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Screening of phenolic substances in the Nordic environments

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TemaNord 2008:530

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TemaNord 2008:530

ISBN 978-92-893-1681-1

Print: Ekspressen Tryk & Kopicenter

Copies: 0
Printed on environmentally friendly paper
This publication can be ordered on www.norden.org/order. Other Nordic publications are available at www.norden.org/publications

Printed in Denmark

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Nordic co-operation

Nordic cooperation is one of the world's most extensive forms of regional collaboration, involving Denmark, Finland, Iceland, Norway, Sweden, and three autonomous areas: the Faroe Islands, Greenland, and Åland.

Nordic cooperation has firm traditions in politics, the economy, and culture. It plays an important rol in European and international collaboration, and aims at creating a strong Nordic community in a strong Europe.

Nordic cooperation seeks to safeguard Nordic and regional interests and principles in the global community. Common Nordic values help the region solidify its position as one of the world's most innovative and competitive.

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Preface

In 2001 the Nordic countries initiated screening projects for potentially hazardous substances in the environment. Among the substances screened so far are synthetic musk substances (2002), perfluorinated alkylated (PFAS) substances (2003) and siloxanes (2004), and bronopol, resorcinol, m-cresol and triclosan (2005), where the specific years represents the time of sampling. In 2006, a new screening project covering selected phenols in the Nordic environment was initiated.

The phenolic substances selected for this screening project include both long and short chain alkylphenols (from 4-*tert*-buylphenol to dodecylphenol), some bisphenols (bisphenol A and tetrabromobisphenol A) and monoethoxylates of octyl- and nonylphenols. All of the selected substances are considered High Production Volume (HPV) chemicals and are likely to be more or less persistent in the environment and/or hazardous to aquatic organisms. More of the substances are of even greater concern due to their suspected endocrine mimicking effects.

The screening project has been initiated and run by a project group under the Nordic Chemicals Group with representatives from environmental institutions in the Nordic countries including the National Environmental Research Institute of Denmark, the Food-, Veterinary and Environmental Agency of the Faroe Islands, the Finnish Environment Institute, the Environment and Food Agency of Iceland, the Norwegian Pollution Control Authority and the Swedish Environmental Protection Agency.

The project has been financed and supported by the Nordic Council of Ministers as well as the participating institutions. The chemical analyses and reporting of results have been carried out by the National Environmental Research Institute of Denmark (NERI).

The overall sampling strategy regarding sample types and sampling sites has been decided by the project Steering Group, while the collection of samples from the various environmental compartments based on a sampling protocol provided by NERI and the transport of samples to the analytical laboratory at NERI been has been organized by each of the participation countries.

Summary

This project on the cooperation of screening of selected phenolic substances in the Nordic environment was initiated by the Nordic Chemicals Group and financed by the Nordic Council of Ministers.

All six Nordic countries participated in the project that included the sampling and analysis of 120 samples from different environmental compartments. The study included the analyses of 13 different phenolic compounds covering alkylphenols (*tert*-butylphenols, di-*tert*-butylphenol, octyl-, nonyl- and dodecyl phenols), 4-cumylphenol, some bisphenols (BPA, TBBPA and its dimethyl ether) and octyl- and nonylphenol monoethoxylates. Different environmental institutions in the member countries were responsible for the selection and the collection of the samples and for the transportation of these to the National Environmental Research Institute of Denmark, who had been selected for carrying out the chemical analyses and the reporting of the results.

The samples were of three main types: water, solids and biota. Water samples included waste water (influents and effluents) from sewage treatment plants (STPs) and effluents from landfills; besides surface runoff and recipient water samples from both freshwater/brackish and marine environments were included. The solid samples also included several types: sewage sludge from STPs, soil from landfills and sediments from both marine and freshwater environments. Biological samples included mussels from marine environments, fish from both freshwater/brackish and marine environments, marine mammals (seal and pilot whales) and two egg samples from seabirds (black guillemots).

For the water samples the following results were obtained:

	STP		Landfill	Surface	Recipient	Background
In ng/L	influent/ sewage	effluent	effluent	runoff	marine/ fresh	marine/ fresh
4-*tert*-Butylphenol	<10	<10	N/A-834	<10-32	<10	N/A
2,6-di-*tert*-butylphenol	<25	<45	<30-254	<30	<1-65	<15
4-*tert*-octylphenol	8.5-73	<5-2,099	<10-2,372	<10-379	<10	<10
n-octylphenol	<1-67	<1-43	3.6-5.9	<5	<2	<2
nonylphenol-mix	133-5,688	<15-2,173	27-16,997	<15-359	<10-4,199	<20-107
n-Nonylphenol	<1-54	<1-72	<1-71	<1-18	<1-287	<1-1.5
4-dodecylphenol	<125-4,096	<100-2,206	241-4,902	<50-4,280	<50	<125
4-cumylphenol	<1-61	<1-8	8-988	<1-154	<1-454	<1
Bisphenol-A	204-9,828	<1-561	711-5,910	<1-5,910	<1-22	<1-11
TBBPA	<25	<10-59	<20	<25	<10	<10
Methylated-TBBPA	<10	<10	<5	<10	<2	<10
octylphenolethoxylate	14-157	<1-239	<1-413	<1-31	<1-118	<1-2
nonylphenol-ethoxylate	1,142-4,896	<2-1,585	<2-85	<1-102	<1-61	<1

The NP-mix (various nonylphenol isomers), dodecylphenol (DDP), bisphenol A (BPA), 4-*tert*-octylphenol and nonylphenol monoethoxylate (NP1EO) were those substances found in highest concentrations in all sewage water samples. Overall, recipient water and background water samples, however, generally had relatively low concentrations of most substances; NP-mix, DDP, BPA and NP1EO were present in detectable amounts, and surface water from Tórshavn had the highest estimated concentrations of NP-mix.

For the solid samples the following results were obtained:

	STP	Landfill	Sediment	
In µg/kg dw	**sludge**	**soil**	**non-marine**	**marine**
4-*tert*-Butylphenol	<5-4,474	N/A	40-134	80
2,6-di-*tert*-butylphenol	<2-104	<5	<5	<5
4-*tert*-octylphenol	<3.5-1,386	3-23	<1-9	<1
n-octylphenol	<0.1-44	<0.2-1	<0.2-25	<0.2-25
nonylphenol-mix	1,460-28,360	<3.5-47	<3.5-485	<3.5-340
n-Nonylphenol	<0.1-5.6	<0.1	<0.1-2	<0.1-3
4-dodecylphenol	8,463-47,396	<25	<25-216	<25-529
4-cumylphenol	<0.1-115	<0.6-8	<0.1-115	<0.1-180
Bisphenol-A	<0.4-1914	<0.1-3	<0.1-40	<0.1-74
TBBPA	<5-1138	<1.0	<1	<1
Methylated-TBBPA	<20	<5-57	<5	<5
octylphenolethoxylate	<1-97	0.1-0.4	<0.2-1.3	<0.2-1.5
nonylphenol-ethoxylate	11-363	1-2	<0.1-67	<0.1-1.4

The sludge samples had the highest content of the analysed substances, and as for the sewage water samples NP-mix and DDP were detected in highest concentrations, whereas the ethoxylates had been significantly reduced. Compared to sludge, both soil from landfill sites and sediments were low in concentrations of most substances.

For the biological samples the following results were obtained:

	Fish		Mussels	Egg	Marine mammals	
In µg/kg ww	**non-marine**	**marine**	**marine/ non-marine**	**seabird**	**seal**	**whale**
4-*tert*-Butylphenol	<4-449	<10-1,079	<10-424	<10	29-109	100
2,6-di-*tert*-butylphenol	12-5,081	81-4,064	<2.5-92	<5	45-677	27-42
4-*tert*-octylphenol	13-355	<12	<3-7,362	15-27	<25-472	<25
n-octylphenol	<1-8	<2	<1-4	<1	<1-4	1.5-3
nonylphenol-mix	44-989	165-1,085	<1-908	10-16	<6-97	52-197
n-Nonylphenol	<10	<1-44	<1-37	<1	<1	<1-2
4-dodecylphenol	<100-253	N/A	<100-181	<100	<100	<100
4-cumylphenol	<1-16	<2-30	<1-3	<1-3	<1	3-7
Bisphenol-A	<1-57	<10	<1-3	6-9	N/A	N/A
TBBPA	<10	N/A	<5	<10	<10	<10
Methylated-TBBPA	<5	<10	<5	<5	<5	<5
octylphenolethoxylate	18-4,035	<5-31,697	<5-28	7-8	<1	36-356
nonylphenol-ethoxylate	18,821	N/A	<5-39	<5	N/A	N/A

In contrast to the other sample types the biota samples have relatively high concentrations of 4-*tert*-butylphenol (4-tBuP) and especially 2,6-di-*tert*-butylphenol (2,6-di-tBuP), but the reason for that is unknown. Otherwise, 4-tOP, NP-mix, DDP and octyl- and nonylphenol monoethoxylates were detected in fish and mussels, while levels were low and close to detection limits in both eggs and seals. Regarding NP-mix and OP1EO, higher levels were detected in pilot whales than in seals.

Apart from the screening results this report also compiles a range of physico-chemical data on the studied substances together with experimental and estimated data on their environmental distribution and partitioning, persistence and toxic effects on various test organisms.

1. Introduction

1.1 Background of the study

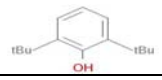
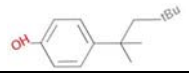
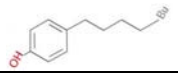
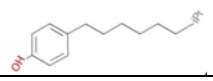
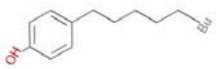
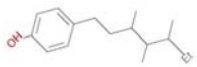
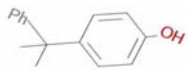
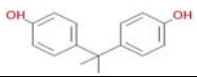
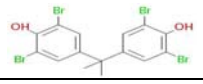
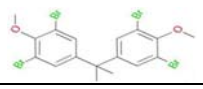
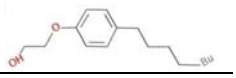
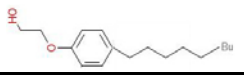
In 2006 the three working groups under the Nordic Council of Ministers (NCM) decided to support cooperation on screening of selected alkylphenols (APs), some of their ethoxylates and the brominated flame retardant TBBPA and its methylated metabolite in Nordic environments. The supporting groups were: The Nordic Chemicals Group (NCG), The Environment and Data Group and the Ocean and Air Group. The project was initiated by the National Environmental Research Institute of Denmark, the Veterinary, Food and Environment Agency of the Faroe Islands, the Finnish Environment Institute, the Environment and Food Agency of Iceland, the Norwegian Pollution Control Authority and the Swedish Environmental Protection Agency.

The National Environmental Research Institute (NERI) in Denmark was assigned the task of carrying out this project, which included analysis of selected compounds in several environmental compartments and sample types. Sampling was performed by the individual Nordic countries.

Most of the individual compounds included in the study are so-called high production volume (HPV) chemicals that furthermore have been identified as bioaccumulative and/or persistent to some extent just as most are potentially toxic to aquatic organisms; in addition some compounds have also been characterized as endocrine disruptors. This causes great concern, and hence several of the compounds are included on international or national priority list of hazardous compounds.

