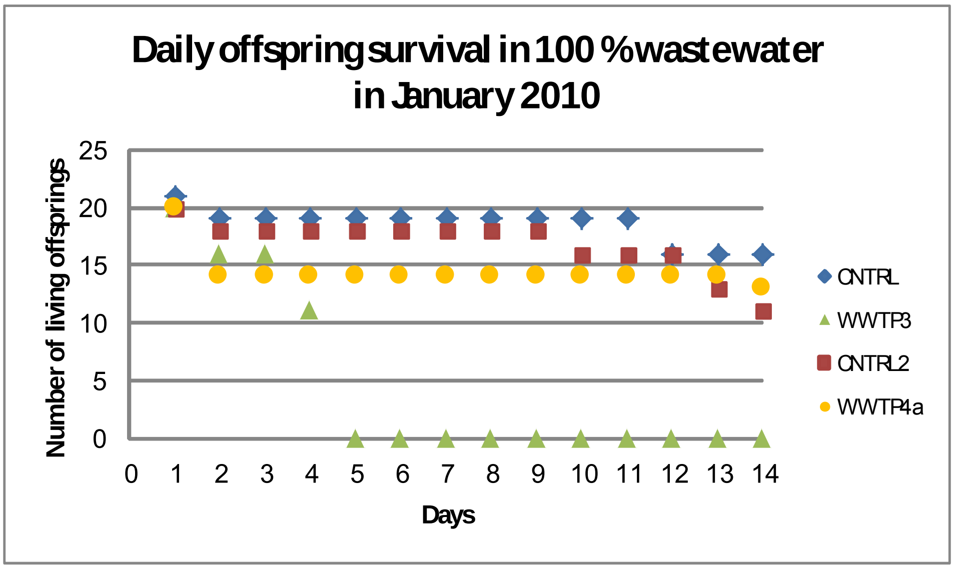
P. subcapitata **Sample**	**WWTP1**	**MWWTP**	**WWTP3**	**WWTP4**	**Landfill**	**Storm water**
2009-5	0	10.14	43.17	0	na	na
2009-7	50 (100)	0	0	0	na	na
2009-9 (Landfill 2009-10)	100 (55.3)	0	4.66	10.89	100 (22.56)	na
2009-11	0	59.52 (69.63)	0	14.49	na	na
2010-1(Storm water 2010-3)	0	0	na	na	na	11.11
2010-4	0	0	10	0	na	0
2010-6	na	na	na	100(53,28)	100(24.95)	na
2010-8	na	na	na	0	na	na

5.2 Optional tests

The optional tests in COHIBA project were: Egg-larvae test of zebrafish, Lemna minor (or duckweeds) test, Fish hepatocyte vitellogenin induction test, Determination of fish hepatocyte ethoxyresorufin-O-deethylase (EROD) activity test, and umu-test.

5.2.1 Egg-larvae test of zebrafish (Danio rerio)

The egg-larvae test of zebrafish showed high toxicity for sample of WWTP3 and some toxicity for sample of WWTP4 (**Figure 5**). Mortality of eggs was 75% in undiluted wastewater of WWTP3 (100% two days later). Sample from WWTP4 showed 30% mortality, according the WEA recommendations the toxicity limit for egg-larvae test is 40% mortality for undiluted water. The mortality results of diluted sample were on the level of controls, WWTP3 still somewhat higher.



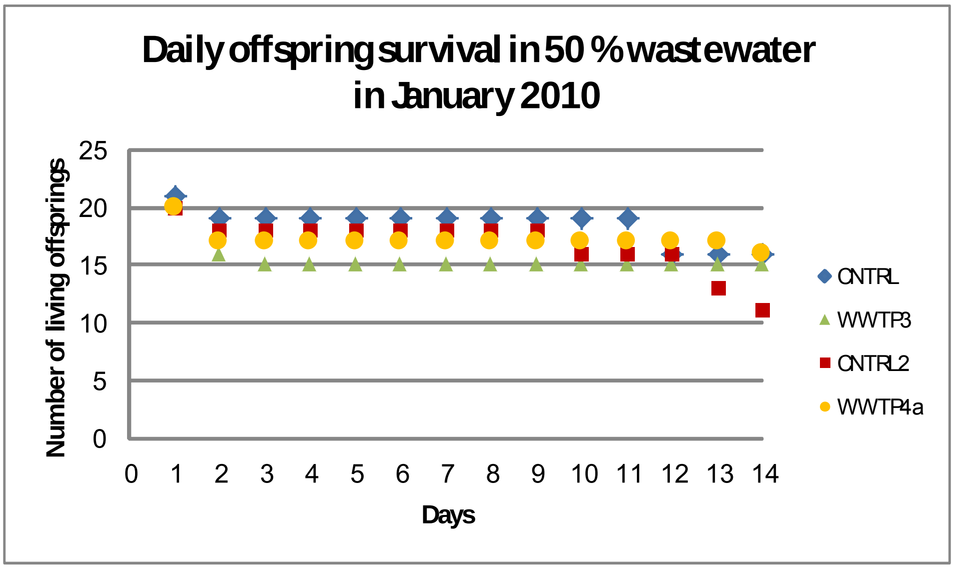


Figure 5. Results of egg-larvae test.

5.2.2 *Lemna minor* test (Duckweeds)

There was no negative effect on *Lemna minor* frond number. The sample from WWTP3 promoted the growth of fronds and area of *Lemna* remarkably. Inhibition was only detected with area measurements for sample from WWTP4a, but the sample was not toxic according the *Lemna minor* test (**Table 39**).

Table 39. Results of *Lemna minor* tests.

	Inhibition %, µ frond number		**Inhibition %, µ area**	
Lemna minor	**5d**	**7d**	**5d**	**7d**
WWTP3	-13,2	-16,4	-15,6	-27,8
WWTP4a	-5,6	-6,6	7,4	2,5

5.2.3 Fish hepatocyte vitellogenin induction

According to this test both our samples had remarkable effect even in low concentrations. WWTP4a was somewhat more effect in low concentrations than WWTP3 and there was no increase of effect with more concentrated sample (**Figure 6**).

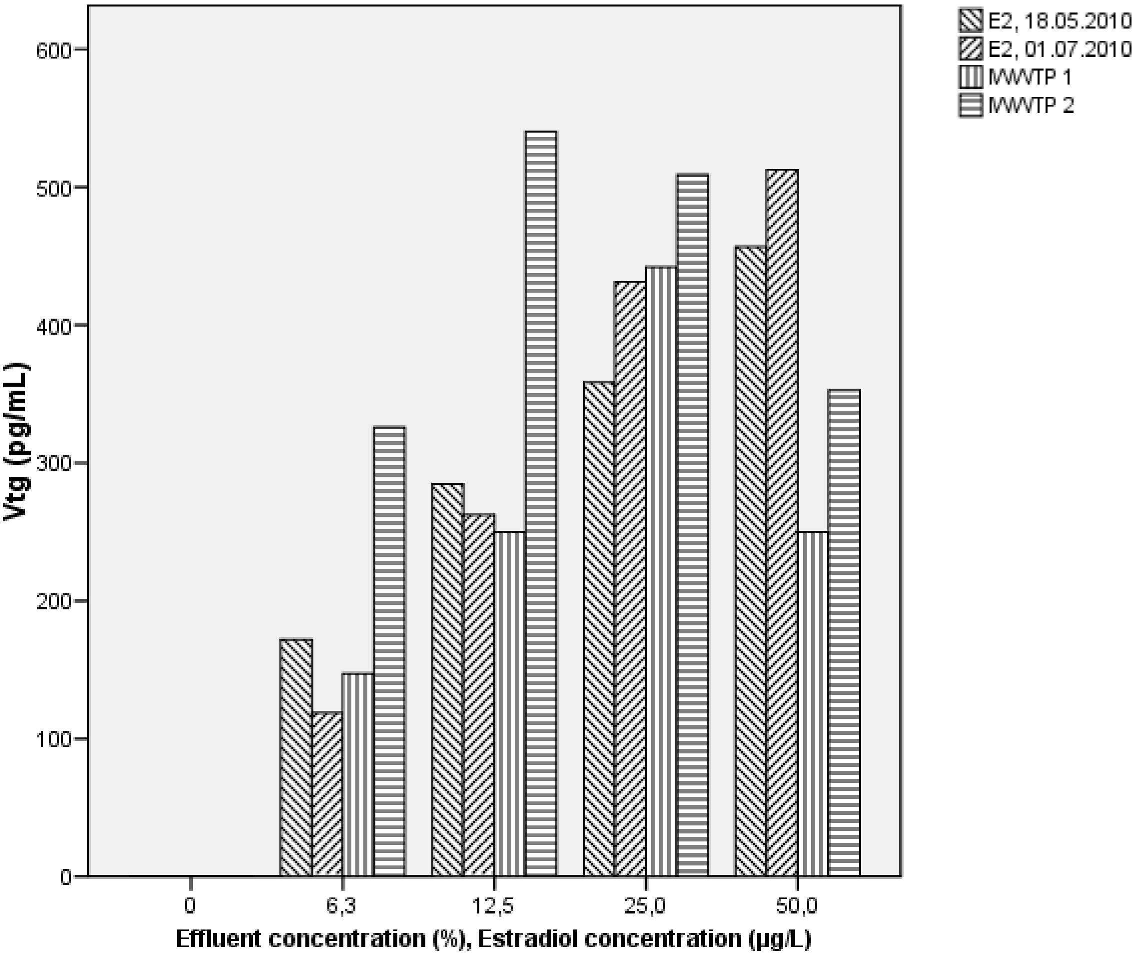


Figure 6. Results of fish hepatocyte vitellogenin induction (IWWTP1=WWTP3; IWWTP2=WWTP4a).

5.2.4 Determination of fish hepatocyte ethoxyresorufin-O-deethylase (EROD) activity

EROD activity test showed high effect for both samples even at the lowest concentrations (**Figure** 7).

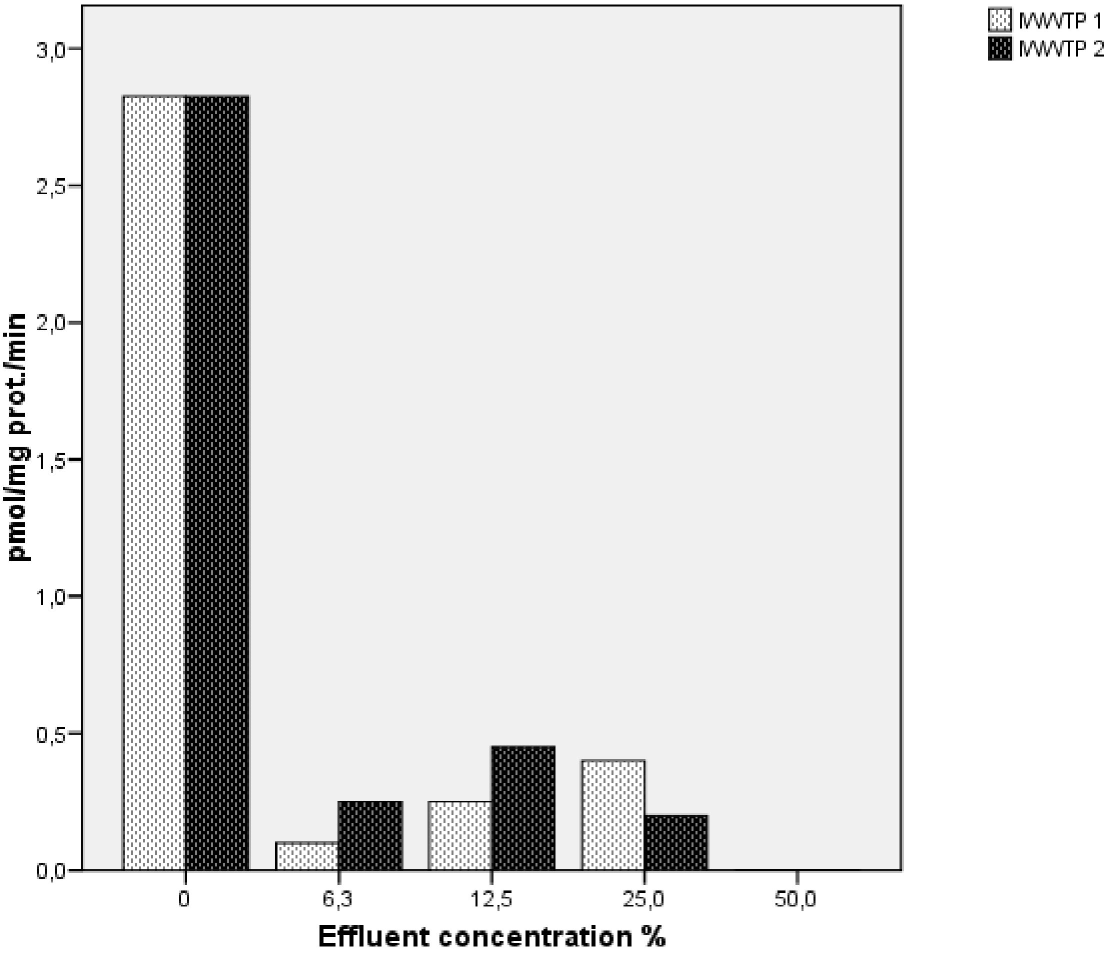


Figure 7. Results of fish hepatocyte ethoxyresorufin-O-deethylase (EROD) activity test (IWWTP1=WWTP3; IWWTP2=WWTP4a).

5.2.5 umu-test

Both samples were showing no genotoxicity at the maximal test concentration (67%), there was no genotoxicity found even at the 1:30 concentrated samples (**Table 40**).