In this screening project the following suite of phenolic substances have been included (*cf.* Table 1):

Table 1. Phenolic compounds included in this screening project

Common name	*Abbreviation*	*CAS no.*	*EINECS no.*	*Structure*
*4-*tert*-Butylphenol*	*4-tBuP*	*98-54-4*	*202-679-0*	
*2,6-di(*tert*-Butyl)phenol*	*2,6-di-tBuP*	*128-39-2*	*204-884-0*	
*4-*tert*-Octylphenol*[1]	*4-tOP*	*140-66-9*	*205-426-2*	
4-Octylphenol	*4-OP*	*1806-26-4*	*217-302-5*	
4-Nonylphenol, branched[2]	*4-NP(b)*	*84852-15-3*	*284-325-5*	
4-n-Nonylphenol	*4-nNP*	*104-40-5*	*203-199-4*	
Dodecylphenol, mixture of isomers[3]	*DDP(m)*	*27193-86-8*	*248-312-8*	
4-Cumylphenol	*4-CP*	*599-64-5*	*209-968-0*	
Bisphenol A	*BPA*	*80-05-7*	*201-245-8*	
Tetrabromobisphenol A	*TBBPA*	*79-94-7*	*201-236-9*	
Tetrabromobisphenol A, dimethylated	*di-Me-TBBPA*	*37853-61-5*	*253-693-9*	
Octylphenol monoethoxylates	*OP1EO*	*See note*[4]	*See note*[4]	
Nonylphenol monoethoxylates	*NP1EO*	*See note*[5]	*See note*[5]	

Notes: [1]Other tert*-octylphenols isomers are described by CAS no. 27193-28-8 (EINECS no. 248-310-7). [2]Mixtures of other nonylphenol isomers are described by CAS no. 25154-52-3 (EINECS no. 246-672-0). [3]CAS no. 121158-58-5 (EINECS no. 310-154-3) also describes mixtures of dodecylphenol isomers, while CAS no. 104-43-8 (EINECS no. 203-202-9) and CAS no. 210555-94-5 describe linear 4-dodecylphenol and branched 4-dodecylphenol isomers, respectively. [4]CAS no. 9063-89-2 describes octylphenol ethoxylates in general, while CAS no. 2315-67-5, CAS no. 1322-97-0 and CAS no. 51437-89-9 (EINECS no. 257-203-4) describe 4-*tert*-Octylphenol monoethoxylate, 4-Octylphenol monoethoxylate and Octylphenol monoethoxylate isomers, respectively. [5]CAS no. 9016-45-9 describes Nonylphenol ethoxylates in general, while CAS no. 27986-36-3 (EINECS no. 248-762-5) and CAS no. 104-35-8 describe Nonylphenol monoethoxylate isomers and linear 4-Nonylphenol monoethoxylate, respectively.*

1.2 Objectives

The overall objective of this Nordic screening project has been to determine concentrations of the selected phenolic compounds in various environmental compartments and media that include a) aqueous samples: influents and effluents from waste water treatment plants (STP), surface runoffs and recipient water (marine and lacustrine), b) solid samples: stabilized sludge from STP, soil and sediment (marine and lacustrine) and c) biological samples: mussels, fish liver, birds egg, seal liver and pilot whale liver. The sampling strategy and selection of sample types were determined individually by each of the six Nordic countries, i.e. Denmark, Faroe Islands, Finland, Iceland, Norway and Sweden; in total 129 samples have been collected and analysed.

2. Physico-chemical properties

The substances involved in this screening project on selected phenols includes a complex mixture of alkylphenols with varying substituents, alkylphenol ethoxylates, bisphenols and brominated compounds with highly varying physico-cheminal properties as described in the table below.

The physico-chemical properties have been retrieved from various sources some of which are based on experimental measurements while others are based on model estimations. Generally, some scatter in the reported values is observed which mostly reflects that different experimental techniques or mathematical models have been applied to generate the data. Another point worth mentioning is that some of the data are also generated from technical and not necessarily pure substances or even from isomeric mixtures. Further details can be obtained from the listed references.

2.1 Physical properties of selected phenols

The physical properties of alkylphenols are comparable to those of phenol, but the properties are strongly influenced by the type and position of the alkyl substituent (Lorenc et al., 2003).

Like phenol, most alkylphenols are solids at room temperature. Para-alkylphenols have higher melting points and boiling points than the ortho-substituted analogs, and the melting points and boiling points go through a maximum for *tert*-butylphenol and then decrease. As the carbon chain of the alkyl group becomes longer and branched, the alkylphenol may become waxy or even supercool; nonylphenol and dodecylphenol are oily liquids.

Alkyl groups in the ortho position affects the intramolecular hydrogen bonding of the hydroxyl group, and the larger the group the bigger the effect. A *tert*-butyl group in the ortho position lowers the boiling with about 20 °C, and the introduction of another *tert*-butyl group in the other ortho position (i.e. 2,6-di-*tert*-butylphenol) effectively precludes any hydrogen bonding.

The solubility of alkylphenols in water decreases as the number of carbon atoms attached to the aromatic ring increases. Alkylphenols are generally soluble in organic solvents like acetone, alcohols, hydrocarbons and toluene. However, the more polar the alkylphenol the greater it's solubility in alcohols and the lower in e.g. hexane or heptane, where the solubility increases with increasing carbon number of the alkyl chain.

All phenols are characterized by a common functional group, the phenolic hydroxyl. The acidic character of the hydroxyl group of alkylphenols is imparted by the aromatic ring leading to acid dissociation constants (pKa-values) of 10-11 for unhindered alkylphenols. Both alkyl and benzyl substituents have a small positive inductive effect while halogen substituents have a negative induction effect. Therefore, most of the phenols in this study, except for TBBPA, are expected to have slightly higher (pKa) than the phenol itself (pKa = 10); TBBPA is more acidic than phenols with pKa values of 7.5 and 8.5. Alcohols, like the alkylphenol ethoxylates, on the other side, generally have pKa values around 16, and hence do not easily dissociate.

Alkylphenols unsubstituted in the ortho position dissolve in alkalized water (pH > 13), but as the carbon number of the alkyl chain increases the solubility decreases.

Generally, water solubility and vapour pressure decrease with increasing molecular weight while the octanol/water partition coefficient (log K_{ow}) increases. These properties, however, are dependent on the actual pH value of the test mixture, just as they are dependent on the actual temperature; most substances are insoluble or only slightly soluble in water. Furthermore, most substances are solid at room temperature with very low vapour pressures, which means that their emission to the atmosphere is rather low.

2.2 Chemical properties of selected phenols

Alkylphenols can undergo a variety of chemical reactions involving either the hydroxyl group or the aromatic nucleus and be converted into valuable products. The unshared electron pair on the hydroxyl group acts as a nucleophile by being attracted to electron deficient centres; however, alkylphenols tend to be less nucleophilic than aliphatic alcohols as the aromatic nucleus attracts the electron density at the oxygen atom. Bulky alkyl groups in ortho position to the hydroxyl group also decreases or excludes reactions involving the hydroxyl functionality (Lorenc et al., 2003). Specifically, it has not been possible to derivatize the 2,6-di-*tert*-Butylphenol with a silylating reagent in this project.

Table 2. Physico-chemical properties of phenolic substances included in the screening project

Name [CAS no.]	Common name	Chemical formula	MW[a] (amu)	Mp[b] (°C)	Vp[c] (Pa/°C)	Wsol[d] (mg/L)/°C	Log K_{ow}[e]	Ref.
4-(tert-butyl)phenol [98-54-4]	p-tert-Butylphenol	C10H14O	150.22	100	0.5/20	500-800/20	2.44-3.45	4
							3.3	7
2,6-di(tert-butyl)phenol [128-39-2]	2,6-di-tert-butyl-phenol	C14H22O	206.33	36-37	1.01/20	4.11	4.5	3
				34-39	1.33/20			4
							4.9	7
4-(1,1,3,3-tetramethyl-butyl)-phenol [140-66-9]	4-tert-Octylphenol	C14H22O	206.33	79-82	0.21/20	17-19/22	3.7-5.3	4
				83.5-84	0.064/25			5
					1	19	4.1	6
				73	0.09/25	4.8/25	5.3	7
4-(n-octyl)phenol [1806-26-4]	p-Octylphenol	C14H22O	206.33	41	0,013/25	3.1/25		1
				83			5.5	7
4-nonylphenol (branched) [84852-15-3]	p-Nonylphenol	C15H24O	220.36	290-302[f]	0.002/20	3-11/20	3.28-4.77	4
					0.3	6	6/4.48	6/8
					0.008	1.2	5.9	7
4-(n-nonyl)phenol [104-40-5]	4-n-Nonylphenol	C15H24O	220.36	42	0.109/25	7/25		5
					0,09	1.6		6
				92	0,005/25	1.6	5.8	7
Dodecylphenol, mixed isomers [27193-86-8]	Dodecylphenol	C18H30O	262.44	310-335[f]	0.0092/25	0.031/22		[g]
					3.1E-4/25	0.032	7.5[h]	7
							7.9[i]	7
				180-270	0.0092/25	2.1/25	7.14	10
4-(1-methyl-1-phenylethyl)-phenol [599-64-4]	p-Cumylphenol	C15H16O	212.29	72	0.003/25	43.3/25	4.12-4.49	3
							4.1	7
4,4'-isoproylidenediphenol [80-05-7]	BPA	C15H16O2	228.29	150-155	4.1E-7/25	120-300/25	2.2-3.8	4
				156	5E-6/20	120/25	3.32	5
				130	5.2E-5/25	170	3.4	7
2-(4-tert-Octylphenoxy) ethanol [2315-67-5]	p-tert-Octylphenol mono-ethoxylate	C16H26O2	250.38				4.96	7
2-(4-n-Octylphenoxy) ethanol [51437-89-9]	p-Octylphenol monoethoxylate	C16H26O2	250.38				5.1	7
						0.26		
						1.1		
							5.58	2
2-(nonylphenoxy)ethanol [27986-36-3]	Nonylphenol mono-ethoxylate	C17H28O2	264.41		2.4E-5/25	0.26	5.6	7
						1.1		
							5.58	2
2-(4-n-nonylphenoxy)ethanol [104-35-8]	p-Nonylphenol mono-ethoxylate	C17H28O2	264.41		2.4E-5/25	0.15-2.34/25	5.6	7
						0.001/25		
2,2',6,6'-tetrabromo-4,4'-iso-propylidenediphenol [79-94-7]	Tetrabromobisphenol A	C15H12Br4O2	543.87	180-184	<1.2E-5		4.54/8.02	1
				181	2.4E-9/25		7.20	3
				210			5.9	7
						1.26/25	8.3	8
				178;181-182	<1.19E-5/20	0.063/21[j]	5.90	9
4,4'-isopropylidene-bis(2,6-dibromoanisole) [37853-61-5]	Tetrabromobisphenol A dimethyl ether	C17H16Br4O2	571.93	200	4.7E-7/25	1.9E-5/25	8.3	7
						6.8E-5	6.7	9

Notes: [a]Molecular weight; [b]Melting point in °C; [c]Vapor pressure in Pascal at specific temperature (°C). [d]Water solubility at specific temperature (°C); for phenolic substances the water solubility generally depends on the pH value. [e]The logarithm of the octanol-water partition coefficient (K_{ow}); as for the water solubility, log K_{ow} is also expected to be dependent on the water pH value; [f]Boiling point in °C at 1013 hPa. [g]Data from EU ECBI/131/06 Rev.1 that covers several Dodecylphenol isomers. [h]This value is an average value for a mixture of several isomers. [i]This value has been reported for the 4-dodecylphenol isomer (CAS no. 104-43-8). [j]pure water.

Refs.: 1) ChemFinder (http://chemfinder.cambridgesoft.com/reference/chemfinder.asp); 2) US-EPA ECOSAR v/0.99g, Jan. 2000 (http://www.epa.gov/opptintr/newchems/tools/21ecosar.htm); 3) US-EPA HPVIS (http://www.epa.gov/hpvis/); 4) EU IUCLID (http://ecb.jrc.it/documentation/); 5) NITE (http://www.safe.nite.go.jp/english/Haz_start.html); 6) OSPAR, Hazardous Substances (http://www.ospar.org/eng/html/welcome.html); 7) US-EPA PBT Profiler (http://www.pbtprofiler.net/default.asp/); 8) OECD SIDS (http://cs3-hq.oecd.org/scripts/hpv/); 9) Environment Agency, UK (2007); 10) OECD SIDS SIAM 22 (ECBI/131/06 ED. 1, 2006).

3. Environmental fate, toxicity and effects

3.1 Recent relevant studies

A study on alkylphenols, their properties, usage and emission to the atmosphere and occurrence, fate and effects in the aquatic environment has recently been performed by the Directoraat-Generaal Rijkswaterstaat, The Netherlands (Groshart et al., 2001), and in 2003 the Swedish Environmental Research Institute (IVL) performed a screening for butylphenols, methylphenols, and long-chain alkylphenols in the Swedish environment (Remberger et al., 2003).

Furthermore, Ying et al. (2002) recently reviewed the environmental fate of alkylphenols and alkylphenol ethoxylates, while Glezer (2003) has reviewed the environmental effects of substituted phenols. In another recent paper Langston et al. (2005) reviewed the partitioning, bioavailability and effects of oestrogens and xeno-oestrogens in the aquatic environment, and Klecka et al. (2005) performed an assessment of the persistence and bioaccumulation potential of nonylphenol, octylphenol and their ethoxylates for the Alkylphenols & Ethoxylates Research Council of Canada. In 2006, Ying published another review on the fate, behaviour and effects of surfactants and their degradation products in the environment.

3.1 The PBT Profiler

The first part of this section includes a description of the behaviour and fate of the studied compounds if released to the environment. Most of the data are model estimates retrieved from the US Environmental Protection Agency (US-EPA) PBT Profiler (see below). This on-line facility has been used to estimate data on a compounds partitioning and persistency in the environment and its toxicity towards aquatic organisms. The estimates are calculated using available physico-chemical properties of the selected substances. A list of various PBT criteria (e.g. UN-ECE, UNEP, OSPAR, EU, Canada) has been compiled by Euro Chlor (2003).

Not only data from the PBT Profiler are included in this section, but also experimental data from OECD and US-EPA and other relevant studies are included.

3.1.1 Partitioning

The PBT profiler uses three environmental compartments (water, soil and sediment) to determine a chemical's persistence if released to the environment, while atmosphere and groundwater are not explicitly considered.

3.1.2 Transformation and persistence

The PBT Profiler considers in which compartment the chemical is most likely found and estimates the persistence based on its transformation in that medium expressed as its half-life, t½ (days); this value does not take into account the fluxes of the chemical in and out of the considered compartment. US-EPA and the corresponding EU/ECB (2003) current cut-off values regarding persistence are (Table 3):

Table 3. US-EPA[1] and EU/ECB[2] cut-off values regarding persistence in environmental compartments.

Environmental compartment	*Half-life ($t_{½}$, days)*		
	Not persistent	*Persistent*	*Very persistent*
Water	*≤ 60[1]*		
Marine	*≤ 60[2]*	*> 60[1,2]*	*> 60[2]*
Freshwater	*≤ 40[2]*	*> 40[2]*	*> 60[2]*
Soil	*≤ 60[1]*	*> 60[1]*	*> 180[1]*
Sediment	*≤ 60[1]*	*> 60[1]*	*> 180[1]*
Marine	*≤ 180[2]*	*> 180[2]*	*> 180[2]*
Freshwater	*≤ 120[2]*	*> 120[2]*	*> 180[2]*

To be able to compare the persistence of various chemicals, the PBT Profiler also calculates an overall persistence, P0 (days). This term is based on the theoretical release of 300 kg/hr in three different scenarios: 1) 100 kg/hr parallel to each of air, water and soil; 2) 150 kg/hr parallel to each of water and soil; 3) 300 kg/hr to water. The overall persistence takes into account both the released chemical's transport (between compartments) and transformation and should therefore not be interconverted with its half-life mentioned above.

Another parameter used to describe a chemicals fate in the environment is its biodegradability. OECD and US-EPA has developed a series of test to determine that. Two different terms are used: "ready" and "inherent" biodegradability; the first is determined under very stringent (low concentrations, small amount of inoculum) and the second under more favourable conditions (higher concentrations, higher of amount inoculum, acclimatization). The recommended mineralisation half-lives (days) for use in marine risk assessment in EU when only screening data are available are shown in Table 4 (EU/ECB, 2003).

Table 4. EU/ECB recommend mineralisation half-lives (days) for use in marine risk assessment.

Environmental compartment	*Half-life ($t_{½}$, days)*		
	Freshwater	*Estuaries*[1]	*Marine environments*
Degradable in marine tests	*n.a.*	*15*	*50*
Readily degradable[2]	*15*	*15*	*50*
Inherently degradable[3]	*150*	*150*	*> 150*
Persistent	*> 150*	*> 150*	*> 150*

[1]also includes shallow marine water closest to shoreline; [2]pass level > 70% DOC in 28 days; [3]a half-life of 150 days must be used only for those inherently degradable substances that are quickly mineralised in various tests – it reflects a "guesstimate consensus" among a number of experts.

3.1.3 Bioaccumulation

Bioaccumulation is a result of a chemical's uptake in an aquatic organism through all possible routes of exposure; as such it includes both biomagnification and bioconcentration. The PBT profiler uses estimates of the bioconcentration factor (BCF) to predict the importance of bioaccumulation, where the bioconcentration factor is ratio between the concentration in biota, CB, and the concentration in water, CW, at equilibrium, i.e. BCF = CB/CW. Lipophilic compounds are most likely to bioaccumulate, as the lipophilicity, or hydrophobicity, measured as the octanol-to-water partition coefficient (K_{ow}) is the driving force for bioconcentration, increasing with increasing K_{ow} value. US-EPA uses the following cutoff values regarding bioaccumulation: BCF < 1,000 (not bioaccumulative, BCF ≥ 1,000 (bioaccumulative) and BCF > 5,000 (very bioaccumulative); for the EU PBT criteria the corresponding values are: BCF > 2,000 (bioaccumulative) and BCF > 5,000 (very bioaccumulative).

3.1.4 Toxicity

The second part of this section considers the ecotoxicity of studied chemicals towards aquatic organisms and estimated effects. The PBT Profiler uses a chronic (long-term) toxicity value called ChV (mg/L) (from ECOSAR ver. 0.99h) to estimate a chemical's relative toxicity towards fish with the following cut-off values: ChV > 10 mg/L (not toxic); ChV < 10 mg/L (toxic); ChV < 0.1 mg/L (very toxic). The ChV value is the geometric mean of the maximum allowable toxicant concentration (MATC), i.e. the maximum concentration a chemical substance can have without being toxic to the test organism; this is the same as the chronic no-effect-concentration (NEC) value. For the EU PBT criteria the corresponding cut-off value is: chronic NOEC < 0,01 mg/L.

Table 5. Estimates of and experimental data on partitioning, persistence, degradation and bioaccumulation of selected phenolic compounds in water, soil and sediments

Name	Partitioning (%)			$t_{½}$ (days)	Overall Persistence (P_{ov} days)			Biodeg.[1]	Bioaccumulation		Ref.[12]
	water	soil	sedim.[2]	wat/soi/sed[3]	100/100/100[4]	---/150/150[5]	---/300/---[6]	ready/inh[7]	Log K_{ow}[8]	BCF[9]	
4-tBuP	*18*	*80*	*1*	*38/75/340*	*55*	*81*	*56*		*3.3*	*71*	*pbt*
[98-54-4]								*y/n*	*2*	*240*	*oecd*
										120	*euses*
2,6-di-tBuP	*12*	*64*	*24*	*38/75/340*	*83*	*120*	*140*		*4.9*	*430*	*pbt*
[128-39-2]								*n/-*			*oecd*
4-tOP	*9*	*53*	*38*	*38/75/340*	*100*	*160*	*200*		*5.3*	*2,300*	*pbt*
[140-66-9]								*n/n*		*297*	*oecd*
4-OP	*12*	*48*	*39*	*15/30/140*	*38*	*57*	*70*		*5.5*	*340*	*pbt*
[1806-26-4]									*4*		
4-NP(b)	*4*	*37*	*58*	*38/75/340*	*150*	*220*	*330*		*5.9*	*7,200*	*pbt*
[84852-15-3]								*n/y*		*1280*	*oecd*
4-nNP	*9*	*42*	*48*	*15/30/140*	*43*	*64*	*84*		*5.8*	*540*	*pbt*
[104-40-5]								*n/n*	*4.48*	*550*	*oecd*
DDP(m)	*4*	*28*	*68*	*15/30/140*	*62*	*93*	*140*		*7.5*	*480*	*pbt*
[27193-86-8]									*7.2*		*oecd*
	0.006	*97.7*	*2.2*					*n/n*	*7.1/5.5*[10]	*~ 6,000*[11]	*oecd/sids*
4-CP	*15*	*81*	*5*	*38/75/340*	*69*	*90*	*72*		*4.1*	*300*	*pbt*
[599-64-4]										*69-187*	*nite*
BPA	*12*	*88*	*1*	*39/75/340*	*89*	*82*	*57*		*3.3*	*72*	*pbt*
[80-05-7]									*3.4*		*oecd*
OP1EO	*16*	*62*	*22*	*15/30/140*	*33*	*45*	*47*		*5.1*	*37*	*pbt*
*[2315-67-5]**											
NP1EO	*11*	*48*	*41*	*15/30/140*	*42*	*60*	*77*		*5.6*	*88*	*pbt*
[27986-36-3]											
4-NP1EO	*11*	*49*	*40*	*15/30/140*	*43*	*60*	*77*		*5.6*	*88*	*pbt*
[104-35-8]											
TBBPA	*1*	*53*	*46*	*180/360/1600*	*1,100*	*1,300*	*2,200*		*7.2*	*14,000*	*pbt*
[79-94-7]											
Di-Me-TBBPA											
[37853-61-5]											

Notes: [1]Biodegradation; [2]sediment; [3]water/soil/sediment; [4]release of 100 kg parallel to water, soil and sediment; [5]release of 150 kg parallel to soil and sediment; [6]release of 300 kg to soil; [7]readily/inherent biodegradable (n=no; y=yes); [8]octanol-to-water partition coefficient; [9]biocon-centration factor; [10]5.5 refers to an experimental value for unspecified DDP; [11]refers to an average log K_{ow} of 6.0; 12References: pbt, US-EPA PBT Profiler (http://www.pbtprofiler.net/default.asp); oecd, OECD (http://cs3-hq.oecd.org/scripts/hpv/); ecb, EU-ECB/ESIS (http://ecb.jrc.it/esis/index.php?PGM=pbt); nite, National Institute of Technology and Evaluation (http://www.safe.nite.go.jp/english/Haz_start.html); oecd/sids (2006).

Table 6. US-EPA cut-off criteria regarding environmental persistence, bioaccumulation and toxicity

Persistence (P)[1]			Bioaccumulation (B)[2]			Toxicity (T)[3]		
Not persistent (--)	Persistent (P)	Very persistent (vP)	Not bioaccum. (--)	Bioaccumulat (B)	Very bioaccum (vB)	Not toxic (--)	Toxic (T)	Very toxic (vT)
P < 60	*60 ≤ P < 180*	*P > 180*	*B < 1000*	*1000 ≤ B < 5000*	*B > 5000*	*T >10*	*10 ≥ T > 0.1*	*T < 0.1*

Notes: [1]Environmental persistence expressed as half-lives in days in most predominant compartment; [2]Bioaccumulation expressed by bioconcentration factor (BCF); [3]Toxicity expressed as chronic toxicity value (fish ChV) in mg/L

Table 7. PBT evaluation of selected phenolic substances according to the US-EPA cut-off criteria[1]

Substance	Persistence (P)	Bioaccumulation (B)	Toxicity (T)
4-tBuP (98-54-4)	*P*	---	***vT***
2,6-di-tBuP (128-39-2)	*P*	---	***vT***
4-tOP (140-66-9)	*P*	*B*	***vT***
4-OP branched (27193-28-8)	---	---	***vT***
4-n-OP (1806-26-4)	---	---	***vT***
NP mixed isomers (25154-52-3)	*P*	---	***vT***
4-NP branched (84852-15-3)	***vP***	***vB***	***vT***
DDP branched (27193-86-8)	*P*	***vB***[2]	***vT***
4-CP (599-64-4)	*P*	---	***vT***
BPA (80-05-7)	*P*	---	***vT***
TBBPA (79-947)	***vP***	***vB***	***vT***
NP1EO (27986-36-3)	---	---	***vT***
4-NP1EO mixture (104-35-8)	---	---	***vT***

*Notes: [1]Data retrieved from PBT Profiler (http://www.pbtprofiler.net/default.asp); ---, below cut-off limit; P/B, persistent/bioaccumulative; **vP/vB/vT**; very persistent/very bioaccumulative/very toxic; [2]Based on BCF = 6,000 (from log K_{ow} = 6.0; oecd/sids, 2006).*

3.2 ECOSAR

More detailed information on the toxicity has been obtained from model estimates using the US-EPA ECOSAR programme (ver. 0.99h), which is based on SAR (structure – activity relationships) model calculations using K_{ow} and MW data. Output from the ECOSAR are acute (short-term) and chronic (long-term) toxicity data regarding green algae (not reported here), daphnid and fish. Acute toxicity end points are typically based on LC50 values obtained through 48-hr and 96-hr tests for both daphnid and fish, respectively. For chronic values (ChV) endpoints are not specified, but it may be either lethality or reproduction.