Table 40. Results of umu-test.

	Original samples, max test conc 67 % = dilution factor 1,5		**1:30 concentrated samples**			
umu-test	**-S9**	**+S9**	**-S9**		**+S9**	
WWTP			induction ratio	dilution factor	induction ratio	dilution factor
IWWTP1	NT	NT	0,94	1,5	0,81	1,5
IWWTP2a	NT	NT	0,78	1,5	0,76	1,5

6 Toxicity tests conclusions

Algae growth inhibition test was the most sensitive of the obligatory tests and luminescent bacteria test the least sensitive.

Samples from landfill were very toxic according all tests.

Storm water samples were not toxic.

Except landfill highest number of toxic samples was collected from WWTP1, but at least one toxic sample was obtained from every treatment plant.

Two effluent samples collected in winter and tested with optional tests showed various results. Samples were not toxic according *Lemna minor* and umu-test, but toxic according fish hepatocyte vitellogenin induction and EROD activity test. According egg-larvae test only one sample was toxic.

7 Conclusions

For a number of substances, COHIBA project was one of the first times to estimate the discharges to and the concentrations in the Estonian environment. The dioxins have not been measured from the waters (effluents) before. All the measured substances were found at least once from some sampling point, endosulfan and Cd being the rarest substances.

Basic parameters

In addition to the hazardous substances, there were problems with basic parameters in WWTPs. Almost all of the basic parameters exceeded the limits at some samples. The most problematic parameter was P-tot that was over the limits in all samples from three WWTPs and three times in one WWTP.

The results of all the basic parameters were over the limits at some point in the landfill leachate. Therefore it is clear that the leachate treatment system must be revised. The landfill leachate shows also very high acute toxicity and has a high direct impact on the environment. In the COHIBA study, it was found that the most toxic samples according to the obligatory toxtest results were the samples from landfill. All three tests (*Vibrio fischeri* luminescent bacteria test, *Daphnia magna* acute toxicity, Algae growth inhibition test) showed rather high toxicity for both samples.

Flow rates

It is important to consider the flow rates when assessing the amounts of hazardous substances led to the environment. High precipitation makes the flow rates also high and dilutes the water, making it difficult to detect the substances that are analysed by concentration. However, even if the substances are not detected by concentration, the amounts of hazardous substances by mass led to the environment with higher flow rates are higher than those led to the environment with lower flow rates. The hazardous substances pose risk to the environment, no matter the what the concentration is.

In Estonia, one maximum concentration of hazardous substances is given in the environmental permits for companies. This practice completely ignores the changing weather conditions and flow rates that can vary more than two-fold as seen in this study. According to those environmental permits it is possible that huge amounts of hazardous substances are led to the environment. It is of utmost importance to change this system and consider the effect of seasonal changes in flow rates in order to protect and achieve a good status for the Baltic Sea environment.

Landfill leachate

In landfill leachate, the hazardous substances that exceeded the EQS were: Hg, endosulfan, SCCP, PFOS, pentaBDEs (BDE-47, BDE-99, BDE-153, BDE-154) and from decaBDEs the congener BDE-183. PFOA and BDE-209 were also found in high concentrations, but there are no EQSs for these substances yet. Most of the measured dioxins, furans and PCB-s were present in a landfill leachate in concentrations over LOQ, no EQS or other limit values in water are set. The concentration of PCB-s (sum of 28, 52, 101, 118, 138, 153, 180 for them the sludge limit value is set) was 6,99 ng/l. The concentration of PCCD/F in landfill leachate was 1,3 WHO-TEQ 2005 pg/g (mediumbound).

HBCD was found once from the landfill leachate and the result did not exceed the EQS. As HBCD was found from all other types of samples, i.e. storm waters and WWTPs, and not found from the landfill, it can be concluded that the substance is mainly used in long-life products and this kind of products have not been dumped yet.

Wastewater treatment plants (WWTPs)

In WWTPs, Cd was found in concentrations close to the EQS, but never over the limits. MCCP and SCCP were found from all the WWTPs from all the samples, and the concentrations of SCCP exceeded the EQS in 22 samples out of 24. This might indicate that there are great problems with chloroalkanes in Estonia and that existing water treatment facilities are not able to remove those substances.

PFOS was measured from WWTP samples over the EQS in 17 samples out of 24. There is no EQS for PFOA, but the substance was found constantly in high concentrations, indicating that the substance is commonly and abundantly used all over the country and that there is a high environmental risk included. HBCD was also found from all the effluent samples and therefore the presence of this substance can be considered problematic. As the HBCD was found over the EQS also in storm water, it is clear that the substance is in common use. Therefore educating the public and finding new treatment options is highly needed.

Organotin substances were found from the effluents and sludge. TBT was found twice over the LOQ, but it must be noted that the LOQ for TBT was 1 ng/l whereas the EQS was 0,2 ng/l which means that no conclusions can be drawn if the samples were over the EQSs or not. It can be concluded, however, that organotin substances have been used in other areas than antifouling paint, as the substances were found all over. More research is definitely needed on the occurrence of organotin substances in Estonia.

Under COHIBA study, dioxins were measured from water for the first time in Estonia and the results were over the LOQ in numerous cases. According to our results, at least some further studies about the concentrations of dioxins in effluents should be considered. The effluents are led directly to the surface waters or recipient waters, affecting the water-living organisms. If the dioxins could be removed by more efficient treatment processes, the levels of dioxins in the environment, including the biota, could be reduced. It is also necessary to examine whether the dioxins in effluents originate mainly from the air or wastes, so that the cheapest and most efficient method to reduce the amount of dioxins reaching the environment could be found.

In WWTP3, the picture of phenolic substances was clearly different from other WWTPs, indicating a high impact from the industry. In WWTP3, all phenolic substances were found over the LOQ, and NP and NPEs were over the LOQ at all times. OP was over the LOQ once and OPEs over half of the times. It should also be noted that the LOQ for NP and OP is higher than the EQS, therefore all the results over the LOQ are also over the EQS. Phenolic substances were also found from the sludge of WWTP3.

In other WWTPs, phenolic substances were found quite uniformly from the effluents and sludge. NP was found to be over the LOQ in six samples out of 18. NP diethoxylates were found over LOQ in four samples; NP monoethoxylates were often detected but not measured over LOQ. OP was found to be over the LOQ three times. OPEs were rarely detected and never measured over LOQ.

In contrast, only NPs were found from the landfill samples, OPs and OPEs were sometimes detected but not measured in concentrations over the LOQ. In storm waters, phenolic substances were detected but not measured in concentrations over the LOQ.

Comparison of biotests and chemical analyses

It is not possible to compare the chemical analyses and biotests as there are many more factors that affect the organisms in biotests than hazardous substances. There is a mixture of chemicals in effluents and the interactions between them are not known yet. However, there are some correlations between biological and chemical indicators, therefore more research is needed on that subject.

WWTP1 had a worse treatment efficiency of the basic parameters and higher acute toxicity than other WWTPs. In WWTP1, the most toxic sample was from April 2010. In that sample organotin compounds were also present in very high concentrations: TBT 2,9 ng/l (EQS is 0,2 ng/l), also MBT 8,9 ng/l, DBT 7,5 ng/l and MOT 1,4 ng/l were found in that sample. Organotins were not found in those high concentrations in other sampling rounds. The CO-PCB 77 concentration was also the highest at that time and differed from other sample. As it was also the most toxic sample from WWTPs, we can assume that presence of organotins in such great concentrations was the reason for high acute toxicity in that sample. The presence of toxic compounds can also be the reason why the efficiency of the WWTP1 is not so good. Toxic effects on activated sludge and other biological treatment steps can occur and lower the substance removal processes.

In WWTP3, the acute toxicity tests showed the smallest toxicity level. However, the concentration of hazardous substances was clearly higher and somewhat different from the other WWTPs. For chronic biotests, the sample from WWTP3 was the most toxic for egg-larvae test of zebrafish. In *Lemna minor* test, the effluents from WWTP3 showed growth promotation. In conclusion – the effluents from WWTP3 clearly have an impact on the organisms, but it is difficult to see clear connections. The growth promotation can be the impact of high P-tot, although P-tot was high in other WWTPs and growth promotion was not detected in those samples. In WWTP3, the most common HSs were nonylphenols and other phenolic compounds that were not found in such high concentrations in other WWTPs. The high concentrations of phenols can also have chronic effects on organisms, but it is not possible to conclude that from our study.

It is clear that future complex studies are needed to estimate the connections between different criteria. The real environmental impact and danger may be overlooked if only a few parameters are to be estimated. Hazardous substances are well-known for their long-term impacts; therefore performing only the acute toxicity tests or chemical analyses is not enough. In COHIBA project, a complex method (WEA) for estimating the impacts of effluents was used. Generally, it showed that the impacts of different chemicals may be seen in very different tests, even if the concentrations of single substances do not exceed the standards.

Storm waters

In storm waters, Cd was found in concentrations close to the EQS. SCCP and HBCDs exceeded the EQS is storm waters. Also, a lot of perfluorinated compounds were found from storm waters, PFOS was found over the EQS and PFOA was found in high concentrations. Dioxins and PCB-s were also present in storm waters and the highest concentrations in that study were measured from storm-waters. Dioxins are washed out from the air with rainwater and end up in water environment. Higher concentration can also point to diffused sources in living areas.

The presence of hazardous substances clearly shows that additional treating facilities for storm waters are needed before those waters can be led to recipient. At this moment, some of the storm waters are led directly to the recipient, without any treatment.

In conclusion – the analyses performed under the COHIBA project gave a whole new perspective on hazardous substances in Estonia. The screening of hazardous substances under the COHIBA project was very necessary and gave new information on the presence of hazardous substances in the Estonian environment. Those results have changed the prevalent opinion that there are no problems with hazardous substances in Estonia. It is also clear that there is a great need for additional measures for treating wastewaters. On the basis of COHIBA results, it is possible to plan future studies, reduction measures and national monitoring for those selected substances.

When planning future studies, it is necessary to consider the matrices that the samples should be taken from. Some of the hazardous substances end up in sediments and sludge, therefore analysing said substances from the water may show no results, even if the substances are present in the environment and have the toxic effect. It is also of utmost importance to choose the monitoring points carefully when organising future screening rounds, as those results must be extrapolated for the whole system, such as river or lake. Monitoring of hazardous substances should be more regular as the studies have shown that these substances are present in the environment and pose a threat to the environment and people. This also means that more attention should be paid to improving the capacity of analysing hazardous substances in the Baltic Sea countries.

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Appendix A: COHIBA project partners

Finnish Environment Institute (SYKE)

Baltic Marine Environment Protection Commission (HELCOM)

Baltic Environmental Forum Latvia (BEF - LV)

Latvian Institute of Aquatic Ecology (LHEI)

Baltic Environmental Forum Estonia (BEF - EE)

Estonian Marine Institute, University of Tartu

Estonian Environmental Research Centre

Tallinn University of Technology

Municipality of Copenhagen

Copenhagen Waste Water Treatment Plants

Copenhagen Energy (KE)

Technical University of Denmark (DTU)

Baltic Environmental Forum Lithuania (BEF - LT)

Environmental Protection Agency, Ministry of Environment of Lithuania

Centre of Marine Research (CMR)

Institute for Ecology of Industrial Areas (IETU)

Swedish Environmental Research Institute (IVL)

Swedish Chemicals Agency (KEMI)

City of Stockholm, Environment and Health Administration

Federal Environment Agency (UBA)

Institute of Botany (IB)

State of Mecklenburg-Vorpommern (MV) (Ministry of Agriculture, Environment and Consumer Protection)

APPENDIX B: Sampling schedule

Monitoring point, matrix	Sampling date	Sampling method
WWTP1, waste water	07.05.2009 15.07.2009 16.09.2009 11.11.2009 14.01.2010 14.04.2010 15.06.2010 18.08.2010	24 h composite samples adjusted to the flow rate
WWTP2, waste water	07.05.2009 15.07.2009 16.09.2009 10.11.2009 13.01.2010 14.04.2010 15.06.2010 18.08.2010	24 h composite samples adjusted to the flow rate
WWTP3, waste water	12.05.2009 14.07.2009 15.09.2009 10.11.2009 12.01.2010 13.04.2010 11.06.2010 17.08.2010	24 h composite samples adjusted to the flow rate
WWTP4a, waste water	12.05.2009 15.07.2009 16.09.2009 11.11.2009 13.01.2010	24 h composite samples adjusted to the time interval
WWTP4b, waste water	13.04.2010 10.06.2010 19.08.2010	24 h composite samples adjusted to the time interval
MWWTP, sludge	14.01.2011 11.06.2011	grab samples
SW, storm water	24.03.2010 07.05.2010	grab samples; sampling was started an hour after the start of the rain
LW, landfill leachate (taken from the equalizing tank)	15.10.2009 16.06.2010 (20.09.2010)	Grab samples (additional sample was for the dioxin analyses as the bottle was broken in the laboratory)