Other inputs to the toxicity part come from experimental data provided mostly by OECD.

Table 8. Predicted acute and chronic toxicity and no-effect concentrations of selected phenolic compounds (mg/L)

Name	Acute tox.		Chronic tox.		NEC/NOEC			PNEC		Ref.
	Daphnid (LC50/48h)	Fish (LC50/96h)	Daphnid (21d)	Fish (30d)	Daphnid	Fish	Water	Sedim.	Fish	
4-tBuP	2.12	2.95	0.32	0.44		0.042	0.0016[6]			pbt
[98-54-4]	3.9/EC50	5.14								luclid
2,6-di-tBuP	1.08	0.90	0.098	0.13		0.019				pbt
[128-39-2]	0.45	>1.0-1.4			0.076	0.21-0.30				oecd
4-tOP	0.51	0.29	0.032	0.041		0.008	0.00061[6]		0.0061	pbt
[140-66-9]	0.27	0.25/0.26			0.11/48h	0.077/96h				iuclid
			0.34/21d	0.12/14d	0.03/21d	0.084/14d				luclid
4-OP	0.41	0.21	0.023	0.030		0.007	0.00001[6]			pbt
[1806-26-4]										
4-NP(b)	0.34	0.15	0.017	0.022		0.005	0.00033[6]		0.0074	pbt
[84852-15-3]	0.043/EC50	0.14/0.31			0.018/96h	0.24/96h				iuclid
					0.024/21d	7.4/33d				iuclid
4-NP	0.28	0.11	0.012	0.016		0.004				pbt
[140-40-5]	1.0/EC50	0.13-0.14			0.024	0.0074				oecd
DDP	0.08	0.02	0.0018	0.002		0.0011				pbt
[27193-86-8]*	0.037		0.0024		0.011/48h					ecbi
					0.002/21d					ecbi
	0,093					> 0.5	9.3E-5	0.064	9.3E-5	oecd/sids
4-CP	1.55	1.54	0.17	0.22		0.029				pbt
[599-64-4]		1.6								nite
BPA	2.62	3.28	0.36	0.48		0.05				pbt
[80-05-7]	3.9/EC50	4.6-9.9	>3.2		>3.2/21d					iuclid
			1.1/96h		0.51/96h					iuclid
					3.16/21d[2]	0.016[2]	0.0016[1]			
OP1EO	0.39	0.30	---	0.062						pbt
[2315-67-5]										
4-OP1EO	0.31	0.23	---	0.049		0.049				pbt
[51437-89-9]										
NP1OE	0.12	0.085	---	0.019		0.019				pbt
[27986-36-3]'										
TBBPA	0.22	0.05	0.006	0.007		0.003		0.69[3]	0.00026[3,5]	pbt
[79-94-7]	0.96	0.4-0.54			<0.32	0.1-0.26/96h		0.00094[3,4]		iuclid
			>0.98		0.54*	0.16/35d				iuclid
di-Me-TBBPA	0.0008	0.0005	---	0.0002						pbt
[37853-61-5]			6.5E-4/16d	1.7E-4/30d						ea

Notes: [1]SIAM 14 (2002); [2]http://www.bisphenol-a.org/esafety/enassess.html; [3]SIAM 20 (2005); [4]PNEC value for soil; [5]Indicative PNEC value for oysters; [6]Klein et al. (1999); ea, Environmental Agency, UK (2007). oecd/sids (2006).

3.3 Alkylphenols

3.3.1 4-tert-butylphenol (4-tBuP)

If released to the environment 4-tBuP is expected to be found predominantly in soil (80 % with an estimated half-life of 75 days in this media; it is therefore considered to be persistent in the environment. Its overall persistence, however, depends on the actual release, and considering various release scenarios, the overall persistence may vary between 55 and 81 days. Other studies report that it is readily biodegraded (EU/ECB, 2006a).

Its log K_{ow} is relatively low, and with an estimated BCF of 71, 4-tBuP is not expected to bioaccumulate considerably. For EU risk assessments EUSES (System for Evaluation of Substances) uses a BCF value of 120.

The estimated ChV (NEC) of 4-tBuP is 0.042 mg/L, which means that it according to the EPA cut-off values is very toxic to fish. The lowest acute and chronic toxicity data are a 48 hr. EC50 of 3.4 mg/L for Daphnia magna, and it may be toxic to aquatic organisms.

3.3.2 2,6-di-tert-butylphenol (2,6-di-tBuP)

If released to environment 2,6-di-tBuP is expected to be found predominantly in soil (64 %) and lesser in sediment (24 %), and its estimated half-life in soil is 75 days (persistent). Its overall persistence under various release ratios can be expected to vary between 83 to 140 days.

The log K_{ow} of 4.9 leads to an estimated BCF value of 430; hence it is not expected to bioaccumulate to any significant degree. An unvalidated experimental value of 660 for fish has been reported (OECD SIDS).

ECOSAR estimates a ChV (NEC) value of 0.019 mg/L, and it is therefore expected to be very toxic to fish. Acute toxicity levels are 1.08 and 0.90 mg/L for daphnid (LC50/48-hr) and fish (LC50/96-hr), respectively.

3.3.3 Octylphenols (OPs)

The partitioning of 4-tOP following a release is expected to be predominantly in soil (53 %) and sediment (38%), and the estimated half-lives are 75 and 340 days, respectively. It is therefore considered to be persistent to very persistent in these two compartments. The overall persistence varies between 100 to 200 days, depending on release scenario.

4-OP behaves a little different regarding partitioning between soil (48 %) and sediment (39 %), which result in half-lives of 30 and 140 days, respectively; 4-OP is expected to be persistent in sediment. The overall persistence varies between 38 and 70 days.

The log K_{ow} value of 5.3 of 4-tOP results in an estimated BCF value of 2,300, which means that 4-tOP is expected to be bioaccumulating. The corresponding value for 4-OP is 340, and it is therefore not expected to bioaccumulate significantly. EUSES uses a value of 634 for risk assessment.

According to ECOSAR estimates 4-tOP is also expected to be very toxic to fish with a ChV (NEC) value of 0.008 mg/L. Acute toxic levels are 0.51 and 0.29 mg/L for daphnid (LC50/48-hr) and fish (LC50/96-hr), respectively.

Correspondingly, 4-OP has an estimated ChV (NEC) value of 0.007 mg/L, and hence it is also expected to be very toxic to fish and slightly more toxic than 4-tOP. Acute toxic ECOSAR estimates are 0.41 and 0.21 mg/L for daphnid (LC50/48-hr) and fish (LC50/96-hr), respectively.

3.3.4 Nonylphenols (NPs)

Branched 4-NPs are expected to partition predominantly to sediment (58 %) and lesser to soil (37 %); corresponding half-lives are 75 and 340 days, and hence they are persistent to very persistent in these compartments. Overall persistence varies between 150 and 330 days following various release scenarios.

For 4-NP the partition is expected to be somewhat different and predominantly in sediment (48 %) and slightly less in soil (42 %). Half-lives are estimated to be 30 and 140 days in soil and sediment, respectively, and hence 4-NP is expected to be persistent in sediment. The overall persistence is expected to vary between 43 and 84 days.

With a log K_{ow} value of 5.9 the estimated BCF of branched 4-NP is 7.200, which means very bioaccumulative, according to the US-EPA criteria. For 4-NP the corresponding value of BCF is 540, which is not considered an indication of bioaccumulation. An estimated value of 1280 is used by EUSES for risk assessment.

The chronic toxicity value (NEC) for the branched 4-NPs is estimated to be 0.005 mg/L, which means very toxic to fish. Acute toxicity levels are according to ECOSAR estimates 0.34 and 0.15 mg/L for daphnid (LC50/48-hr) and fish (LC50/96-hr), respectively. That means that NPs are generally slightly more toxic than OPs.

For 4-NP the chronic toxicity value of ChV (NEC) is 0.004 mg/L, which is considered very toxic to fish. Acute toxicity levels are 0.28 and 0.11 mg/L for daphnid (LC50/48-hr) and fish (LC50/96-hr), respectively.

3.3.5 Dodecylphenols (DDPs)

DDPs are expected to partition predominantly into sediment (68 %) and somewhat less into soil (28 %); the expected half-live in sediment is 140 days, which shows that DDPs are expected to be persistent in sediment.

The overall persistence ranges from 62 to 140 days depending on release scenario.

An estimated log K_{ow} is 7.5 for DDPs leads to an expected BCF of 480, a value that shows that DDPs are not likely to bioaccumulate. Experimental data for log K_{ow} of 7.17 and BCF of 823 (for rainbow trout) for a mixture of various DDP isomers (EU/ECB, 2006b) seem to confirm the relatively moderate tendency to bioaccumulate despite the high K_{ow} value. Other data from OECD/SIDS (2006), however, list a range of log K_{ow} from 5.5 to 7.5 (depending on the specific isomer), and with an average value of 6,0 an estimated BCF of at least 6,000 would result. Hence, DDP is considered with a high bioaccumulating potential and being of highest concern.

According to ECOSAR estimates a chronic toxicity value (ChV) for DDPs is 0.0011 mg/L, which shows that DDPs are very toxic to fish. Corresponding acute toxicity values are 0.083 and 0.017 mg/L for daphnid (LC50/48-hr) and fish (LC50/96-hr), respectively. According to OECD/SIAM 22 (2006) a 21-day reproduction NOEC of 0.0037 mg/L was obtained for Daphnia.

3.4 Other phenols

3.4.1 4-Cumylphenol (4-CP)

According to PBT Profiler estimates 4-CP is expected to partition predominantly into soil (81 %) with an expected half-life of 75 days; Thus 4-CP is expected to be persistent in soil. Overall persistence is estimated to range between 69 and 90 days, depending on the release scenario.

4-CP has an estimated log K_{ow} of 4.1 which leads to an expected BCF value of 300; thus, 4-CP is not expected to bioaccumulate.

The chronic toxicity to fish has a ChV value of 0.029 mg/L, which shows that 4-CP is expected to be very toxic to fish. For the acute toxicity the following values have been estimated: 1.55 and 1.54 mg/L for daphnid (LC50/48-hr) and fish (LC50/96-hr), respectively.

3.4.2 Bisphenol A (BPA)

If released to the environment BPA is expected to partition predominantly into soil (88 %) with an estimated half-life of 75 days; therefore, BPA is expected to persistent in soil. The overall persistence, depending on release scenario, is estimated to range between 57 and 89 days.

BPA has en estimated log K_{ow} of 3.3 and that leads to an expected BCF value of 72; BPA is therefore not expected to bioaccumulate. These model estimates are supported by test values that range from about 5 to

68 for fish (Staples et al., 1998). An experimental of 67 is used by EUSES for risk assessments.