Appendix C: Results of Waste water treatment plant 1

Basic data from the WWTPs needed for the chemical screening of effluents

Sampling date	**07.05.09**	**15.07.09**	**16.09.09**	**11.11.09**	**14.01.10**	**14.04.10**	**15.06.10**	**18.08.10**
Sampling time	5:00	5:00	5:00	9:00	---	---	---	7:00
Flow rate (m^3/d)	13500	13605	12593	22770	13328	37311	16955	11668
Number of inhabitants	92 000	92 000	92 000	92 000	92 000	92 000	92 000	92 000
BOD_7 (mg/l)	5,5	6,1	5,2	---	6,1	<3	<3	<3
COD_{Cr} (mg/l)	58	69	120	82	104	63,00	99,00	113
Suspended solids (mg/l)	2	4	24	18	19	7,00	16,00	12
Tot-P (mg P/l)	0,18	10	18	---	0,44	0,11	0,33	2,9
PO_4-P (mg P/l)	0,07	9,9	14	0,05	0,03	0,03	0,04	0,03
Tot-N (mg N/l) *(Kjeldahl)*	5,9	12	16	4,2	4,2	3,60	6,50	7,8
NH_4-N (mg N/l)	0,12	0,27	9,3	< 0,01	<0,01	0,02	<0,01	0,02
Alkalinity (mmol/l)	3,85	3,41	4,06	3,92	2,86	4,49	2,57	2,55
pH	8,13	6,95	7,31	7,71	6,97	7,01	6,33	6,87
Conductivity (µS/m)	2020	1940	2090	---	2090	1460,00	2010,00	1917
Fe (mg Fe/l)	0,10	0,11	0,67	1,3	0,41	0,09	0,17	0,2
t (^{0}C)	15	22,6	19,8	---	10,0	10,70	21,30	24,2
Sulphur (S) (mg/l) dissolved	101	102	106	35,31	110	94,00	118,00	94
TOC (mg C/l)	---	24	38	19	24	16,00	28,00	34

Biotests

Acute tests	May-09	Jul-09	Sep-09	Nov-09	Jan-10	Apr-10
luminescent bacteria	nt(80%)	Inhibition = 5,0%	Inhibition = 14,3%	nt (80%)	nt (80%)	nt (80%)
Daphnia magna, acute	no toxicity	no toxicity	Inhibition= 10%	no toxicity	no toxicity	EC50= 49.5% (24h)
algae growth inhibition.	no toxicity	EC50= 100% Inhibition =50%	EC50= 55,3% Inhibition=100 %	no toxicity	no toxicity	no toxicity

Chemical analysis

		MWWTP effluent							MWWTP Sludge	
	CAS	**Unit**	**Sep-09**	**Nov-09**	**Jan-10**	**Apr-10**	**Jun-10**	**Aug-10**	**Unit**	**Jan-10**
PBDEs										
BDE-17	147217-75-2	ng/l	nd	nd	nd	nd	nd	nd	µg/kg	nd
BDE-28	41318-75-6	ng/l	nd	nd	nd	nd	nd	nd	µg/kg	nd
BDE-47	5436-43-1	ng/l	0,23	0,08	nd	0,07	0,08	nd	µg/kg	8,65
BDE-66	189084-61-5	ng/l	nd	nd	nd	nd	0,16	nd	µg/kg	nd
BDE-85	182346-21-0	ng/l	nd	nd	nd	nd	nd	nd	µg/kg	nd
BDE-99	60348-60-9	ng/l	0,24	0,16	nd	nd	0,28	nd	µg/kg	12,08
BDE-100	189084-64-8	ng/l	0,05	nd	nd	nd	nd	nd	µg/kg	2,74
BDE-153	68631-49-2	ng/l	0,05	nd	nd	nd	nd	nd	µg/kg	3,11
BDE-154	207122-15-4	ng/l	nd	nd	nd	nd	nd	nd	µg/kg	nd
BDE-183	207122-16-5	ng/l	nd	nd	nd	nd	nd	nd	µg/kg	1,07
BDE-203		ng/l	nd	nd	nd	nd	nd	nd	µg/kg	1,18
BDE-209	1163-19-5	ng/l	1,70	0,44	2,28	0,13	0,21	0,32	µg/kg	303,6
HBCDs										
α-HBCD		ng/l	1,28	0,38	0,65	0,41	0,46	0,68	µg/kg	2,7
β-HBCD		ng/l	nd	nd	nd	0,13	nd	0,2	µg/kg	nd
γ-HBCD		ng/l	1,77	0,02	1,27	0,82	nd	0,52	µg/kg	19,8
HBCD sum			3,05	0,4	1,92	1,36	0,46	1,4		22,5
Perfluorinated substances										
perfluoro-n-hexanoic acid (PFHxA)	307-24-4	ng/l	nd	nd	nd	nd	nd	3,1	µg/kg	nd
perfluorooctane sulfonate (PFOS)	1763-23-1	ng/l	0,7	0,7	0,5	0,7	nd	0,7	µg/kg	2,2
perfluorooctanoic acid (PFOA)	335-67-1	ng/l	5,1	3,4	4,4	2,0	5,6	5,5	µg/kg	0,6

		MWWTP effluent							MWWTP Sludge	
	CAS	**Unit**	**Sep-09**	**Nov-09**	**Jan-10**	**Apr-10**	**Jun-10**	**Aug-10**	**Unit**	**Jan-10**
perfluoro-n-decanoic acid (PFDA)	335-76-2	ng/l	0,8	0,33	0,3	nd	0,3	0,7	µg/kg	2,3
Phenolic substances										
bisphenol a	80-05-7	µg/l	0,15	3,0	1,59	nd	0,64	0,33	mg/kg	nd
4-nonylphenol (mix.)	84852-15-3	µg/l	nd	0,33	0,54	0,42	nd	0,25	mg/kg	3,88
4-nonylphenol monoethoxylate (mix.)	-	µg/l	nd	nd	0,06	0,06	nd	0,06	mg/kg	nd
4-nonylphenol diethoxylate (mix.)	-	µg/l	nd	0,19	0,10	nd	0,02	0,06	mg/kg	0,10
octylphenol	140-66-9	µg/l	nd	0,21	0,07	nd	0,06	nd	mg/kg	nd
octylphenol monoethoxylate	-	µg/l	nd	nd	nd	nd	0,02	nd	mg/kg	nd
octylphenol diethoxylate	-	µg/l	nd	nd	nd	nd	nd	nd	mg/kg	nd
Chlorinated paraffins										
SCCP	85535-84-8	µg/l	0,44	2	0,99	0,81	0,64	1,67	mg/kg	10,50
MCCP		µg/l		3,93	2,72	3,21	4,80	0,73	mg/kg	1,23
Endosulfan										
α-Endosulfan	959-98-8	ng/l	<5	<5	<5	<5	<5	<5	µg/kg	<1
β-Endosulfan	33213-65-9	ng/l	<5	<5	<5	<5	<5	<5	µg/kg	<1
Endosulfan sulphate	1031-07-8	ng/l	<5	<5	<5	<5	<5	<5	µg/kg	<1
Cadmium										
	7440-43-9	µg/l	< 0,1	< 0,1	< 0,1	0,07	0,05	0,14	mg/kg	<1
Mercury										
	7439-97-6	µg/l	< 0,05	0,05	< 0,05	< 0,05	< 0,05	< 0,05	mg/kg	0,23

Organotins

		MWWTP effluent						
	CAS	**Unit**	**Sep-09**	**Nov-09**	**Jan-10**	**Apr-10**	**Jun-10**	**Aug-10**
Monobutyltin cation, MBT		ng/l	<1	3,4	4,7	8,9	<1	<1
Dibutyltin cation, DBT		ng/l	<1	<1	1	7,5	<1	<1
Tributyltin cation, TBT	3664-73-3	ng/l	<1	<1	<1	2,9	<1	<1
Tetrabutyltin, TTBT	1461-25-2	ng/l	<1	<1	5,5	<1	<1	<1
Monooctyltin cation, MOT		ng/l	<1	<1	3,5	1,4	<1	<1
Dioctyltin cation, DOT		ng/l	<1	<1	<1	<1	<1	<1
Triphenyltin cation, TPhT		ng/l	<1	<1	<1	<1	<1	<1
Tricyclohexyltin cation, TCyT		ng/l	<1	<1	<1	<1	<1	<1

	CAS	**Unit**	**Apr-10**	**Jun-10**	**Aug-10**
Dioxins					
2,3,7,8-TCDD	1746-01-6	pg/l	<0.086	<0.32	<0.30
2,3,7,8-TCDF	51207-31-9	pg/l	<0.061	<0.18	<0.030
1,2,3,7,8-PeCDD	40321-76-4	pg/l	<0.14	<0.36	<0.031
1,2,3,7,8-PeCDF	57117-41-6	pg/l	<0.040	<0.18	<0.039
2,3,4,7,8-PeCDF	57117-31-4	pg/l	<0.049	<0.20	<0.081
1,2,3,4,7,8-HxCDD	39227-28-6	pg/l	<0.20	<0.46	<0.044
1,2,3,6,7,8-HxCDD	57653-85-7	pg/l	<0.21	<0.46	<0.044
1,2,3,7,8,9-HxCDD	19408-74-3	pg/l	<0.19	<0.45	<0.042
1,2,3,4,7,8-HxCDF	70648-26-9	pg/l	<0.090	<0.23	<0.098
1,2,3,6,7,8-HxCDF	57117-44-9	pg/l	<0.077	<0.22	<0.068
1,2,3,7,8,9-HxCDF	72918-21-9	pg/l	<0.41	<0.33	<0.10

	CAS	Unit	Apr-10	Jun-10	Aug-10
2,3,4,6,7,8-HxCDF	60851-34-5	pg/l	<0.13	<0.76	<0.062
1,2,3,4,6,7,8-HpCDD	35822-46-9	pg/l	<0.28	<0.65	0,3486
1,2,3,4,6,7,8-HpCDF	67562-39-4	pg/l	<0.085	<0.30	0,1199
1,2,3,4,7,8,9-HpCDF	55673-89-7	pg/l	<0.49	<1.0	<0.047
OCDD	3268-87-9	pg/l	<0.70	<1.4	4,2626
OCDF	39001-02-0	pg/l	<1.7	<2.7	0,7774
Total TCDD	41903-57-5	pg/l	<0.086	<0.32	<0.30
Total TCDF	55722-27-5	pg/l	<0.061	<0.18	<0.030
Total PeCDD	36088-22-9	pg/l	<0.14	<0.36	<0.031
Total PeCDF	30402-15-4	pg/l	<0,089	<0,38	<0,12
Total HxCDD	34465-46-8	pg/l	<0,6	<1,37	<0,13
Total HxCDF	55684-94-1	pg/l	<0,707	<1,54	<0,328
Total HpCDD	37871-00-4	pg/l	<0.28	<0.65	0,3486
Total HpCDF	38998-75-3	pg/l	<0,575	<1,3	<0,1669
sum (pg/l)		pg/l	< 4.9	< 10	< 6.5
WHO-TEQ 2005 pg/g (upperbound)		pg/l	0,3925	1,0707	0,4174
WHO-TEQ 2005 pg/g (mediumbound)		pg/l	0,1963	0,5353	0,2118
WHO-TEQ 2005 pg/g (lowerbound)		pg/l	0,0000	0,0000	0,0062
Non-ortho PCBs i.e. co-planar PCBs					
CO-PCB-77		pg/l	5,3337	1,7621	2,1994
CO-PCB-81		pg/l	0,2495	<0.14	0,0897
CO-PCB-126		pg/l	<0.060	<0.14	<0.095
CO-PCB-169		pg/l	<0.051	<0.14	<0.068
Sum		pg/l	< 5.7	< 2.2	< 2.5
WHO-TEQ 2005 pg/l (upperbound)		pg/l	0,0081	0,0180	0,0118

	CAS	Unit	Apr-10	Jun-10	Aug-10
Other PCBs					
PCB-18		ng/l	<0.012	0,0824	0,0712
PCB-28/31		ng/l	<0.027	0,0854	0,0544
PCB-33		ng/l	<0.012	0,0348	0,0235
PCB-47		ng/l	0,2362	0,9362	0,8664
PCB-49		ng/l	<0.0075	0,0414	0,0195
PCB-51		ng/l	0,0560	0,1939	0,1887
PCB-52		ng/l	<0.025	0,0741	0,0503
PCB-60		ng/l	<0.0032	0,0041	<0.0029
PCB-66		ng/l	<0.014	0,0273	0,0192
PCB-74		ng/l	<0.0079	0,0141	0,0078
PCB-99		ng/l	0,0212	0,0319	0,0313
PCB-101		ng/l	0,0249	0,0501	0,0455
PCB-105		ng/l	0,0188	0,0154	0,0107
PCB-110		ng/l	0,0255	0,0496	0,0426
PCB-114		ng/l	<0.0027	<0.0025	<0.0005
PCB-118		ng/l	0,0460	0,0402	0,0354
PCB-122		ng/l	<0.0033	<0.0028	<0.0005
PCB-123		ng/l	<0.0022	<0.0022	<0.0004
PCB-128		ng/l	0,0092	0,0081	0,0062
PCB-138		ng/l	0,0363	0,0385	0,0370
PCB-141		ng/l	0,0103	0,0068	0,0060
PCB-153		ng/l	0,0300	0,0371	0,0502
PCB-156		ng/l	0,0096	0,0042	0,0047
PCB-157		ng/l	<0.0038	<0.0020	0,0011

	CAS	**Unit**	**Apr-10**	**Jun-10**	**Aug-10**
PCB-167		ng/l	<0.0027	<0.0022	0,0009
PCB-170		ng/l	0,0191	<0.0043	0,0142
PCB-180		ng/l	0,0294	0,0084	0,0306
PCB-183		ng/l	<0.0074	<0.0048	0,0079
PCB-187		ng/l	<0.0057	<0.0041	0,0150
PCB-189		ng/l	<0.0037	<0.0031	0,0006
PCB-194		ng/l	<0.0067	<0.0033	0,0061
PCB-206		ng/l	<0.0076	<0.0027	<0.0009
PCB-209		ng/l	<0.0056	<0.0028	<0.0005
All PCBs together (ng/l)		ng/l	< 0.74	< 1.8	< 1.7
WHO-TEQ 2005 pg/g (upperbound)		pg/l	0,0110	0,0202	0,0136
WHO-TEQ 2005 pg/g (mediumbound)		pg/l	0,0071	0,0111	0,0078
WHO-TEQ 2005 pg/g (lowerbound)		pg/l	0,0031	0,0021	0,0020