The estimated chronic ChV value for BPA is 0.05 mg/L, and BPA is therefore expected to be very toxic to fish. Corresponding acute toxicity values are 2.62 and 3.28 mg/L for daphnid (LC50/48-hr) and fish (LC50/96-hr), respectively.

3.5 Brominated compounds

3.5.1 Tetrabromobisphenol A (TBBPA)

TBBPA is expected to partition both into soil (53 %) and sediment (46 %) with half-lives of 360 and 1,600 days, respectively; only 1 % will be in the aqueous environment, and it also has a relatively low solubility of 0.001 mg/L. As it binds strongly to both soil and sediment, TBBPA is therefore expected to be very persistent in these compartments. The overall persistence of TBBPA, depending on the release, is expected to range from 1,100 to 2,200 days. TBBPA is not readily biodegradable, but it degrades slowly in soil and sediment under both aerobic and anaerobic conditions. According to a recent update on the risk assessment by the Environment Agency, UK (2007) it was concluded that TBBPA is persistent to very persistent (P to vP).

TBBPA has a high estimated log K_{ow} value of 7.2 and leads to a very high expected BCF value of 14,000, and TBBPA is thus expected to bioaccumulate strongly. The Environment Agency, UK (2007) reports an experimental log K_{ow} of 5.9, and that experimental data does not clearly indicate a bioaccumulation potential (BCF ~ 1,300; i.e. not B).

The chronic toxicity data gives an estimated ChV value of 0.003 mg/L, which indicates that it is expected to be very toxic to fish. For the acute toxicity ECOSAR gives the following values, 0.22 and 0.05 mg/L for daphnid (LC50/48-hr) and fish (LC50/96-hr), respectively. Experimental data (Environment Agency, 2007) give a NOEC of 0.30 mg/L for daphnia (21-d test) and 0.16 mg/L for fish (35-d test). According to this TBBPA is not considered toxic to marine organisms (i.e. not T).

3.5.2 Tetrabromobisphenol A dimethylether (di-Me-TBBPA)

As for TBBPA its dimethylether is expected to partition almost equally to soil (49 %) and sediment (51 %) with expected half-lives of 360 and 1,600 days, respectively, in these compartments. The overall persistence is expected to range from 1,100 to 2,200 days, and TBBPA is therefore expected to be very persistent in the environment; this conclusion is consistent with a recent risk assessment from the Environment Agency, UK (2007).

The dimethylether of TBBPA has an even higher estimated log K_{ow} than TBBPA, but the value of 8.3 only leads to an expected BCF value of 990; therefore, it is not expected to bioaccumulate significantly. This conclusion is in contrast with that of the recent risk assessment from the Environment Agency, UK (2007), which gives a corrected log K_{ow} value of 6.7 and reports a high bioaccumulation potential.

ECOSAR does not report any chronic toxicity (ChV value) towards fish, only data for a 30-day period is available with a value of 0.00017 mg/L. For the acute toxicity the following values are estimated: 0.00079 and 0.00048 mg/L for daphnid (LC50/48-hr) and fish (LC50/96-hr), respectively. According to these values, TBBPA is expected to very toxic to aquatic organisms. Corresponding chronic values reported by the Environment Agency, UK (2007) are: 0.00065 mg/L for daphnia (21-d test) and 0.00017 mg/L for fish (30-d test), according to which it is considered toxic to marine organisms.

3.6 Alkylphenol ethoxylates (APEOs)

3.6.1 Octylphenol ethoxylates (OPEOs)

Following a release OP1EOs are expected to partition predominantly into soil (62 %) while only about 22 % are expected to be found in water and sediment. The expected half-life in soil is 30 days, and hence OP1EOs are not considered persistent.

With an estimated log K_{ow} of about 5 the expected BCF is about 30, and OP1EOs are therefore not likely to bioaccumulate.

The chronic toxicity data with a ChV of 0.062 mg/L shows that OP1EOs are expected to be very toxic to fish. For the acute toxicity ECOSAR gives the following data of 0.39 and 0.30 mg/L for daphnid (LC50/48-hr) and fish (LC50/96-hr), respectively.

3.6.2 Nonylphenol ethoxylates (NPEOs)

NP1EOs are expected to partition almost equally into soil (48-49 %) and sediment (40-41 %) with expected half-lives in these compartments of 30 and 140 days, respectively; NP1EOs are thus expected to be persistent in sediment according to US-EPA criteria.

For NP1EOs the following log K_{ow} value of 5.6 has been estimated, and that leads to an expected BCF value of 88; hence, NP1EOs are not expected to bioaccumulate.

Regarding chronic toxicity to fish ECOSAR gives a ChV value of 0.019, which shows that NP1EOs are expected to be very toxic to fish. Corresponding value for acute toxicity are 0.116 and 0.085 mg/L for daphnid (LC50/48-hr) and fish (LC50/96-hr), respectively.

3.7 Endocrine disruptors

Some of the phenols selected for this screening study can act like hormones (e.g. estrogens) and interact with the hormonal system; both octyl- and nonylphenols, nonylphenol ethoxylates and Bisphenol A belong to that group (Lintelmann et al., 2003). Recent attention has focussed on the effects on fish, where the feminisation of males has been implicated with estrogenic components in sewage effluents (Christiansen et al., 2002).

The potency of various phenolic compounds relative to 17ß-Oestradiol in rainbow trouts (Oncorhynchus mykiss) have been tested and evaluated by Jobling & Sumpter (1993), who found that the tested compounds had a relative order of potency: 4-tBuP > 4-tOP > 4-NP > NP2EO > NP9EO ranging from $1.6x10^{-6}$ to $2.0x10^{-7}$ times to that of 17ß-Oestradiol. Relative oestrogenic activity of individual nonylphenol isomers has recently been studied by Preuss et al. (2005) and by Katase et al. (2008); the latter found that of 13 branched isomers in technical mixtures one isomer, 4-(3-Ethyl-2-methylhexan-2-yl)phenol, was three to eighteen times more potent than any other isomer. Also BPA is known to be weakly endocrine disrupting.

4. Production, use and occurrence in the environment

4.1 Production and use – general

4.1.1 Alkylphenols

The alkylphenols studied in this project are high production volume (HPV) chemicals. The para-substituted alkylphenols are typically produced from an olefin and phenol using an acid catalyst. Depending on the purity of the olefin used the resulting side chain may be more or less branched, just as a minor part can be attached to the ortho position.

Alkylphenols are produced in high volumes and are primarily used as intermediates in the chemical industry for the production of alkylphenol ethoxylates (non-ionic surfactants and detergents), as resins for phenolic based plastomers and as antioxidants. Octyl- and nonylphenols are the major contributors in this class of compounds with more 95% of market, while other compounds like butyl- and dodecylphenols only add to about 5% of the market. In 1997 the production of octyl- and nonylphenols in Western Europe were about 7,000 and 110,000 tonnes/year. The degradation of alkyphenol ethoxylates in the environment further add to the occurrence of the alkylphenols, primarily in waste water and surface water.

Both octyl- and nonylphenols are on the EU list of priority substances in the field of water policy and the OSPAR list of chemicals for priority action (OSPAR, 2007).

4.1.2 Other phenolic compounds

Other phenolic substances included in this study are 4-Cumylphenol and Bisphenol A, which share a common structure except that BPA incorporates a double hydroxyl functionality.

4.1.3 Alkylphenol ethoxylates

Alkylphenol ethoxylates (APEOs) are mainly used as non-ionic surfactants, detergents and stabilizers, but they also have a wide range of applications as dispersants, emulsifiers, solubilizers and foaming agents. In addition to their use as detergents, wetting and cleaning agents in industry they are used on a smaller scale in the production of pulp and paper, textiles, coatings, pesticides, lubricating oil and fuels and in the metal finishing and plastic industry. In Europe, industrial applications have the

major market share of about 70%, while non-industrial application is about 30%. In 1997 the production of nonylphenol ethoxylates in EU was approximately 118,000 tonnes/year.

In this study is included octyl- and nonyl-phenol ethoxylates, but far the largest usage of alkylphenol ethoxylates is of nonylphenol ethoxylates that in all four countries surpass the usage of octylphenol ethoxylates by several hundred percents. Nonylphenol ethoxylates are on the OSPAR list of chemicals for priority action (OSPAR, 2007).

4.1.4 Brominated flame retardants

Tetrabromobisphenol A (TBBPA) is the largest volume of BFRs in production today to improve fire safety of mainly electrical and electronic equipment. The substance is generally marketed without legislative restrictions and in 2002 more than 130,000 tonnes were produced. Besides TBBPA its bis-methyl ether is also part of this study.
Like the alkylphenols and ethoxylates, TBBPA is also on the OSPAR list of chemicals for priority action (OSPAR, 2007).

4.2 Usage of phenolic compounds and alkylphenol ethoxylates in Nordic countries

Specifically, data on the use of the phenols substances selected for this study in the Nordic countries have been extracted from the SPIN database. SPIN is a database on the use of Substances in Products in the Nordic countries. It compiles data from the Product Registries of Norway, Sweden, Denmark and Finland, and it is financed by the Nordic Council of Ministers, Chemical group. At present, SPIN does not include data from Iceland and the Faroe Islands.

In all Denmark, Norway and Sweden companies are liable of registrating produced or imported substances in excess of 100 kg; in Finland there is no such fixed limit. In Denmark, Finland and Norway dangerous products must be registered, while in Sweden all chemical products regardless of their danger classification shall be registered. Sweden has the largest number of active products registered per year (about 70,000 in 2005), while Norway had the largest turnover (sum of import and production) in 2005 (approximately 175 mio. tonnes).

SPIN includes data from 2000 to 2005, and the compilation includes both total use, the substance categories and the number of preparations a specific substance has been used for. In Figure 1 is shown the total amount of specific substances that have been consumed in individual countries during 2000-2005. Denmark seems to have had the largest accumulated consumption of all listed compounds during 2000-2005 with a few exceptions. Finland has had the largest accumulated consumption of

BPA (> 2,000 tonnes), except for a very large consumption in Norway of > 9,000 tonnes in 2002. Besides that, Sweden has had the largest accumulated consumption of TBBPA (> 1,400 tonnes). Nonylphenol ethoxylates are the substances used in largest amount in Denmark with an average > 1,000 tonnes/year.

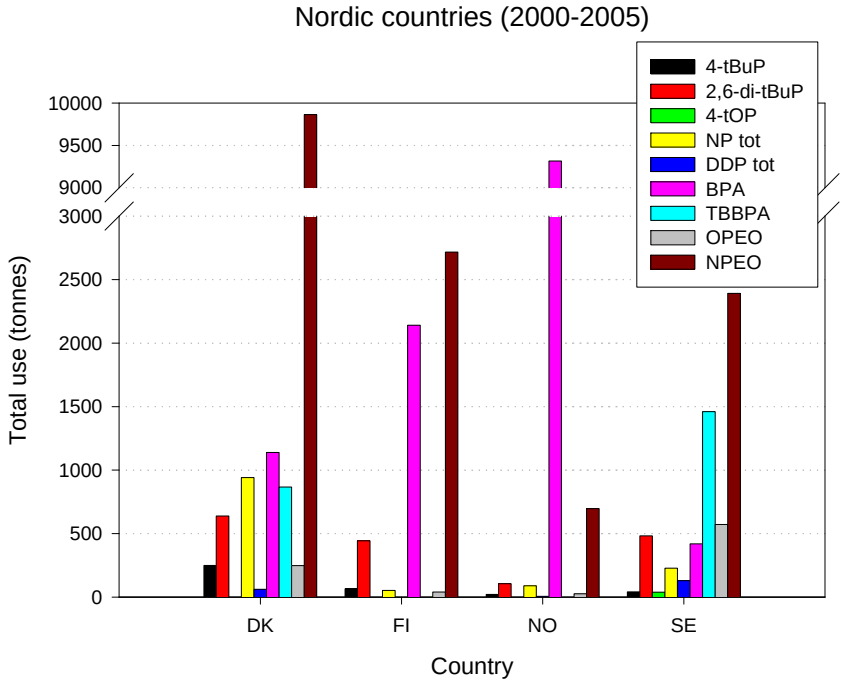


Figure 1. Accumulated use of selected phenolic substances in Nordic countries (DK, FI, NO and SE) during 2000-2005 (extracts from SPIN database).