Appendix D: Results of Waste water treatment plant 2

Basic data from the WWTPs needed for the chemical screening of effluents

Sampling date	**07.05.09**	**15.07.09**	**16.09.09**	**10.11.09**	**13.01.10**	**14.04.10**	**15.06.10**	**18.08.10**
Sampling time	8:00	8:00	8:00	5:00	---	---	---	9:00
Flow rate (m^3/d)	17760	16090	27250	38282	14096	44899	20080	---
Number of inhabitants	84 600	84 600	84 600	84 600	84 600	84 600	84 600	84 600
BOD_7 (mg/l)	5,4	3,1	< 3	---	4,4	9,00	<3	<3
COD_{Cr} (mg/l)	21	25	16	37	79	32,00	27,00	38
Suspended solids (mg/l)	<2	6	9	5	5	7,00	3,00	8
Tot-P (mg P/l)	0,32	0,37	0,17	---	0,28	0,16	0,74	0,4
PO_4-P (mg P/l)	0,19	0,30	0,06	---	0,15	0,07	0,63	0,03
Tot-N (mg N/l) *(Kjeldahl)*	4	6,1	3,8	---	11	6,60	4,70	8,4
NH_4-N (mg N/l)	0,13	0,08	0,08	0,46	0,06	4,50	1,40	1,2
Alkalinity (mmol/l)	4,08	3,4	4,41	3,95	3,80	5,10	4,29	3,39
pH	7,85	7,26	8,16	7,60	7,10	7,25	6,38	7,17
Conductivity (µS/m)	816	703	794	820	1200	898,00	801,00	699
Fe (mg Fe/l)	0,10	0,08	0,12	0,14	0,26	0,10	0,18	0,55
t (^{0}C)	12,7	18,2	16,1	11,9	9,1	8,00	14,60	20
Sulphur (S) (mg/l) dissolved	23	21	20	13,86	37	25,00	21,00	21
TOC (mg C/l)	---	14	7,9	10	12	9,90	12,00	12

Biotests

Acute tests	May-09	Jul-09	Sep-09	Nov-09	Jan-10	Apr-10
luminescent bacteria	no toxicity	no toxicity	no toxicity	no toxicity	no toxicity	no toxicity
Daphnia magna, acute	no toxicity	no toxicity	no toxicity	no toxicity	no toxicity	no toxicity
algae growth inhibition.	Inhibition= 10.14%	no toxicity	no toxicity	EC50=69.63% Inhibition= 59.52%	no toxicity	no toxicity

Chemical analysis

	CAS	Unit	Sep-09	Nov-09	Jan-10	Apr-10	Jun-10	Aug-10
PBDEs								
BDE-17	147217-75-2	ng/l	nd	nd	nd	nd	nd	nd
BDE-28	41318-75-6	ng/l	nd	nd	nd	nd	nd	nd
BDE-47	5436-43-1	ng/l	0,03	0,07	nd	0,08	0,08	nd
BDE-66	189084-61-5	ng/l	nd	nd	nd	nd	0,18	nd
BDE-85	182346-21-0	ng/l	nd	nd	nd	nd	nd	nd
BDE-99	60348-60-9	ng/l	0,05	0,15	nd	nd	0,32	nd
BDE-100	189084-64-8	ng/l	nd	nd	nd	nd	nd	nd
BDE-153	68631-49-2	ng/l	nd	nd	nd	nd	nd	nd
BDE-154	207122-15-4	ng/l	nd	nd	nd	nd	nd	nd
BDE-183	207122-16-5	ng/l	nd	nd	nd	nd	nd	nd
BDE-203		ng/l	nd	nd	nd	nd	nd	nd
BDE-209	1163-19-5	ng/l	0,21	0,81	2,16	0,17	1,63	0,36

	CAS	Unit	Sep-09	Nov-09	Jan-10	Apr-10	Jun-10	Aug-10
HBCDs								
α-HBCD		ng/l	0,27	0,02	0,42	0,61	0,45	0,71
β-HBCD		ng/l	nd	nd	0,67	0,33	0,54	nd
γ-HBCD		ng/l	0,39	nd	2,23	1,08	2,51	nd
HBCD sum			0,66	0,02	3,32	2,02	3,5	0,71
Perfluorinated substances								
perfluoro-n-hexanoic acid (PFHxA)	307-24-4	ng/l	0,45	1,2	0,8	0,1	0,2	1,5
perfluorooctane sulfonate (PFOS)	1763-23-1	ng/l	0,13	0,9	1,1	1,0	nd	0,9
perfluorooctanoic acid (PFOA)	335-67-1	ng/l	3,1	8,6	12	2,0	1,6	5,7
perfluoro-n-decanoic acid (PFDA)	335-76-2	ng/l	nd	2,1	4,2	nd	nd	0,8
Phenolic substances								
bisphenol a	80-05-7	µg/l	nd	0,26	nd	0,18	5,79	2,12
4-nonylphenol (mix.)	84852-15-3	µg/l	0,52	0,20	0,29	0,23	0,24	0,25
4-nonylphenol monoethoxylate (mix.)	-	µg/l	nd	0,08	0,05	0,10	0,09	0,04
4-nonylphenol diethoxylate (mix.)	-	µg/l	nd	0,04	0,02	0,04	0,03	0,02
octylphenol	140-66-9	µg/l	nd	0,26	0,11	0,07	nd	0,07
octylphenol monoethoxylate	-	µg/l	nd	nd	nd	nd	0,02	nd
octylphenol diethoxylate	-	µg/l	nd	nd	nd	nd	nd	nd
Organotins								
Monobutyltin cation, MBT		ng/l	<1	<1	3,3	5	2,6	<1
Dibutyltin cation, DBT		ng/l	<1	<1	1,1	1,4	1,2	<1
Tributyltin cation, TBT		ng/l	<1	<1	<1	2,2	<1	<1
Tetrabutyltin, TTBT		ng/l	<1	<1	<1	<1	<1	<1
Monooctyltin cation, MOT		ng/l	<1	<1	<1	<1	3,7	<1
Dioctyltin cation, DOT		ng/l	<1	<1	<1	<1	1,3	<1

	CAS	**Unit**	**Sep-09**	**Nov-09**	**Jan-10**	**Apr-10**	**Jun-10**	**Aug-10**
Triphenyltin cation, TPhT		ng/l	<1	<1	<1	<1	<1	<1
Tricyclohexyltin cation, TCyT		ng/l	<1	<1	<1	<1	<1	<1
Chlorinated paraffins								
SCCP	85535-84-8	µg/l	0,38	1,32	0,78	1,57	1,14	1,98
MCCP		µg/l		1,11	2,20	4,84	1,26	2,29
Endosulfan								
α-Endosulfan	959-98-8	ng/l	<5	<5	<5	<5	<5	<5
β-Endosulfan	33213-65-9	ng/l	<5	<5	<5	<5	<5	<5
Endosulfan sulphate	1031-07-8	ng/l	<5	<5	<5	<5	<5	<5
Cadmium								
	7440-43-9	µg/l	< 0,1	0,14	< 0,1	0,07	<0,02	<0,02
Mercury								
	7439-97-6	µg/l	< 0,05	0,05	< 0,05	< 0,05	< 0,05	< 0,05

	CAS	**Unit**	**Apr-10**	**Jun-10**	**Aug-10**
Dioxins					
2,3,7,8-TCDD	1746-01-6	pg/l	<0.086	<0.32	<0.30
2,3,7,8-TCDF	51207-31-9	pg/l	<0.061	<0.18	<0.030
1,2,3,7,8-PeCDD	40321-76-4	pg/l	<0.14	<0.36	<0.031
1,2,3,7,8-PeCDF	57117-41-6	pg/l	<0.040	<0.18	<0.039
2,3,4,7,8-PeCDF	57117-31-4	pg/l	<0.049	<0.20	<0.081
1,2,3,4,7,8-HxCDD	39227-28-6	pg/l	<0.20	<0.46	<0.044
1,2,3,6,7,8-HxCDD	57653-85-7	pg/l	<0.21	<0.46	<0.044
1,2,3,7,8,9-HxCDD	19408-74-3	pg/l	<0.19	<0.45	<0.042
1,2,3,4,7,8-HxCDF	70648-26-9	pg/l	<0.090	<0.23	<0.098

	CAS	Unit	Apr-10	Jun-10	Aug-10
1,2,3,6,7,8-HxCDF	57117-44-9	pg/l	<0.077	<0.22	<0.068
1,2,3,7,8,9-HxCDF	72918-21-9	pg/l	<0.41	<0.33	<0.10
2,3,4,6,7,8-HxCDF	60851-34-5	pg/l	<0.13	<0.76	<0.062
1,2,3,4,6,7,8-HpCDD	35822-46-9	pg/l	<0.28	<0.65	0.3486
1,2,3,4,6,7,8-HpCDF	67562-39-4	pg/l	<0.085	<0.30	0.1199
1,2,3,4,7,8,9-HpCDF	55673-89-7	pg/l	<0.49	<1.0	<0.047
OCDD	3268-87-9	pg/l	<0.70	<1.4	4.2626
OCDF	39001-02-0	pg/l	<1.7	<2.7	0.7774
Total TCDD	41903-57-5	pg/l	<0.086	<0.32	<0.30
Total TCDF	55722-27-5	pg/l	<0.061	<0.18	<0.030
Total PeCDD	36088-22-9	pg/l	<0.14	<0.36	<0.031
Total PeCDF	30402-15-4	pg/l	<0,089	<0,38	<0,12
Total HxCDD	34465-46-8	pg/l	<0,6	<1,37	<0,13
Total HxCDF	55684-94-1	pg/l	<0,707	<1,54	<0,328
Total HpCDD	37871-00-4	pg/l	<0.28	<0.65	0.3486
Total HpCDF	38998-75-3	pg/l	<0,575	<1,3	<0,1669
sum (pg/l)		pg/l	< 4.9	< 10	< 6.5
WHO-TEQ 2005 pg/g (upperbound)		pg/l	0.3925	1.0707	0.4174
WHO-TEQ 2005 pg/g (mediumbound)		pg/l	0.1963	0.5353	0.2118
WHO-TEQ 2005 pg/g (lowerbound)		pg/l	0.0000	0.0000	0.0062
Non-ortho PCBs i.e. co-planar PCBs					
CO-PCB-77		pg/l	5.3337	1.7621	2.1994
CO-PCB-81		pg/l	0.2495	<0.14	0.0897
CO-PCB-126		pg/l	<0.060	<0.14	<0.095
CO-PCB-169		pg/l	<0.051	<0.14	<0.068

	CAS	Unit	Apr-10	Jun-10	Aug-10
Sum		pg/l	< 5.7	< 2.2	< 2.5
WHO-TEQ 2005 pg/l (upperbound)		pg/l	0.0081	0.0180	0.0118
Other PCBs					
PCB-18		ng/l	<0.012	0.0824	0.0712
PCB-28/31		ng/l	<0.027	0.0854	0.0544
PCB-33		ng/l	<0.012	0.0348	0.0235
PCB-47		ng/l	0.2362	0.9362	0.8664
PCB-49		ng/l	<0.0075	0.0414	0.0195
PCB-51		ng/l	0.0560	0.1939	0.1887
PCB-52		ng/l	<0.025	0.0741	0.0503
PCB-60		ng/l	<0.0032	0.0041	<0.0029
PCB-66		ng/l	<0.014	0.0273	0.0192
PCB-74		ng/l	<0.0079	0.0141	0.0078
PCB-99		ng/l	0.0212	0.0319	0.0313
PCB-101		ng/l	0.0249	0.0501	0.0455
PCB-105		ng/l	0.0188	0.0154	0.0107
PCB-110		ng/l	0.0255	0.0496	0.0426
PCB-114		ng/l	<0.0027	<0.0025	<0.0005
PCB-118		ng/l	0.0460	0.0402	0.0354
PCB-122		ng/l	<0.0033	<0.0028	<0.0005
PCB-123		ng/l	<0.0022	<0.0022	<0.0004
PCB-128		ng/l	0.0092	0.0081	0.0062
PCB-138		ng/l	0.0363	0.0385	0.0370
PCB-141		ng/l	0.0103	0.0068	0.0060
PCB-153		ng/l	0.0300	0.0371	0.0502

	CAS	Unit	Apr-10	Jun-10	Aug-10
PCB-156		ng/l	0.0096	0.0042	0.0047
PCB-157		ng/l	<0.0038	<0.0020	0.0011
PCB-167		ng/l	<0.0027	<0.0022	0.0009
PCB-170		ng/l	0.0191	<0.0043	0.0142
PCB-180		ng/l	0.0294	0.0084	0.0306
PCB-183		ng/l	<0.0074	<0.0048	0.0079
PCB-187		ng/l	<0.0057	<0.0041	0.0150
PCB-189		ng/l	<0.0037	<0.0031	0.0006
PCB-194		ng/l	<0.0067	<0.0033	0.0061
PCB-206		ng/l	<0.0076	<0.0027	<0.0009
PCB-209		ng/l	<0.0056	<0.0028	<0.0005
All PCBs together (ng/l)		ng/l	< 0.74	< 1.8	< 1.7
WHO-TEQ 2005 pg/g (upperbound)		pg/l	0.0110	0.0202	0.0136
WHO-TEQ 2005 pg/g (mediumbound)		pg/l	0.0071	0.0111	0.0078
WHO-TEQ 2005 pg/g (lowerbound)		pg/l	0.0031	0.0021	0.0020