4.2.1 4-tert-butylphenol [98-54-4]

4-*tert*-Butylphenol is a stable solid that is used as an intermediate for phenolic and polycarbonate resins. It is also used as a raw material for construction elements and floors in buildings. It is also being used as an antioxidant/stabilizer in rubber, plastic, food and oils; it is also used in fragrances. In 1993 it was produced at a yearly rate of 5,000 tonnes in Japan (SIAM 16, 27-30 May 2003). It is being considered a HPV chemical by ESIS, but it has not been classified as a dangerous substance (Directive 67/548/EEC). The consumption of 4-tBuP is expected to grow slightly (Lorenc et al., 2003).

The largest consumption has been in Denmark with an average 50 tonnes/year, and after a declining use from 2000 to 2004, the use of 4-tBuP seems to have increased again in 2005. In the other Nordic countries the average consumption has been < 10 tonnes/year (*cf.* Figure 2).

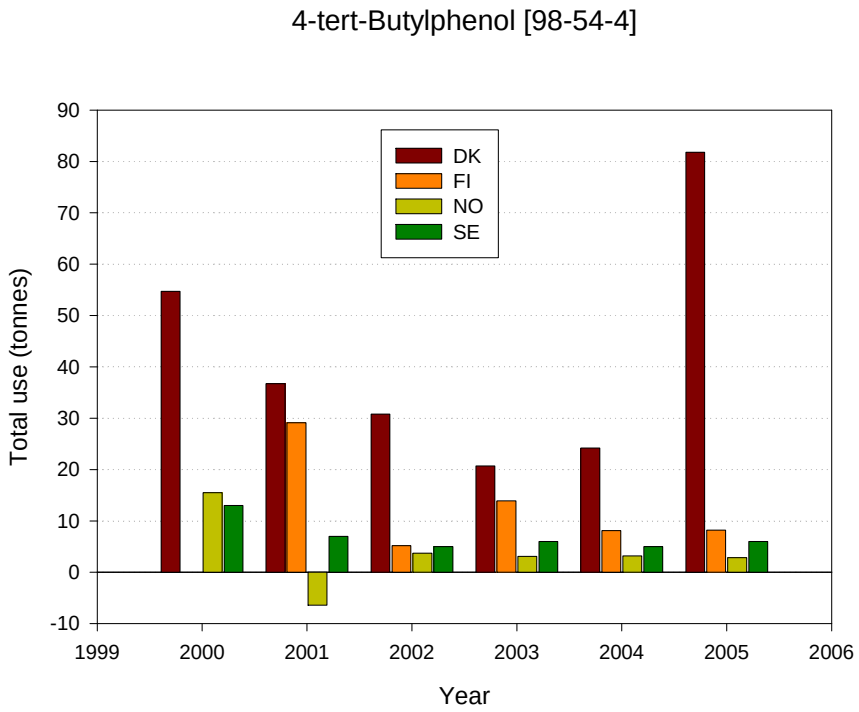


Figure 2. Yearly use of 4-tert-Butylphenol in Nordic countries during 2000-2005 (extracts from SPIN database).

4.2.2 2,6-di-tert-butylphenol [128-39-2]

2,6-di(*tert*-Butyl)phenol (2,6-di-tBP) is primarily used as an antioxidant, lubricant and transmission agent, while there is a small scale use for incorporation in plastics and rubber and for the production of chemicals for agriculture. In the US this is a HPV chemical with the production exceeding 450,000 tonnes per year. In ESIS this is also considered a HPV chemical, but it has not yet been included in a priority list. The quantities released to the environment are expected to be small and mainly to the atmosphere although 2,6-di-tBuP has a low volatility.

In Scandinavia the use of 2,6-di-tBP from 2000 to 2004 is shown in Figure 3. While the use of 2,6-di-tBP seems to level off in Denmark (from about 140 to < 50 tonnes/year) it seems to be increasing in Finland (up to about 125 tonnes/year); in Norway and Sweden its use seems to be relative constant about 25 and 75 tonnes/year, respectively. For Finland the consumption data for 2001 and 2002 has not been disclosed.

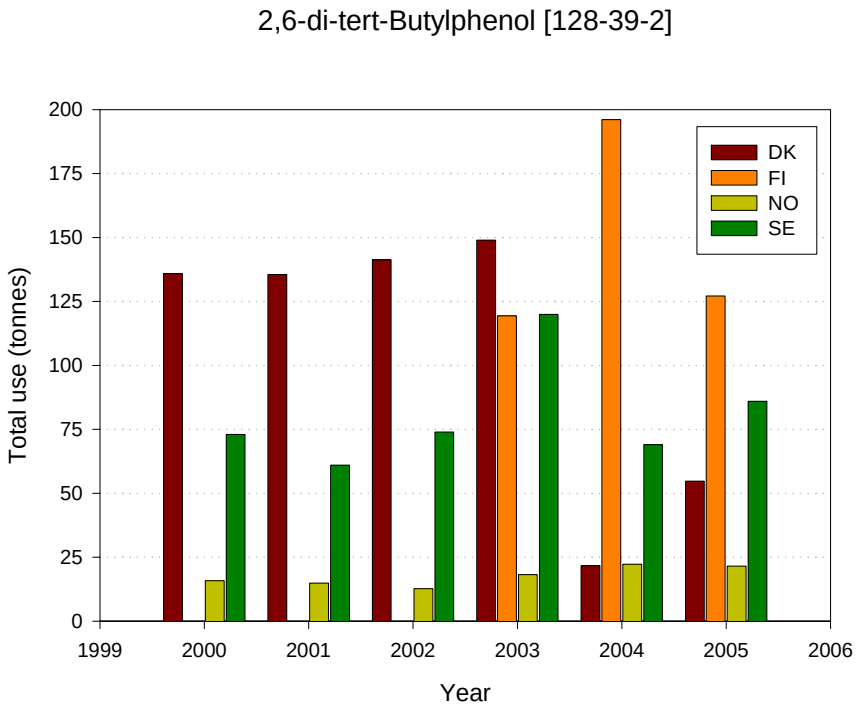


Figure 3. Yearly use of 2,6-di-tert-Butylphenol in Nordic countries during 2000-2005 (extracts from SPIN database).

4.2.3 Octylphenols

Octylphenols (OP) represents a number of isomeric compounds, where the alkyl group (C8H17) may either be straight or be branched in various ways. OP is produced by the reaction of phenol with octene, and commercial synthesis results in a mixture of various octylphenol isomers. Of the potential isomers, 4-*tert*-octylphenol [140-66-9], which is made by using the dimer of isobutylene, is the most commercially important. tOP is avail-able as a technical grade that contains about 90-95 % 4-tOP, 5-8 % 2-t-OP and 1-2 % butyloctylphenol (BOP). A high purity grade contains approximately 98-99 % 4-tOP, < 2 % 2-tOP and only traces of BOP (Lorenc et al., 2003).

OP is produced in high volume for use as an intermediate in the production of surfactants, formaldehyde resins etc. and octylphenol ethoxylates. In the European Union the production of 4-*tert*-octylphenol has increased from about 17,500 tonnes in 1997 to about 22,600 tonnes in 2001. Most of the production is being used within EU, and together with a small amount (< 1,000 tonnes/year) of imported bulk material the usage was slightly below 23,000 tonnes in 2001.

OP is also formed following the breakdown of octylphenol ethoxylates in the environment and is thus subject to wide dispersive use and distribution. OP is very toxic to aquatic organisms, is not easily degraded in the environment and has been detected in surface waters. Because OP

is considered to show significant endocrine disrupting effects, it is included in the OSPAR 1998 List of Candidate Substances (*cf.* List 6 in Annex 3 of the OSPAR Strategy with regard to Hazardous Substances, 2000). Under this entry is also included 4-n-octylphenol [1806-26-4] and octylphenols (branched) [27193-28-8].

It is uncertain to estimate the world consumption of 4-tOP because some producers keep their consumption confidential. The overall growth is expected the growth in GNP, in particular in phenolic resins and polycarbonates. However, due to concerns over endocrine disrupting effects, aquatic toxicity and biodegradability market shares for ethoxylates has been lost to alcohol ethoxylates (Lorenc et al., 2003).

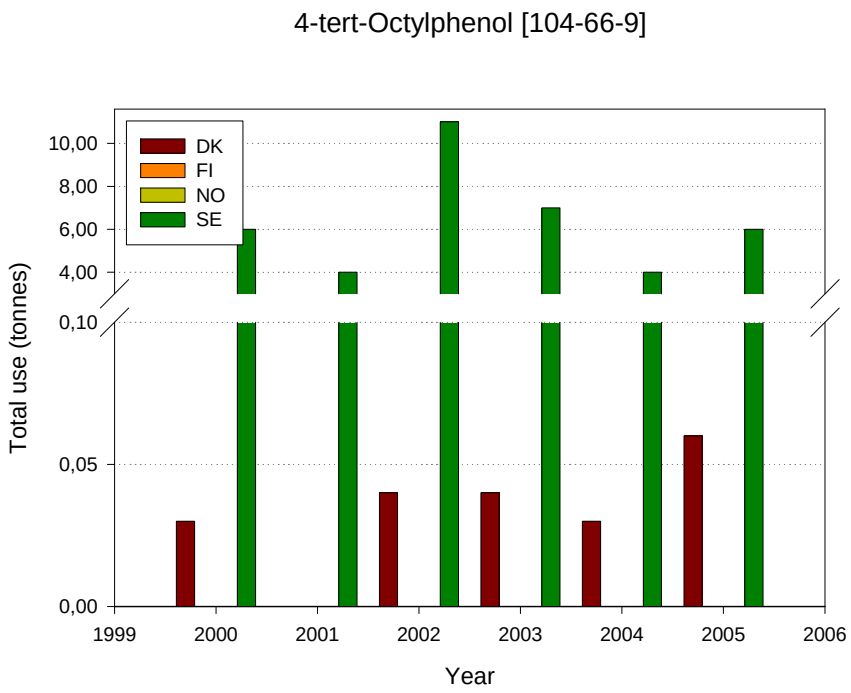


Figure 4. Yearly use of 4-tert-Octylphenol[a] [140-66-9] in Nordic countries during 2000-2005 (extracts from SPIN database); aincludes a small contribution of 4-n-OP [1806-26-4] in Denmark in 2000 (0.03 tonnes).

In the Nordic countries only a minor use in Sweden has been recorded. Data on the use of 4-tOP [140-66-9] has not been disclosed in Denmark for 2000 and 2001, and in Norway not for 2001-2005. For 4-OP [1806-26-4] data has not been disclosed for Denmark for 2001-2005. Regarding branched OP [27193-28-8] data has not been disclosed for Denmark in 2000, not for Finland in 2001 and not for Sweden in 2000-2005 (*cf.* Figure 4.).

4.2.4 Nonylphenols

Nonylphenol (NP) covers the commercial description of complex mixtures of C9-carbon alkyl-chain substituted phenols. NP is produced through the reaction of phenol with nonene, and the substitution predominantly takes place at the para position. As commercial nonene does not contain the linear C9-α-olefin, but a rather complex mixture of branched C9-olefins, the produced NP also consists of complex mixture of C9-phenols. GC analysis has revealed at least 22 isomers of p-NP. The commercially purity grades of NP include a technical grade comprising 10-12 % 2-NP, 85-90 % 4-NP and up to 5 % 2,4-di-nonylphenol (2,4-di-NP), while a high purity grade is composed of approximately 95 % 4-NP, 5 % 2-NP and only traces of 2,4-di-NP (Lorenc et al., 2003).