Appendix E: Results of Waste water treatment plant 3

Basic data from the WWTPs needed for the chemical screening of effluents

Sampling date	**12.05.09**	**14.07.09**	**15.09.09**	**10.11.09**	**12.01.10**	**13.04.10**	**11.06.10**	**17.08.10**
Sampling time	**15:30**	**15:00**	**15:00**	**14:00**	**---**	**---**	**---**	**11:00**
Flow rate (m^3/d)	1170	2800	1077	1657	975	3532	1325	1249
Number of inhabitants	9000	9000	9000	9000	9000	9000	9000	9000
BOD_7 (mg/l)	17	31	<3	---	7,6	8,30	3,50	<3
COD_{Cr} (mg/l)	53	41	16	21	48	37,00	48,00	14
Suspended solids (mg/l)	14	5	<2	4	6	4,00	8,00	4
Tot-P (mgP/l)	0,41	1,2	0,52	0,72	0,60	0,10	0,14	0,2
PO_4-P (mgP/l)	0,14	1,0	0,40	0,56	0,44	0,02	0,02	<0,02
Tot-N (mg N/l) *(Kjeldahl)*	36	16	8,3	11	35	19,00	41,00	9,8
NH_4-N (mg N/l)	32	7,7	1,3	0,42	25	15,00	40,00	0,7
Alkalinity (mmol/l)	7,62	4,84	3,76	4,10	5,13	5,57	6,84	3,76
pH	7,96	7,61	7,55	7,46	7,75	7,30	7,16	6,99
Conductivity (μS/m)	309	2990	2430	1392	2120	1766,00	2630,00	2470
Fe (mg Fe/l)	0,25	0,18	0,14	0,09	0,16	0,05	0,08	0,05
t (^{0}C)	12	20	16,6	12,1	8,8	15,10	19,90	20,07
Sulphur (S) (mg/l) dissolved	52	78	51	37	48	36,00	55,00	49
TOC (mg C/l)	130	11	8,8	8,6	15	11,00	14,00	10

Biotests

Acute tests	May-09	Jul-09	Sep-09	Nov-09	Jan-10	Apr-10
luminescent bacteria	no toxicity	no toxicity	no toxicity	no toxicity	no toxicity	no toxicity
Daphnia magna, acute	no toxicity	no toxicity	no toxicity	no toxicity	NA	no toxicity
algae growth inhibition.	Inhibition= 43.17%	no toxicity	Inhibition= 4.66%	no toxicity	NA	Inhibition= 10%

Chemical analysis

		MWWTP effluents							MWWTP Sludge		
	CAS	Unit	Sep-09	Nov-09	Jan-10	Apr-10	Jun-10	Aug-10	Unit	Jan-10	Jun-10
PBDEs											
BDE-17	147217-75-2	ng/l	nd	nd	nd	nd	nd	nd	µg/kg	0.35	nd
BDE-28	41318-75-6	ng/l	nd	nd	nd	nd	nd	nd	µg/kg	0.66	nd
BDE-47	5436-43-1	ng/l	0.03	0.08	nd	0.08	0.08	0.23	µg/kg	11.03	10.8
BDE-66	189084-61-5	ng/l	nd	0.08	nd	nd	nd	nd	µg/kg	nd	0.87
BDE-85	182346-21-0	ng/l	nd	nd	nd	nd	nd	nd	µg/kg	nd	nd
BDE-99	60348-60-9	ng/l	nd	0.16	nd	nd	0.31	nd	µg/kg	12.95	12.0
BDE-100	189084-64-8	ng/l	nd	nd	nd	nd	nd	nd	µg/kg	2.61	1.9
BDE-153	68631-49-2	ng/l	nd	nd	nd	nd	nd	nd	µg/kg	2.61	2.3
BDE-154	207122-15-4	ng/l	nd	nd	nd	nd	nd	nd	µg/kg	nd	nd
BDE-183	207122-16-5	ng/l	nd	nd	nd	nd	nd	nd	µg/kg	0.92	0.98
BDE-203		ng/l	nd	nd	nd	nd	nd	nd	µg/kg	1	1.1
BDE-209	1163-19-5	ng/l	0.23	1.21	2.42	0.17	1.31	0.26	µg/kg	1183	1010
HBCDs											
α-HBCD		ng/l	0.34	0.14	0.28	0.63	0.39	0.58	µg/kg	33.1	96.7
β-HBCD		ng/l	nd	nd	nd	0.23	0.22	0.29	µg/kg	14	nd

		MWWTP effluents							MWWTP Sludge		
	CAS	**Unit**	**Sep-09**	**Nov-09**	**Jan-10**	**Apr-10**	**Jun-10**	**Aug-10**	**Unit**	**Jan-10**	**Jun-10**
γ-HBCD		ng/l	nd	0.03	0.5	1.53	nd	0.48	µg/kg	74.8	86.2
HBCD sum			0.34	0.17	0.78	2.39	0.61	1.35		121.9	182.9
Perfluorinated substances											
perfluoro-n-hexanoic acid (PFHxA)	307-24-4	ng/l	1.8	0.7	0.7	0.6	0.9	1.5	µg/kg	0.1	0.2
perfluorooctane sulfonate (PFOS)	1763-23-1	ng/l	0.7	0.6	0.7	2.3	1.0	1.2	µg/kg	2.4	3.0
perfluorooctanoic acid (PFOA)	335-67-1	ng/l	14	3.7	3.5	3.2	3.9	5.0	µg/kg	0.7	0.4
perfluoro-n-decanoic acid (PFDA)	335-76-2	ng/l	0.42	0.30	0.2	nd	nd	0.3	µg/kg	2.7	2.4
Phenolic substances											
bisphenol a	80-05-7	µg/l	nd	0.19	nd	0.11	1.08	0.28	mg/kg	nd	nd
4-nonylphenol (mix.)	84852-15-3	µg/l	0.75	0.47	1.75	2.62	0.64	1.12	mg/kg	24.2	2.01
4-nonylphenol monoethoxylate (mix.)	-	µg/l	0.73	0.55	5.89	6.43	0.38	0.85	mg/kg	31.1	7.53
4-nonylphenol diethoxylate (mix.)	-	µg/l	0.61	0.85	6.96	6.78	1.18	1.35	mg/kg	26.4	13.88
octylphenol	140-66-9	µg/l	0.15	0.22	0.14	0.13	0.06	nd	mg/kg	0.77	0.12
octylphenol monoethoxylate	-	µg/l	0.14	0.08	1.29	0.08	0.05	nd	mg/kg	5.08	0.09
octylphenol diethoxylate	-	µg/l	0.12	0.23	3.62	0.07	0.03	nd	mg/kg	9.64	0.07
Chlorinated paraffins											
SCCP	85535-84-8	µg/l	2.94	1.06	0.74	0.48	1.59	0.56	mg/kg	6.37	5.99
MCCP		µg/l		3.01	1.02	2.14	1.04	1.00	mg/kg	0.03	2.27
Endosulfan											
α-Endosulfan	959-98-8	ng/l	<5	<5	<5	<5	<5	<5	µg/kg	<1	<1
β-Endosulfan	33213-65-9	ng/l	<5	<5	<5	<5	<5	<5	µg/kg	<1	1.3
Endosulfan sulphate	1031-07-8	ng/l	<5	<5	<5	<5	<5	<5	µg/kg	<1	<1
Cadmium											
	7440-43-9	µg/l	< 0,1	< 0,1	< 0,1	0.04	0.03	0.06	mg/kg	<1	<1

		MWWTP effluents							MWWTP Sludge		
	CAS	**Unit**	**Sep-09**	**Nov-09**	**Jan-10**	**Apr-10**	**Jun-10**	**Aug-10**	**Unit**	**Jan-10**	**Jun-10**
Mercury											
	7439-97-6	µg/l	< 0,05	0.05	< 0,05	< 0,05	< 0,05	< 0,05	mg/kg	0.5	0.44

		MWWTP effluents							MWWTP Sludge		
	CAS	**Unit**	**Sep-09**	**Nov-09**	**Jan-10**	**Apr-10**	**Jun-10**	**Aug-10**	**Unit**	**Jan-10**	**Jun-10**
Organotins											
Monobutyltin cation, MBT		ng/l	<1	1.4	9.5	10	8.3	1.8	µg/kg	420	
Dibutyltin cation, DBT		ng/l	<1	<1	5.6	2.1	1.4	<1	µg/kg	230	
Tributyltin cation, TBT		ng/l	<1	<1	<1	<1	<1	<1	µg/kg	4.1	
Tetrabutyltin, TTBT		ng/l	<1	<1	<1	13	<1	<1	µg/kg	-	
Monooctyltin cation, MOT		ng/l	<1	<1	5.3	8.5	6.2	<1	µg/kg	83	
Dioctyltin cation, DOT		ng/l	<1	<1	<1	<1	<1	<1	µg/kg	33	
Triphenyltin cation, TPhT		ng/l	<1	<1	<1	<1	<1	<1	µg/kg	<5	
Tricyclohexyltin cation, TCyT		ng/l	<1	<1	<1	<1	<1	<1	µg/kg	-	

		MWWTP effluents			
	CAS	**Unit**	**Sep-09**	**Nov-09**	**Jan-10**
Dioxins					
2,3,7,8-TCDD	1746-01-6	pg/l	<0.088	<0.20	<0.30
2,3,7,8-TCDF	51207-31-9	pg/l	<0.054	<0.13	<0.030
1,2,3,7,8-PeCDD	40321-76-4	pg/l	<0.15	<0.40	<0.23
1,2,3,7,8-PeCDF	57117-41-6	pg/l	<0.047	<0.12	<0.039
2,3,4,7,8-PeCDF	57117-31-4	pg/l	<0.043	<0.17	<0.081
1,2,3,4,7,8-HxCDD	39227-28-6	pg/l	<0.21	<0.36	<0.050
1,2,3,6,7,8-HxCDD	57653-85-7	pg/l	<0.21	<0.35	<0.13
1,2,3,7,8,9-HxCDD	19408-74-3	pg/l	<0.20	<0.35	<0.024
1,2,3,4,7,8-HxCDF	70648-26-9	pg/l	<0.071	<0.17	<0.098
1,2,3,6,7,8-HxCDF	57117-44-9	pg/l	<0.061	<0.15	<0.068
1,2,3,7,8,9-HxCDF	72918-21-9	pg/l	<0.25	<0.22	<0.10
2,3,4,6,7,8-HxCDF	60851-34-5	pg/l	<0.093	<0.51	<0.11
1,2,3,4,6,7,8-HpCDD	35822-46-9	pg/l	<0.25	<0.47	<0.11
1,2,3,4,6,7,8-HpCDF	67562-39-4	pg/l	<0.10	<0.22	<0.11
1,2,3,4,7,8,9-HpCDF	55673-89-7	pg/l	<0.51	<0.88	<0.18
OCDD	3268-87-9	pg/l	0.8027	<0.96	0.5838
OCDF	39001-02-0	pg/l	<1.6	<2.4	0.2611
Total TCDD	41903-57-5	pg/l	<0.088	<0.20	<0.30
Total TCDF	55722-27-5	pg/l	<0.054	<0.13	<0.030
Total PeCDD	36088-22-9	pg/l	<0.15	<0.40	<0.23
Total PeCDF	30402-15-4	pg/l	<0,09	<0,29	<0,12
Total HxCDD	34465-46-8	pg/l	<0,62	<1,06	<0,204

		MWWTP effluents			
	CAS	**Unit**	**Sep-09**	**Nov-09**	**Jan-10**
Total HxCDF	55684-94-1	pg/l	<0,475	<1,05	<0,376
Total HpCDD	37871-00-4	pg/l	<0.25	<0.47	<0.11
Total HpCDF	38998-75-3	pg/l	<0,61	<1,1	<0,29
sum (pg/l)		pg/l	< 4.7	< 8.1	< 2.5
WHO-TEQ 2005 pg/g (upperbound)		pg/l	0.3732	0.9013	0.6229
WHO-TEQ 2005 pg/g (mediumbound)		pg/l	0.1867	0.4507	0.3116
WHO-TEQ 2005 pg/g (lowerbound)		pg/l	0.0002	0.0000	0.0003
Non-ortho PCBs i.e. co-planar PCBs					
CO-PCB-77		pg/l	0.9554	< 8.1	1.4239
CO-PCB-81		pg/l	0.1642	0.9013	0.0789
CO-PCB-126		pg/l	<0.059	0.4507	<0.095
CO-PCB-169		pg/l	<0.15	0.0000	<0.068
Sum		pg/l	< 1.3	< 0.93	< 1.7
WHO-TEQ 2005 pg/l (upperbound)		pg/l	0.0104	0.0138	0.0118
Other PCBs					
PCB-18		ng/l	0.0458	0.0378	0.0391
PCB-28/31		ng/l	0.0423	0.0715	0.0571
PCB-33		ng/l	0.0150	0.0209	0.0094
PCB-47		ng/l	0.0753	<0.054	0.1074
PCB-49		ng/l	0.0267	0.0172	0.0089
PCB-51		ng/l	0.0188	0.0124	0.0139
PCB-52		ng/l	0.0593	0.0365	0.0245
PCB-60		ng/l	0.0034	0.0035	<0.0029
PCB-66		ng/l	0.0153	0.0151	0.0110