Concerning the CAS registration numbers there seems to have been some confusion. The EU Risk Assessment on NP simultaneously addressed CAS RN 84852-15-3 (4-NP, branched) and CAS RN 25154-52-3 (NP, unspecified) as equivalent compounds. Later, however, the CAS RN has been redefined so that CAS RN 25154-52-3 now only covers mixed isomers of straight-chain NP, while CAS RN 84852-15-2 describes the commercially relevant branched 4-NP. CAS RN 104-40-5 is used exclusive for the specifically laboratory synthesized 4-nNP.

The worldwide consumption of 4-NP is difficult to estimate because of confidentiality by some producers. Future growth has been predicted to increase but some market share in ethoxylates has been substituted by alcohol ethoxylates because of the rising concern over endocrine interference potential, aquatic toxicity and biodegradability of alkylphenol ethoxylates (Lorenc et al., 2003).

The total use of NP in EU has been estimated by HELCOM to approximately 78,500 tonnes in 1997; of this about 47,000 tonnes were used as intermediates for the production of ethoxylates (HELCOM, 2002). Major releases to the environment are expected to arise from degradation of nonylphenol ethoxylates being discharged in industrial and domestic wastewater.

In the Nordic countries the largest use has been in Sweden, but the use seems to be declining to about 10 tonnes/year. In Denmark the use of 4-NPs is < 5 tonnes/year and seems to be declining; for 4-nNP [104-40-5] data for 2004-2005 has not been disclosed.

For the mixed NP isomers the largest use has been in Denmark with more than 100 tonnes/year in 2000-2002; the consumption then dropped to < 50 tonnes/year in 2003-2004, but eventually increased again to about 470 tonnes in 2005 (*cf.* Figure 5).

Major releases to the environment are probably related to cleaning activities, to manufacturing processes of chemical products and fibres, and to municipal waste treatment (incl. sludge and storm water runoff), while minor sources may include household consumption, paint applications, use of pesticides and refinery and offshore activities.

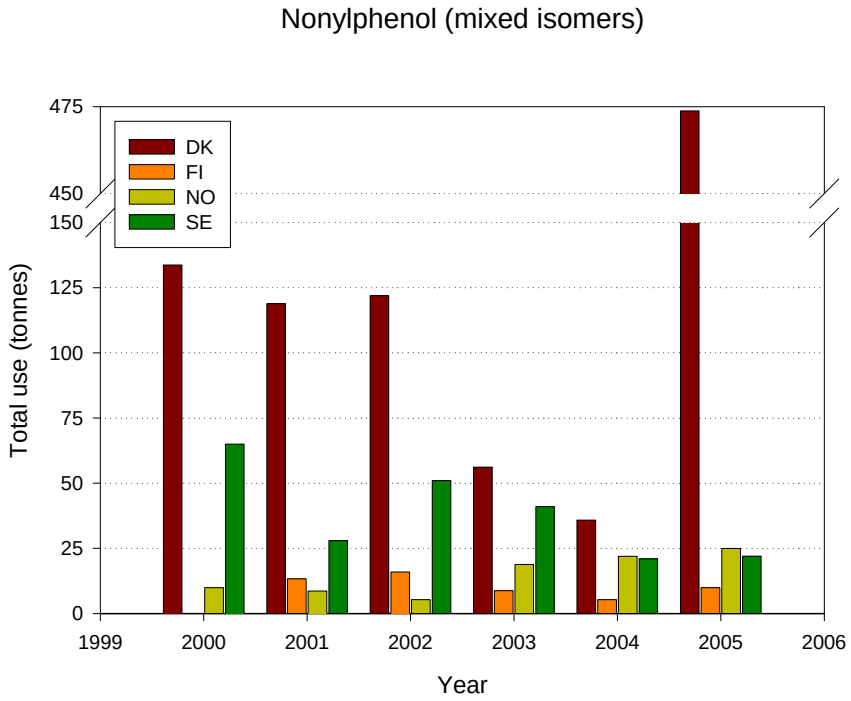


Figure 5. Yearly use of nonylphenol, mixed isomers[a], in Nordic countries during 2000-2004 (extracts from SPIN database); aincludes the following substances (listed according to importance of consumption): NP [25154-52-3], 4-nNP [104-40-5] and 4-NP, branched [84852-15-3].

4.2.5 Dodecylphenols

Besides 4-Dodecylphenol [104-43-8] this entry also covers other dodecylphenol isomers like 4-Dodecylphenol (branched) [210555-94-5], Dodecylphenol, mixed isomers (branched) [121158-58-5] and Dodecylphenol (unspecified) [21793-86-8]. Two grades of DDP are commercially available. A technical grade (an amber liquid) that contains approximately 85 % 4-DDP, 10 % 2-DDP and 5 % 2,4-didodecylphenol (2,4-di-DDP), and a high purity grade (colourless liquid) that contains approximately 95 % 4-DDP, 2 % 2-DDP and only traces of 2,4-di-DDP (Lorenc et al., 2003).

High purity 4-DDP is used to produce specialty surfactants by its reaction with ethylene oxide. According to CEPAD (2003), branched DDPs [121158-58-5] was produced and used in the European Union with an estimated tonnage of 280 tonnes in 2002, predominantly as an antioxidant in rubber and phenolic resins. At the same time, unspecified DDPs [21793-86-8] were used in quantities up to 38 tonnes for the production of oil and lubricant additives. DDPs are produced in closed and controlled processes with only a small likelihood of release to environment. It is not used directly in consumer products and only used by a few companies, and is thus not likely to have a widely dispersive release. Test

data on the dodecylphenol indicate that it is of high aquatic toxicity, highly bioaccumulative and will not degrade rapidly in the environment.

In the Nordic countries DDPs has only been used in significant amount in Sweden in 2000 and 2001 (up to 75 tonnes/year) and in Denmark in 2005 (about 53 tonnes). Data for the use of 4-DDP [104-43-8] and DDPs (unspecified) [27193-86-8] in Denmark has not been disclosed for 2000; Norway and Finland have not disclosed data on the use of DDPs (unspecified) in 2003-2005 and 2004, respectively. For use of the branched DDPs [121158-58-5] the data has been treated confidentially by all four countries for most of the period 2000-2005. Additionally, Denmark has reported a small use of 4-DDP, branched, approximately 0.02 tonnes/year during 2005-2005 (*cf.* Figure 6).

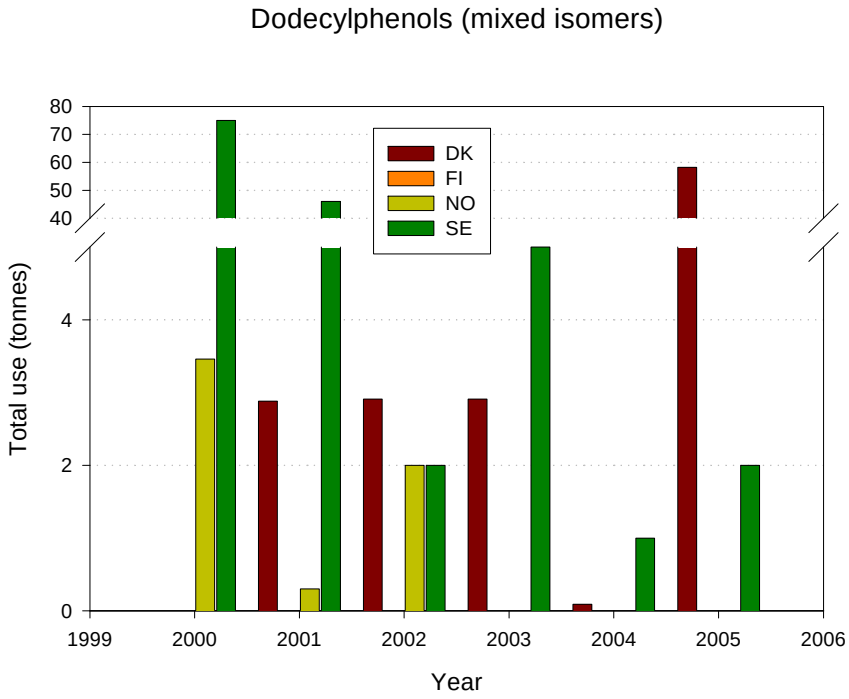


Figure 6. Yearly use of dodecylphenol (isomer mixtures)[a] in the Nordic countries during 2000-2005 (extracts from SPIN database); aincludes the following substances (listed according to importance of consumption): DDPs [27193-86-8], DDPs, branched [121158-58-5] and 4-DDP, branched [210555-94-5].

Exposure to DDPs is expected to be very low based on the physico-chemical properties and the patterns of handling and using it, and its subsequent potential release to environment may occur during production, its use as additive in petroleum products and the subsequent disposal of these.

4.2.6 4-Cumylphenol [599-64-4]

4-Cumylphenol, 4-(1-methyl-phenylethyl)phenol, a white solid, is being used as an industrial and institutional surfactant, as a tackifier in rubber manufacturing, as a lube oil additive and in polymers either as a polymer stabilizer and plasticizer. Another application is as a specialty surfactant produced by its reaction with ethylene oxide. Its major use is as chain terminator and molecular weight modifier for polycarbonates. It is also being used in pesticides and as an anti-sludge agent.

No data is available on the use of 4-Cumylphenol, neither globally, in Europe nor in Scandinavia. According to SPIN, Denmark has reported the use of 4-CP in 2000-2005, but the data has been treated confidentially. The growth rate of 4-CP is expected to parallel that of polycarbonates, in particular the grades used for producing compact discs.

4.2.7 Bisphenol A [80-05-7]

About 800,000 tonnes of Bisphenol A are manufactured in Europe pr. year (in 2002). It is primarily used for the production of epoxy and polycarbonate resins with minor uses for thermal paper and PVC industries. It is also used as an antioxidant in the polymer industry.

For the Nordic countries the use has been reported in the SPIN database as shown in Figure 7. The largest use has been reported by Finland with numbers from a little less than 400 tonnes/year to more than 600 tonnes/year except for 2003, where only 100 tonnes were used. For Denmark an unsteady use has been reported ranging from less than 50 tonnes/year in 2000, 2001 and 2004 to more than 350 tonnes/year in 2002, 2003 and 2005. For both Sweden and Norway a relatively small and steady use of less than 100 tonnes/year has been reported, except for 2002 where Norway has reported an unusually high use of about 9,000 tonnes.

The main route of environmental exposure is from its use in thermal paper and PVC industries. It is considered readily and inherently biodegradable. Its log K_{ow} value of 3.4 implies a low to moderate bioaccumulation potential in aquatic species and moderate adsorption to soil. It is supposed to partition primarily to water, and it may be relatively mobile in the environment (SIAM 14, 2002).

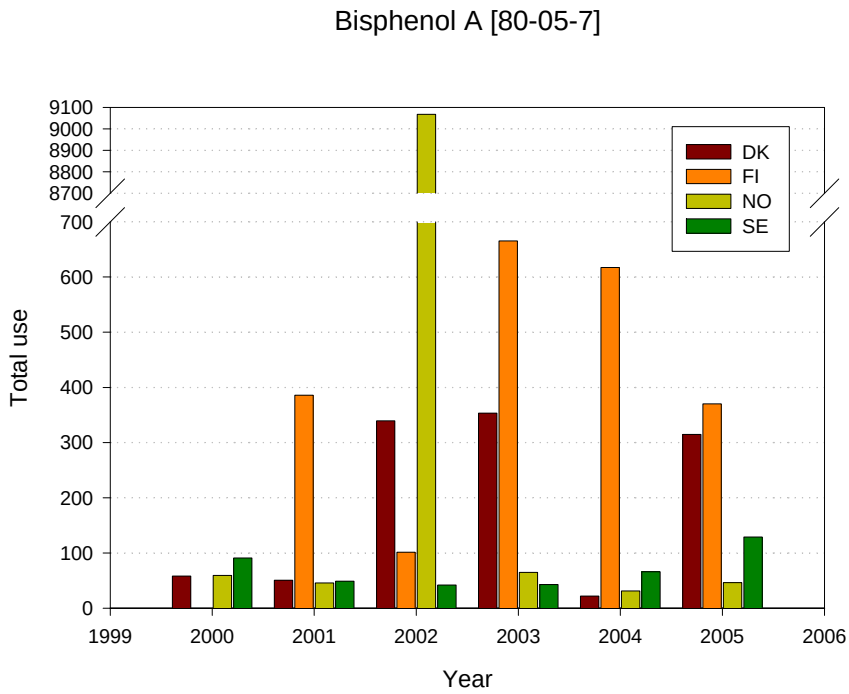


Figure 7. Yearly use of Bisphenol A in Nordic countries during 2000-2005 (extracts from SPIN database).