		MWWTP effluents			
	CAS	**Unit**	**Sep-09**	**Nov-09**	**Jan-10**
PCB-74		ng/l	0.0103	0.0095	0.0078
PCB-99		ng/l	0.0149	0.0112	<0.0094
PCB-101		ng/l	0.0396	0.0285	<0.023
PCB-105		ng/l	0.0089	0.0063	<0.0087
PCB-110		ng/l	0.0231	0.0244	<0.024
PCB-114		ng/l	<0.0027	<0.0026	<0.0005
PCB-118		ng/l	0.0301	0.0220	<0.022
PCB-122		ng/l	<0.0033	<0.0030	<0.0005
PCB-123		ng/l	<0.0024	<0.0024	<0.0005
PCB-128		ng/l	0.0073	0.0109	<0.0045
PCB-138		ng/l	0.0360	0.0701	<0.021
PCB-141		ng/l	0.0098	0.0186	0.0044
PCB-153		ng/l	0.0356	0.0741	0.0259
PCB-156		ng/l	0.0053	0.0136	<0.0023
PCB-157		ng/l	<0.0034	<0.0019	0.0007
PCB-167		ng/l	<0.0022	<0.0014	<0.0006
PCB-170		ng/l	0.0148	0.0473	0.0073
PCB-180		ng/l	0.0291	0.0776	0.0139
PCB-183		ng/l	0.0104	0.0116	0.0051
PCB-187		ng/l	0.0111	0.0167	0.0079
PCB-189		ng/l	<0.0040	<0.0035	<0.0004
PCB-194		ng/l	<0.0050	0.0124	<0.0012
PCB-206		ng/l	<0.0062	<0.0027	<0.0008
PCB-209		ng/l	<0.0040	<0.0020	<0.0005

		MWWTP effluents			
	CAS	**Unit**	**Sep-09**	**Nov-09**	**Jan-10**
All PCBs together (ng/l)		ng/l	< 0.62	< 0.74	< 0.47
WHO-TEQ 2005 pg/g (upperbound)		pg/l	0.0123	0.0158	0.0129
WHO-TEQ 2005 pg/g (mediumbound)		pg/l	0.0069	0.0088	0.0065
WHO-TEQ 2005 pg/g (lowerbound)		pg/l	0.0016	0.0017	0.0002

Additional findings from Keila sludge in June

Substance	Concentration	Unit
endrin	4.9	µg/kg
heptachlor exoepoxid	1.0	µg/kg
heptachlor endoepoxid	5.5	µg/kg
CB-118	2.3	µg/kg
CB-28	1.1	µg/kg
CB-52	2.1	µg/kg
CB-101	4.8	µg/kg
CB-153	5.9	µg/kg
CB-138	6.0	µg/kg
CB-180	3.1	µg/kg
dieldrin	2.6	µg/kg
p,p'-DDE	14.53	µg/kg
p,p'-DDT	4.7	µg/kg

Appendix F: Results of Waste water treatment plant 4a

Basic data from the WWTPs needed for the chemical screening of effluents

Sampling date	**12.05.09**	**15.07.09**	**16.09.09**	**11.11.09**	**13.01.10**
Sampling time	11:30	11:30	11:30	16:00	---
Flow rate (m^3/d)	750	800	1080	875	800
Number of inhabitants	2000	2000	2000	2000	2000
BOD_7 (mg/l)	3,8	7,8	< 3	---	3,2
COD_{Cr} (mg/l)	21	30	16	37	34
Suspended solids (mg/l)	5	<2	10	4	8
Tot-P (mgP/l)	1,5	2,9	5,2	2,8	3,3
PO_4-P (mgP/l)	1,3	2,7	4,5	2,4	3,0
Tot-N (mg N/l) *(Kjeldahl)*	15	18	17	11	17
NH_4-N (mg N/l)	0,06	8,5	3,5	0,50	0,40
Alkalinity (mmol/l)	2,88	3,48	2,74	3,10	2,58
pH	7,66	7,23	7,60	7,82	7,20
Conductivity (µS/m)	735	680	758	---	671
Fe (mg Fe/l)	0,21	0,2	0,30	0,40	0,52
t (^{0}C)	10,6	17,3	16,1	---	6,2
Sulphur (S) (mg/l) dissolved	18	16	18	7,59	19
TOC (mg C/l)	115	11	13	11	10

Biotests

Acute tests	May-09	Jul-09	Sep-09	Nov-09
luminescent bacteria	no toxicity	Inhibition= 1.5%	no toxicity	no toxicity
Daphnia magna, acute	no toxicity	no toxicity	no toxicity	no toxicity
algae growth inhibition.	no toxicity	no toxicity	Inhibition= 10.89%	Inhibition= 14.49%

Chemical analysis

	CAS	Unit	Sep-09	Nov-09	Jan-10
PBDEs					
BDE-17	147217-75-2	ng/l	nd	nd	nd
BDE-28	41318-75-6	ng/l	nd	nd	nd
BDE-47	5436-43-1	ng/l	0.03	0.06	nd
BDE-66	189084-61-5	ng/l	nd	nd	nd
BDE-85	182346-21-0	ng/l	nd	nd	nd
BDE-99	60348-60-9	ng/l	0.05	0.14	nd
BDE-100	189084-64-8	ng/l	nd	nd	nd
BDE-153	68631-49-2	ng/l	nd	nd	nd
BDE-154	207122-15-4	ng/l	nd	nd	nd
BDE-183	207122-16-5	ng/l	nd	nd	nd
BDE-203		ng/l	nd	nd	nd
BDE-209	1163-19-5	ng/l	0.20	0.37	2.76
HBCDs					
α-HBCD		ng/l	0.56	nd	0.27
β-HBCD		ng/l	nd	nd	nd
γ-HBCD		ng/l	0.67	0.04	0.89

	CAS	Unit	Sep-09	Nov-09	Jan-10
	sum		1.23	0.04	1.16
Perfluorinated substances					
perfluoro-n-hexanoic acid (PFHxA)	307-24-4	ng/l	1	0.4	0.7
perfluorooctane sulfonate (PFOS)	1763-23-1	ng/l	0.6	1.2	1.0
perfluorooctanoic acid (PFOA)	335-67-1	ng/l	5.4	2.3	4.0
perfluoro-n-decanoic acid (PFDA)	335-76-2	ng/l	0.2	0.3	0.2
Phenolic substances					
bisphenol a	80-05-7	µg/l	nd	0.11	nd
4-nonylphenol (mix.)	84852-15-3	µg/l	0.22	0.26	0.38
4-nonylphenol monoethoxylate (mix.)	-	µg/l	0.05	nd	nd
4-nonylphenol diethoxylate (mix.)	-	µg/l	nd	0.02	nd
octylphenol	140-66-9	µg/l	nd	nd	0.20
octylphenol monoethoxylate	-	µg/l	0.03	nd	nd
octylphenol diethoxylate	-	µg/l	nd	nd	nd
Organotins					
Monobutyltin cation, MBT		ng/l	<1	2.3	<1
Dibutyltin cation, DBT		ng/l	<1	<1	<1
Tributyltin cation, TBT		ng/l	<1	<1	<1
Tetrabutyltin, TTBT		ng/l	<1	<1	<1
Monooctyltin cation, MOT		ng/l	<1	<1	<1
Dioctyltin cation, DOT		ng/l	<1	<1	<1
Triphenyltin cation, TPhT		ng/l	<1	<1	<1
Tricyclohexyltin cation, TCyT		ng/l	<1	<1	<1
Chlorinated paraffins					
SCCP	85535-84-8	µg/l	0.50	0.64	0.32

	CAS	**Unit**	**Sep-09**	**Nov-09**	**Jan-10**
MCCP	85535-84-9	µg/l		2.22	5.86
Endosulfan					
α-Endosulfan	959-98-8	ng/l	<5	<5	<5
β-Endosulfan	33213-65-9	ng/l	<5	<5	<5
Endosulfan sulphate	1031-07-8	ng/l	<5	<5	<5
Cadmium					
	7440-43-9	µg/l	< 0,1	< 0,1	< 0,1
Mercury					
	7439-97-6	µg/l	< 0,05	< 0,05	< 0,05

Appendix G: Results of Waste water treatment plant 4b

Basic data from the WWTPs needed for the chemical screening of effluents

Sampling date	**12.-13.04.10**	**09.-10.06.10**	**18.-19.08.10**
Sampling time			15:30
Flow rate (m^3/d)	2558	1210	1556
Number of inhabitants	8000	8000	8000
BOD_7 (mg/l)	3,90	5,20	<3
COD_{Cr} (mg/l)	47,00	56,00	32
Suspended solids (mg/l)	3,00	12,00	7
Tot-P (mgP/l)	1,60	3,00	1,9
PO_4-P (mgP/l)	1,50	2,80	0,03
Tot-N (mg N/l) *(Kjeldahl)*	27,00	37,00	38
NH_4-N (mg N/l)	20,00	36,00	32
Alkalinity (mmol/l)	5,25	6,10	5,72
pH	7,40	7,58	7,56
Conductivity (µS/m)	1573,00	1724,00	1659
Fe (mg Fe/l)	0,12	0,11	0,15
t (^{0}C)	9,50	17,10	18,5
Sulphur (S) (mg/l) dissolved	43,00	29,00	27
TOC (mg C/l)	13,00	16,00	11

Biotests

Acute tests	**Jan-10**	**Apr-10**	**Jun-10**
luminescent bacteria	no toxicity	no toxicity	no toxicity
Daphnia magna, acute	NA	no toxicity	no toxicity
algae growth inhibition.	NA	no toxicity	ErC50= 53,28

Chemical analysis

	CAS	**Unit**	**Apr-10**	**Jun-10**	**Aug-10**
PBDEs					
BDE-17	147217-75-2	ng/l	nd	nd	nd
BDE-28	41318-75-6	ng/l	nd	nd	nd
BDE-47	5436-43-1	ng/l	0.09	0.08	nd
BDE-66	189084-61-5	ng/l	0.09	nd	nd
BDE-85	182346-21-0	ng/l	nd	nd	nd
BDE-99	60348-60-9	ng/l	0.18	0.27	nd
BDE-100	189084-64-8	ng/l	nd	nd	nd
BDE-153	68631-49-2	ng/l	nd	nd	nd
BDE-154	207122-15-4	ng/l	nd	nd	nd
BDE-183	207122-16-5	ng/l	nd	nd	nd
BDE-203		ng/l	nd	nd	nd
BDE-209	1163-19-5	ng/l	0.24	0.76	0.46
HBCDs					
α-HBCD		ng/l	0.69	0.71	0.49
β-HBCD		ng/l	0.42	0.41	nd

	CAS	Unit	Apr-10	Jun-10	Aug-10
γ-HBCD		ng/l	1.33	1.64	0.27
HBCD sum			2.44	2.76	0.76
Perfluorinated substances					
perfluoro-n-hexanoic acid (PFHxA)	307-24-4	ng/l	0.4	0.2	0.8
perfluorooctane sulfonate (PFOS)	1763-23-1	ng/l	1.3	nd	0.5
perfluorooctanoic acid (PFOA)	335-67-1	ng/l	1.8	1.0	2.1
perfluoro-n-decanoic acid (PFDA)	335-76-2	ng/l	nd	nd	0.2
Phenolic substances					
bisphenol a	80-05-7	µg/l	0.18	1.64	0.31
4-nonylphenol (mix.)	84852-15-3	µg/l	0.73	0.15	0.34
4-nonylphenol monoethoxylate (mix.)	-	µg/l	0.15	0.12	0.15
4-nonylphenol diethoxylate (mix.)	-	µg/l	0.20	0.05	0.07
octylphenol	140-66-9	µg/l	0.06	nd	0.13
octylphenol monoethoxylate	-	µg/l	nd	0.03	nd
octylphenol diethoxylate	-	µg/l	nd	nd	nd

Dioxins					
2,3,7,8-TCDD	1746-01-6	pg/l	<0.088	<0.11	<0.30
2,3,7,8-TCDF	51207-31-9	pg/l	<0.056	<0.048	<0.030
1,2,3,7,8-PeCDD	40321-76-4	pg/l	<0.14	<0.13	<0.059
1,2,3,7,8-PeCDF	57117-41-6	pg/l	<0.046	<0.068	<0.039
2,3,4,7,8-PeCDF	57117-31-4	pg/l	<0.050	<0.059	<0.081
1,2,3,4,7,8-HxCDD	39227-28-6	pg/l	<0.23	<0.15	<0.069

	CAS	**Unit**	**Apr-10**	**Jun-10**	**Aug-10**
1,2,3,6,7,8-HxCDD	57653-85-7	pg/l	<0.24	<0.15	<0.073
1,2,3,7,8,9-HxCDD	19408-74-3	pg/l	<0.22	<0.14	<0.066
1,2,3,4,7,8-HxCDF	70648-26-9	pg/l	<0.090	<0.076	<0.098
1,2,3,6,7,8-HxCDF	57117-44-9	pg/l	<0.079	<0.067	<0.068
1,2,3,7,8,9-HxCDF	72918-21-9	pg/l	<0.33	<0.10	<0.10
2,3,4,6,7,8-HxCDF	60851-34-5	pg/l	<0.12	<0.17	<0.12
1,2,3,4,6,7,8-HpCDD	35822-46-9	pg/l	<0.26	<0.29	0.1339
1,2,3,4,6,7,8-HpCDF	67562-39-4	pg/l	0.1318	<0.13	<0.11
1,2,3,4,7,8,9-HpCDF	55673-89-7	pg/l	<0.43	<0.15	<0.093
OCDD	3268-87-9	pg/l	1.1615	<1.2	1.9668
OCDF	39001-02-0	pg/l	<1.7	<0.58	0.3549
Total TCDD	41903-57-5	pg/l	<0.088	<0.11	<0.30
Total TCDF	55722-27-5	pg/l	<0.056	<0.048	<0.030
Total PeCDD	36088-22-9	pg/l	<0.14	<0.13	<0.059
Total PeCDF	30402-15-4	pg/l	<0,096	<0,127	<0,12
Total HxCDD	34465-46-8	pg/l	<0,69	<0,44	<0,208
Total HxCDF	55684-94-1	pg/l	<0,619	<0,413	<0,386
Total HpCDD	37871-00-4	pg/l	<0.26	<0.29	0.1339
Total HpCDF	38998-75-3	pg/l	<0,5618	<0,28	<0,203
sum (pg/l)		pg/l	< 5.4	< 3.6	< 3.8
WHO-TEQ 2005 pg/g (upperbound)		pg/l	0.3872	0.3545	0.4566
WHO-TEQ 2005 pg/g (mediumbound)		pg/l	0.1944	0.1772	0.2293
WHO-TEQ 2005 pg/g (lowerbound)		pg/l	0.0017	0.0000	0.0020

	CAS	**Unit**	**Apr-10**	**Jun-10**	**Aug-10**
Non-ortho PCBs i.e. co-planar PCBs					
CO-PCB-77		pg/l	2.9712	4.3979	2.3342
CO-PCB-81		pg/l	0.2255	0.1375	0.1232
CO-PCB-126		pg/l	0.2750	0.2382	<0.095
CO-PCB-169		pg/l	<0.085	<0.061	<0.068
Sum		pg/l	< 3.6	< 4.8	< 2.6
WHO-TEQ 2005 pg/l (upperbound)		pg/l	0.0304	0.0261	0.0119
Other PCBs					
PCB-18		ng/l	0.0830	0.1822	0.1113
PCB-28/31		ng/l	0.0848	0.2927	0.1457
PCB-33		ng/l	0.0239	0.0851	0.0405
PCB-47		ng/l	0.0906	0.3184	<0.083
PCB-49		ng/l	0.0280	<0.024	0.0177
PCB-51		ng/l	0.0199	0.0590	<0.0079
PCB-52		ng/l	0.0547	0.0909	0.0500
PCB-60		ng/l	0.0079	0.0165	0.0064
PCB-66		ng/l	0.0308	0.0648	0.0230
PCB-74		ng/l	0.0219	0.0451	0.0175
PCB-99		ng/l	0.0345	0.0376	0.0235
PCB-101		ng/l	0.0562	0.0898	0.0349
PCB-105		ng/l	0.0311	0.0266	0.0112
PCB-110		ng/l	0.0532	0.0800	0.0371
PCB-114		ng/l	0.0025	<0.0034	0.0014
PCB-118		ng/l	0.0797	0.0841	0.0338

	CAS	Unit	Apr-10	Jun-10	Aug-10
PCB-122		ng/l	<0.0029	<0.0038	<0.0006
PCB-123		ng/l	<0.0022	<0.0028	<0.0006
PCB-128		ng/l	0.0191	0.0176	0.0069
PCB-138		ng/l	0.0864	0.1090	0.0421
PCB-141		ng/l	0.0198	0.0212	0.0087
PCB-153		ng/l	0.0720	0.1115	0.0456
PCB-156		ng/l	0.0157	0.0187	0.0052
PCB-157		ng/l	<0.0032	<0.0025	0.0009
PCB-167		ng/l	0.0038	<0.0022	0.0010
PCB-170		ng/l	0.0369	0.0494	0.0214
PCB-180		ng/l	0.0599	0.0813	0.0368
PCB-183		ng/l	0.0110	0.0172	0.0085
PCB-187		ng/l	0.0174	0.0236	0.0135
PCB-189		ng/l	<0.0040	<0.0038	0.0008
PCB-194		ng/l	0.0100	<0.0055	0.0051
PCB-206		ng/l	<0.0080	<0.010	<0.0015
PCB-209		ng/l	<0.0048	<0.0068	<0.0009
All PCBs together (ng/l)		ng/l	< 1.1	< 2.0	< 0.85
WHO-TEQ 2005 pg/g (upperbound)		pg/l	0.0350	0.0309	0.0136
WHO-TEQ 2005 pg/g (mediumbound)		pg/l	0.0336	0.0298	0.0078
WHO-TEQ 2005 pg/g (lowerbound)		pg/l	0.0322	0.0287	0.0020
Organotins					
Monobutyltin cation, MBT		ng/l	8.3	7.3	3.8
Dibutyltin cation, DBT		ng/l	1.5	2.4	<1

	CAS	Unit	Apr-10	Jun-10	Aug-10
Tributyltin cation, TBT		ng/l	<1	<1	<1
Tetrabutyltin, TTBT		ng/l	8.6	<1	<1
Monooctyltin cation, MOT		ng/l	5.4	3.5	<1
Dioctyltin cation, DOT		ng/l	<1	<1	<1
Triphenyltin cation, TPhT		ng/l	<1	<1	<1
Tricyclohexyltin cation, TCyT		ng/l	<1	<1	<1
Chlorinated paraffins					
SCCP	85535-84-8	µg/l	1.88	1.04	2.85
MCCP	85535-84-9	µg/l	3.08	8.40	0.96
Endosulfan					
α-Endosulfan	959-98-8	ng/l	<5	<5	<5
β-Endosulfan	33213-65-9	ng/l	<5	<5	<5
Endosulfan sulphate	1031-07-8	ng/l	<5	<5	<5
Cadmium					
	7440-43-9	µg/l	0.06	0.05	0.15
Mercury					
	7439-97-6	µg/l	< 0,05	< 0,05	< 0,05

Appendix H: Results of Storm water

Basic data from the WWTPs needed for the chemical screening of effluents

Sampling date	**24.03.10**	**07.05.10**
Sampling time	11:30	13:05
BOD_7 (mg/l)	5,00	5,60
COD_{Cr} (mg/l)	49,00	105,00
Suspended solids (mg/l)	52,00	140,00
Tot-P (mgP/l)	0,16	0,70
PO_4-P (mgP/l)	0,06	0,02
Tot-N (mg N/l) *(Kjeldahl)*	6,10	4,60
NH_4-N (mg N/l)	0,35	0,19
Alkalinity (mmol/l)	3,94	1,46
pH	7,41	7,88
Conductivity (µS/m)	2510,00	322,00
Fe (mg Fe/l)	2,80	5,10
t (^{0}C)	6,40	7,40
Sulphur (S) (mg/l) dissolved	16,83	14,00
TOC (mg C/l)	5,90	5,60

Biotests

Acute tests	**Unit**	**March-10**	**May-10**
luminescent bacteria		no toxicity	no toxicity
Daphnia magna, acute		no toxicity	no toxicity
algae growth inhibition.		Inhibition= 11.11%	no toxicity

Chemical analysis

	CAS	**Unit**	**March-10**	**May-10**
PBDEs				
BDE-17	147217-75-2	ng/l	nd	nd
BDE-28	41318-75-6	ng/l	nd	nd
BDE-47	5436-43-1	ng/l	nd	0.40
BDE-66	189084-61-5	ng/l	nd	nd
BDE-85	182346-21-0	ng/l	nd	nd
BDE-99	60348-60-9	ng/l	nd	0.51
BDE-100	189084-64-8	ng/l	nd	0.18
BDE-153	68631-49-2	ng/l	nd	0.21
BDE-154	207122-15-4	ng/l	nd	nd
BDE-183	207122-16-5	ng/l	nd	0.12
BDE-203		ng/l	nd	0.13
BDE-209	1163-19-5	ng/l	3.73	10.4
HBCDs				
α-HBCD		ng/l	nd	2.42
β-HBCD		ng/l	nd	0.95
γ-HBCD		ng/l	3.94	3.11

	CAS	Unit	March-10	May-10
HBCD sum			3.94	6.48
Perfluorinated substances				
perfluoro-n-hexanoic acid (PFHxA)	307-24-4	ng/l	0.8	nd
perfluorooctane sulfonate (PFOS)	1763-23-1	ng/l	1.5	1.3
perfluorooctanoic acid (PFOA)	335-67-1	ng/l	1.9	0.5
perfluoro-n-decanoic acid (PFDA)	335-76-2	ng/l	nd	nd
Phenolic substances				
bisphenol a	80-05-7	µg/l	0.05	0.24
4-nonylphenol (mix.)	84852-15-3	µg/l	0.23	nd
4-nonylphenol monoethoxylate (mix.)	-	µg/l	0.06	0.08
4-nonylphenol diethoxylate (mix.)	-	µg/l	0.02	0.09
octylphenol	140-66-9	µg/l	nd	nd
octylphenol monoethoxylate	-	µg/l	nd	0.03
octylphenol diethoxylate	-	µg/l	nd	nd
Organotins				
Monobutyltin cation, MBT		ng/l	<1	<1
Dibutyltin cation, DBT		ng/l	5.4	3.4
Tributyltin cation, TBT		ng/l	<1	<1
Tetrabutyltin, TTBT		ng/l	<1	<1
Monooctyltin cation, MOT		ng/l	<1	1.5
Dioctyltin cation, DOT		ng/l	<1	<1
Triphenyltin cation, TPhT		ng/l	<1	<1
Tricyclohexyltin cation, TCyT		ng/l	<1	<1
Chlorinated paraffins				
SCCP	85535-84-8	µg/l	1.84	0.85

	CAS	Unit	March-10	May-10
MCCP		µg/l	2.91	1.11
Endosulfan				
α-Endosulfan	959-98-8	ng/l	<5	<5
β-Endosulfan	33213-65-9	ng/l	<5	<5
Endosulfan sulphate	1031-07-8	ng/l	<5	<5
Cadmium				
	7440-43-9	µg/l	0.05	0.16
Mercury				
	7439-97-6	µg/l	<0,05	<0,05

	CAS	Unit	March-10
Dioxins			
2,3,7,8-TCDD	1746-01-6	pg/l	<0.24
2,3,7,8-TCDF	51207-31-9	pg/l	0.9281
1,2,3,7,8-PeCDD	40321-76-4	pg/l	<0.19
1,2,3,7,8-PeCDF	57117-41-6	pg/l	0.6103
2,3,4,7,8-PeCDF	57117-31-4	pg/l	1.3616
1,2,3,4,7,8-HxCDD	39227-28-6	pg/l	<0.34
1,2,3,6,7,8-HxCDD	57653-85-7	pg/l	0.3892
1,2,3,7,8,9-HxCDD	19408-74-3	pg/l	0.7216
1,2,3,4,7,8-HxCDF	70648-26-9	pg/l	1.3251
1,2,3,6,7,8-HxCDF	57117-44-9	pg/l	1.0586
1,2,3,7,8,9-HxCDF	72918-21-9	pg/l	<0.57
2,3,4,6,7,8-HxCDF	60851-34-5	pg/l	1.2565

	CAS	**Unit**	**March-10**
1,2,3,4,6,7,8-HpCDD	35822-46-9	pg/l	5.2454
1,2,3,4,6,7,8-HpCDF	67562-39-4	pg/l	4.4530667
1,2,3,4,7,8,9-HpCDF	55673-89-7	pg/l	0.9985
OCDD	3268-87-9	pg/l	51.1375
OCDF	39001-02-0	pg/l	10.5312
Total TCDD	41903-57-5	pg/l	<0.24
Total TCDF	55722-27-5	pg/l	0.9281
Total PeCDD	36088-22-9	pg/l	<0.19
Total PeCDF	30402-15-4	pg/l	1.9719
Total HxCDD	34465-46-8	pg/l	<1,4508
Total HxCDF	55684-94-1	pg/l	<4,2102
Total HpCDD	37871-00-4	pg/l	5.2454
Total HpCDF	38998-75-3	pg/l	5.4515667
sum (pg/l)		pg/l	< 81
WHO-TEQ 2005 pg/g (upperbound)		pg/l	1.6361693
WHO-TEQ 2005 pg/g (mediumbound)		pg/l	1.3781693
WHO-TEQ 2005 pg/g (lowerbound)		pg/l	1.1201693
Non-ortho PCBs i.e. co-planar PCBs			
CO-PCB-77		pg/l	264.2970
CO-PCB-81		pg/l	13.0018
CO-PCB-126		pg/l	4.4809
CO-PCB-169		pg/l	0.3203
Sum		pg/l	282.1000
WHO-TEQ 2005 pg/l (upperbound)		pg/l	0.4880
Other PCBs			

	CAS	Unit	March-10
PCB-18		ng/l	4.8894
PCB-28/31		ng/l	7.7242
PCB-33		ng/l	1.8133
PCB-47		ng/l	0.8330
PCB-49		ng/l	2.1335
PCB-51		ng/l	0.1707
PCB-52		ng/l	2.2876
PCB-60		ng/l	0.7463
PCB-66		ng/l	2.4903
PCB-74		ng/l	1.2754
PCB-99		ng/l	0.6736
PCB-101		ng/l	1.1046
PCB-105		ng/l	0.5104
PCB-110		ng/l	1.4437
PCB-114		ng/l	0.0291
PCB-118		ng/l	1.3025
PCB-122		ng/l	0.0110
PCB-123		ng/l	0.0170
PCB-128		ng/l	0.2053
PCB-138		ng/l	0.9382
PCB-141		ng/l	0.1516
PCB-153		ng/l	0.7880
PCB-156		ng/l	0.1064
PCB-157		ng/l	0.0209
PCB-167		ng/l	0.0284

	CAS	Unit	March-10
PCB-170		ng/l	0.1671
PCB-180		ng/l	0.2827
PCB-183		ng/l	0.0741
PCB-187		ng/l	0.1202
PCB-189		ng/l	0.0057
PCB-194		ng/l	0.0322
PCB-206		ng/l	0.0072
PCB-209		ng/l	0.0092
All PCBs together (ng/l)		ng/l	32.6748
WHO-TEQ 2005 pg/g (upperbound)		pg/l	0.5510
WHO-TEQ 2005 pg/g (mediumbound)		pg/l	0.5510
WHO-TEQ 2005 pg/g (lowerbound)		pg/l	0.5510

Appendix I: Results of Landfill leachate

Basic data from the WWTPs needed for the chemical screening of effluents

Sampling date	**15.10.09**	**16.06.10**	**20.09.10***
Sampling time	14:00	---	14:00
BOD_7 (mg/l)	90	130,00	55
COD_{Cr} (mg/l)	980	1300,00	900
Suspended solids (mg/l)	100	300,00	196
Tot-P (mgP/l)	5,1	5,10	5,00
PO_4-P (mgP/l)	3,4	1,60	3,3
Tot-N (mg N/l) *(Kjeldahl)*	244	301,00	268
NH_4-N (mg N/l)	118	244,00	210
Alkalinity (mmol/l)	28,22	54,34	40,5
pH	8,22	---	---
Conductivity (µS/m)	4840	6650,00	---
Fe (mg Fe/l)	3,9	12,00	8,3
t (^{0}C)	6,1	17,20	---
Sulphur (S) (mg/l) dissolved	---	4,00	89
TOC (mg C/l)	263	366,00	---

* additional analyses from the landfill were taken for the dioxin analyses as the original bottle was broken

Biotests

Acute tests	**Oct-09**	**Jun-10**
luminescent bacteria	46,13 (CL lower 41,78 % , CL upper 52,19 %)	**EC50 =39,6%** (CL lower 34.3 % , CL upper 47,37 %)
Daphnia magna, acute	49.05	EC50 =24.41%
algae growth inhibition.	22.56	ErC50=24,95

Chemical analysis

	CAS	Unit	Oct-09	Jun-10
PBDEs				
BDE-17	147217-75-2	ng/l	nd	nd
BDE-28	41318-75-6	ng/l	nd	nd
BDE-47	5436-43-1	ng/l	2.53	2.14
BDE-66	189084-61-5	ng/l	nd	nd
BDE-85	182346-21-0	ng/l	nd	nd
BDE-99	60348-60-9	ng/l	3.41	4.46
BDE-100	189084-64-8	ng/l	nd	nd
BDE-153	68631-49-2	ng/l	nd	1.44
BDE-154	207122-15-4	ng/l	nd	2.63
BDE-183	207122-16-5	ng/l	nd	1.36
BDE-203		ng/l	nd	nd
BDE-209	1163-19-5	ng/l	3.28	3.73
HBCDs				
α-HBCD		ng/l	nd	0.99
β-HBCD		ng/l	nd	0.08
γ-HBCD		ng/l	nd	nd
HBCD sum			nd	1.07

Difficult sample to extract
-> made an awful emulsion
-> poor recovery! (12%)

Difficult sample to extract
-> made an awful emulsion
-> poor recovery! (5-8%)

	CAS	Unit	Oct-09	Jun-10
Perfluorinated substances				
perfluoro-n-hexanoic acid (PFHxA)	307-24-4	ng/l	597	570
perfluorooctane sulfonate (PFOS)	1763-23-1	ng/l	108	11
perfluorooctanoic acid (PFOA)	335-67-1	ng/l	533	590
perfluoro-n-decanoic acid (PFDA)	335-76-2	ng/l	20.7	2.2
Phenolic substances				
bisphenol a	80-05-7	µg/l	0.65	0.56
4-nonylphenol (mix.)	84852-15-3	µg/l	0.99	0.39
4-nonylphenol monoethoxylate (mix.)	-	µg/l	nd	nd
4-nonylphenol diethoxylate (mix.)	-	µg/l	0.09	0.05
octylphenol	140-66-9	µg/l	0.07	nd
octylphenol monoethoxylate	-	µg/l	0.02	0.03
octylphenol diethoxylate	-	µg/l	nd	nd
Organotins				
Monobutyltin cation, MBT		ng/l	21	58
Dibutyltin cation, DBT		ng/l	<1	<5
Tributyltin cation, TBT		ng/l	<1	<5
Tetrabutyltin, TTBT		ng/l	<1	<5
Monooctyltin cation, MOT		ng/l	<1	18
Dioctyltin cation, DOT		ng/l	<1	<10
Triphenyltin cation, TPhT		ng/l	<1	<5
Tricyclohexyltin cation, TCyT		ng/l	<1	<5
Chlorinated paraffins				

	CAS	Unit	Oct-09	Jun-10
SCCP	85535-84-8	µg/l	3.57	10.38
MCCP		µg/l		< 0.2
Endosulfan				
a-Endosulfan	959-98-8	ng/l	<5	<5
b-Endosulfan	33213-65-9	ng/l	<5	<5
Endosulfan sulphate	1031-07-8	ng/l	<5	38.4
Cadmium				
	7440-43-9	µg/l	< 0,02	< 0,02
Mercury				
	7439-97-6	µg/l	0.10	<0,05

	CAS	Unit	Oct-09
Dioxins			
2,3,7,8-TCDD	1746-01-6	pg/l	0.3857
2,3,7,8-TCDF	51207-31-9	pg/l	0.4366
1,2,3,7,8-PeCDD	40321-76-4	pg/l	<0.30
1,2,3,7,8-PeCDF	57117-41-6	pg/l	<0.21
2,3,4,7,8-PeCDF	57117-31-4	pg/l	0.6331
1,2,3,4,7,8-HxCDD	39227-28-6	pg/l	<0.49
1,2,3,6,7,8-HxCDD	57653-85-7	pg/l	0.5355
1,2,3,7,8,9-HxCDD	19408-74-3	pg/l	<0.46
1,2,3,4,7,8-HxCDF	70648-26-9	pg/l	0.6446
1,2,3,6,7,8-HxCDF	57117-44-9	pg/l	0.3582

	CAS	Unit	Oct-09
1,2,3,7,8,9-HxCDF	72918-21-9	pg/l	0.7688
2,3,4,6,7,8-HxCDF	60851-34-5	pg/l	<0.51
1,2,3,4,6,7,8-HpCDD	35822-46-9	pg/l	14.2608
1,2,3,4,6,7,8-HpCDF	67562-39-4	pg/l	2.4998
1,2,3,4,7,8,9-HpCDF	55673-89-7	pg/l	<0.58
OCDD	3268-87-9	pg/l	96.6663
OCDF	39001-02-0	pg/l	7.1487
Total TCDD	41903-57-5	pg/l	0.3857
Total TCDF	55722-27-5	pg/l	0.43659
Total PeCDD	36088-22-9	pg/l	<0.30
Total PeCDF	30402-15-4	pg/l	<0,8431
Total HxCDD	34465-46-8	pg/l	<1,4855
Total HxCDF	55684-94-1	pg/l	<2,2816
Total HpCDD	37871-00-4	pg/l	14.2608
Total HpCDF	38998-75-3	pg/l	<3,0798
sum (pg/l)		pg/l	< 127
WHO-TEQ 2005 pg/g (upperbound)		pg/l	1.5107
WHO-TEQ 2005 pg/g (mediumbound)		pg/l	1.2797
WHO-TEQ 2005 pg/g (lowerbound)		pg/l	1.0487
Non-ortho PCBs i.e. co-planar PCBs			
CO-PCB-77		pg/l	76.1324
CO-PCB-81		pg/l	3.8974
CO-PCB-126		pg/l	2.3693

	CAS	Unit	Oct-09
CO-PCB-169		pg/l	0.2155
Sum		pg/l	82.6147
WHO-TEQ 2005 pg/l (upperbound)		pg/l	0.2522
Other PCBs			
PCB-18		ng/l	1.6213
PCB-28/31		ng/l	2.3288
PCB-33		ng/l	0.7043
PCB-47		ng/l	0.2047
PCB-49		ng/l	0.6496
PCB-51		ng/l	0.0650
PCB-52		ng/l	0.7698
PCB-60		ng/l	0.3073
PCB-66		ng/l	1.1794
PCB-74		ng/l	0.6560
PCB-99		ng/l	0.4817
PCB-101		ng/l	0.7052
PCB-105		ng/l	0.5105
PCB-110		ng/l	1.1019
PCB-114		ng/l	0.0281
PCB-118		ng/l	1.1342
PCB-122		ng/l	0.0102
PCB-123		ng/l	<0.0030
PCB-128		ng/l	0.1925
PCB-138		ng/l	0.9449

	CAS	**Unit**	**Oct-09**
PCB-141		ng/l	0.1259
PCB-153		ng/l	0.6802
PCB-156		ng/l	0.0263
PCB-157		ng/l	<0.0020
PCB-167		ng/l	<0.0060
PCB-170		ng/l	0.2864
PCB-180		ng/l	0.4276
PCB-183		ng/l	0.0799
PCB-187		ng/l	0.1407
PCB-189		ng/l	0.0035
PCB-194		ng/l	0.0671
PCB-206		ng/l	<0.0060
PCB-209		ng/l	0.0361
All PCBs together (ng/l)		ng/l	< 16
WHO-TEQ 2005 pg/g (upperbound)		pg/l	0.3042
WHO-TEQ 2005 pg/g (mediumbound)		pg/l	0.3041
WHO-TEQ 2005 pg/g (lowerbound)		pg/l	0.3040

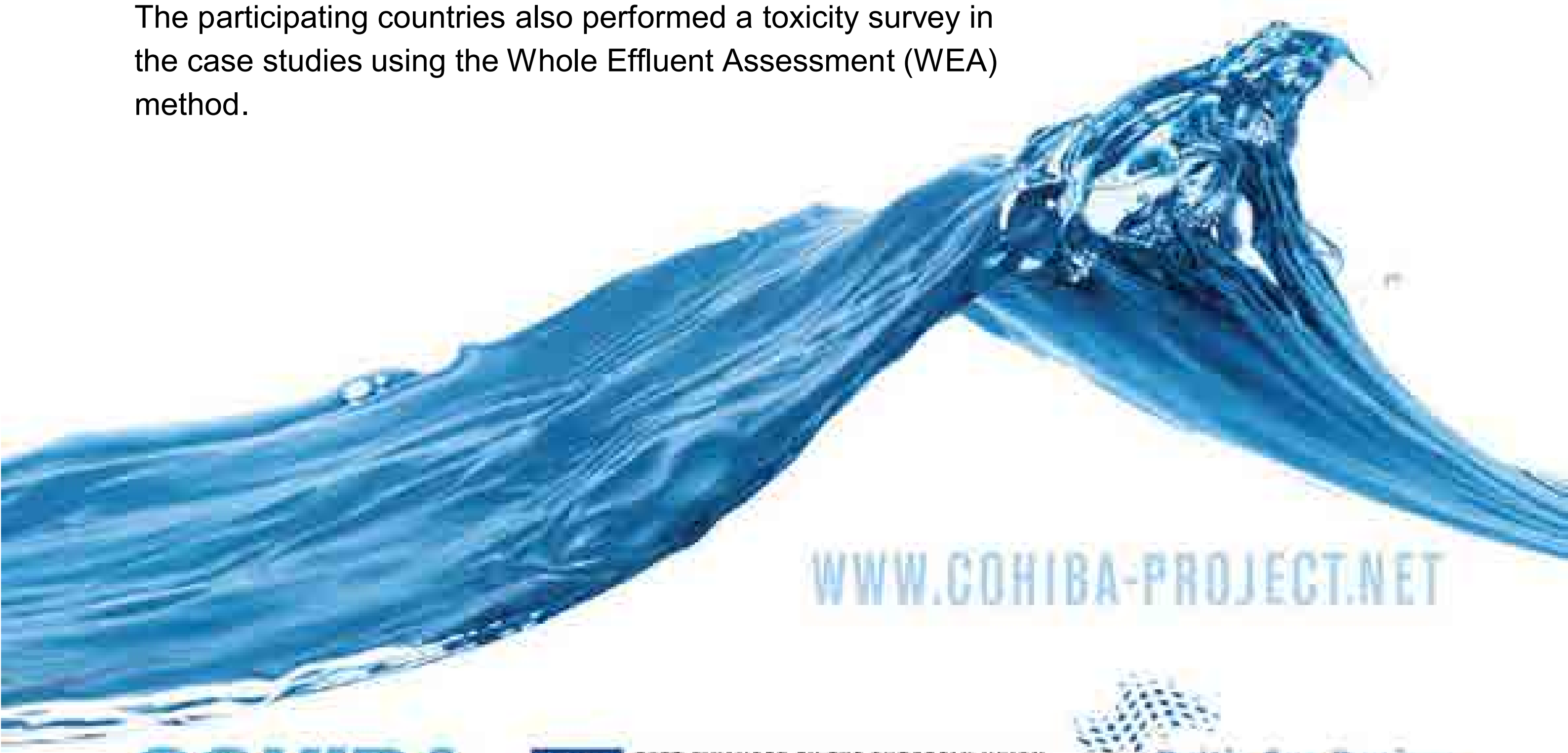
Additional findings from landfill effluent in June

Substance	**Concentration**	**Unit**
CB-28	12.4	ng/l
CB-101	24.2	ng/l
p,p'-DDT	44	ng/l
o,p'-DDE	det	
unidentified halogenorganic compounds	det	

This is the report of Estonian results of COHIBA Work Package 3 work. The goal of this study was to identify sources of 11 hazardous substances of specific concern to the Baltic Sea as listed in HELCOM Baltic Sea Action Plan. The screening of the substances was performed in municipal and industrial wastewaters, landfill effluents and storm waters, in all participating countries.

Estonian sampling sites were located on the Northern coast of Estonia, near the Baltic Sea coastline. Four wastewater treatment plants, treating mostly domestic waste waters but also industrial wastewater, one landfill and one storm water collector were selected as case studies.

The participating countries also performed a toxicity survey in the case studies using the Whole Effluent Assessment (WEA) method.



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