4.2.8 Octylphenol ethoxylates

In the European Union the use of OP ethoxylates was 1,050 tonnes in 2001 (OSPAR, 2006). The SPIN database reports data on the use of several commercial products of Octylphenol ethoxylates including ethoxylates of 4-tOP [9002-93-1], tOP [9036-19-5] and OP [9063-89-2 and 68987-90-6]; the largest use is reported for tOP ethoxylates, somewhat smaller for 4-tOP ethoxylates and very little for OP ethoxylates. For t-OP ethoxylates the largest use has been in Sweden with an average of approximately 80 tonnes/year compared to about 30 tonnes/year in Denmark. For 4-tOP ethoxylates an average use of 12-13 tonnes/year has been reported for both Denmark and Sweden. Finland has not disclosed data on the use of 4-tOP ethoxylates during 2001-2004, and for Denmark and Norway data on OP ethoxylates have been treated confidentially for several years (*cf.* Figure 8).

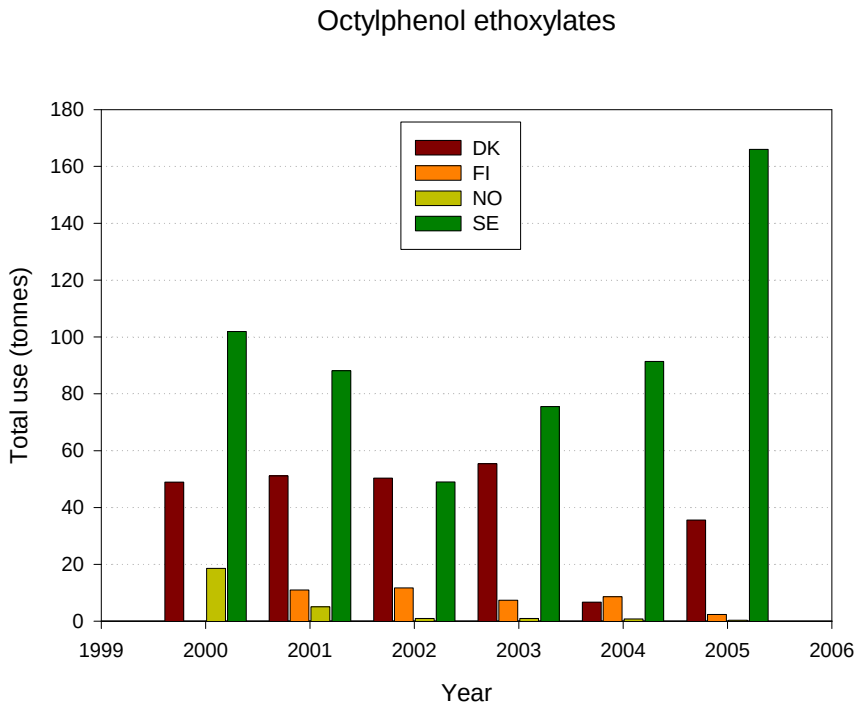


Figure 8. Yearly use of octylphenol ethoxylates[a] in Nordic countries during 2000-2005 (extracts from SPIN database); acovers the following substances (listed according to importance of consumption): tOPnEO [9036-19-5], 4-tOPnEO [9002-93-1] and OPnEO [9063-89-2].

4.2.9 Nonylphenol ethoxylates

Nonylphenol ethoxylates (NPEO) are produced by the reaction of para-NP with ethylene oxide, and the branching of the nonyl group (distribution of NP isomers) gives rise to additional structural isomers of NPEO. The most commonly used NPEO is manufactured to target nine moles of ethoxylation (NP9EO), but products ranging NP1EO to about NP18EO are generally generated. In this study only structural isomers of NP1EO, best described by CAS RN 104-35-8 (4-n-NP1EO) and CAS RN 27986-36-3 (NP1EO) are covered.

In 2002 HELCOM has estimated a total use of NP ethoxylates of some 77,600 tonnes in 1997 (HELCOM, 2002). No data is available from the SPIN database on the use of any of the more specific Nonylphenol ethoxylates mentioned above. SPIN only reports the use of the commercial product (CAS no. 9016-45-9) which is an unspecific mixture of Nonylphenol polyethoxylates. In Denmark this is used in large quantities of more than 1,400 tonnes in 2000 and 2001, down to less than 200 tonnes in 2002 and 2003 and with an increase to more than 800 tonnes in 2004 and 2005. For the other Nordic countries the use has been below 100 tonnes/year for 2000-2005, except for 2000 where Sweden used about 175 tonnes (*cf.* Figure 9).

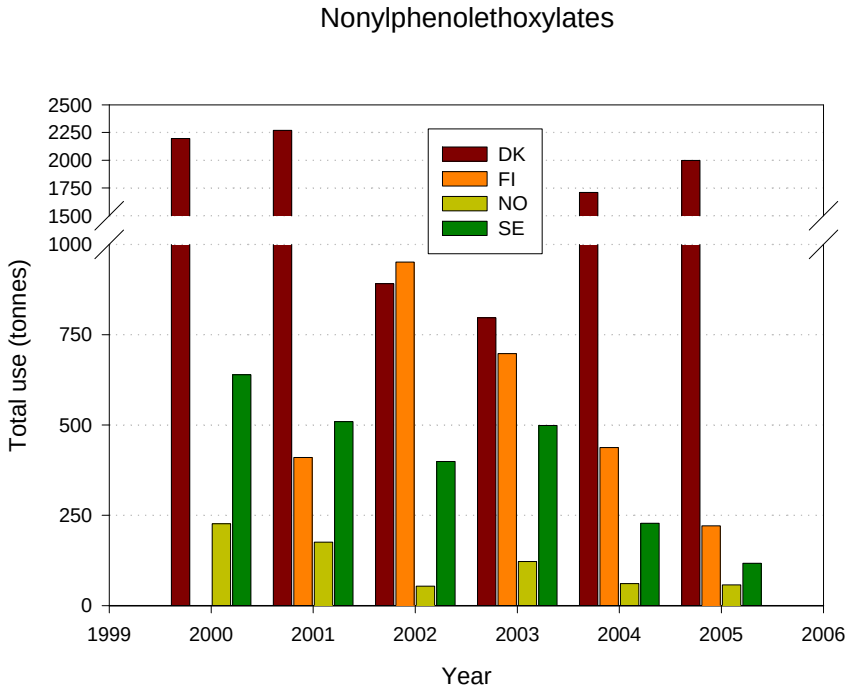


Figure 9. Yearly use of nonylphenol ethoxylatesa in Nordic countries during 2000-2005 (extracts from SPIN database); acovers the following substances (listed according to importance of consumption): NPnEO, branched [68412-54-4], NPnEO [9016-45-9], i-NPnEO [37205-87-1], 4-NPnEO [26027-38-3] and 4-NPnEO, branched [127087-87-0].

4.2.9 Tetrabromobisphenol A [79-94-7]

TBBPA is a white powder, and emissions to the environment can occur both to atmosphere (as vapour and dust) and waste water. Sources of release include BFR production sites, epoxy and polycarbonate production sites; emission sources also include use and disposal of finished articles.

The major application of TBBPA is as a reactive flame retardant in laminates (e.g. epoxy resins) for about 90% of all printed boards. It is also used as an intermediate for the production of other brominated FR products, where it is chemically bound, and thus it poses no immediate risk of emission to the environment. Additionally, TBBPA is used an additive flame retardant in ABS and phenolic plastic and is considered as substitute for polybrominated diphenylethers (PDBEs).

The total current amount produced worldwide is estimated to 150,000 tonnes/year, but it may have increased recently as TBBPA is a potential substitute for octabromodiphenyl ether. TBBPA is not produced in Europe, where the total market in 2005 was about 13,800 tonnes (9% of worldwide use. Since the free residual monomer is likely to be less than 1,000 ppm, consumer exposure to TBBPA is likely to be insignificant. Thus, at present there are no legislative restrictions on the use of TBBPA

in Europe, and it is not part of the Restriction of Hazardous Substances (RoHS) Directive. It is not part of the EU Commission list of prioritised substances, but it has been included in the 4th Priority List for assessment under the EU Existing Substances Regulation, just as it is part of the list of substances for further evaluation of their role in endocrine disruption.

Although, it is both very toxic to aquatic organisms and bioaccumulative TBBPA is not included in the priority list of the Water Framework Directive, neither in the Scandinavian list of undesirable substances nor specified in the OEM blacklist. However, the high tonnage in use and its dangerous properties give rise to concerns regarding long-term exposures, and due to its role as a BFR, TBBPA is included by the OSPAR Commission for the protection of the Marine Environment of the North-East Atlantic. Norway also considers regulating the additive use of TBBPA.

The use of TBBPA in the Nordic countries has only been reported by Denmark and Sweden. Extracts from the SPIN database reports a steady use in Denmark of about 290 tonnes/year in 2002, 2003 and 2005, while in Sweden TBBPA has been used more irregularly from more than 400 tonnes in 2000 to about 130 tonnes in 2005 (*cf.* Figure 10).

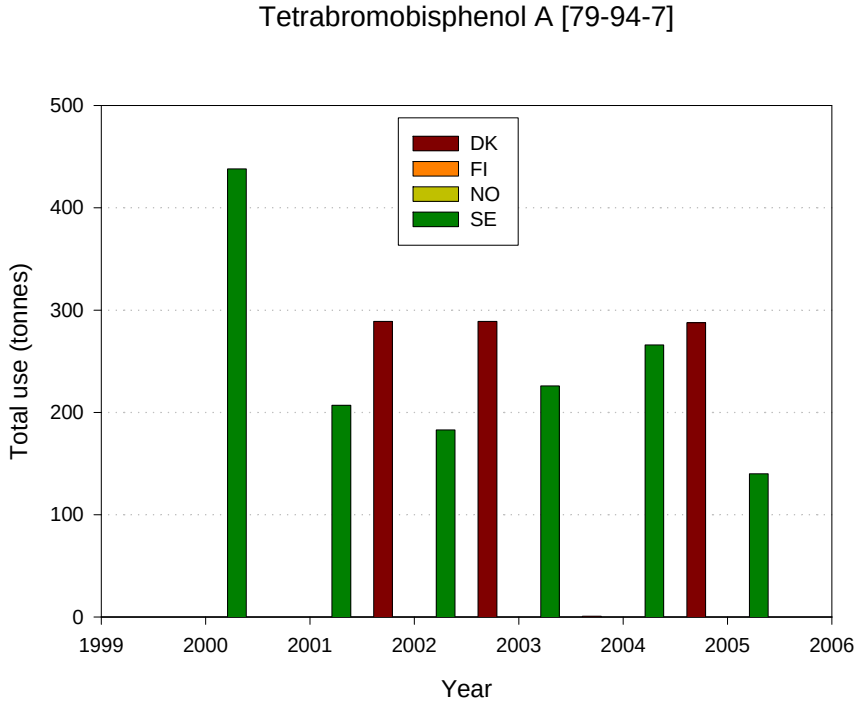


Figure 10. Yearly use of TBBPA in Nordic countries during 2000-2005 (extracts from SPIN database).

TBBPA is not readily biodegradable, but have been shown degrade (but not mineralize) under both aerobic and anaerobic conditions in soil and sediment with Bisphenol A as a major metabolite following debromination.

4.2.10 Tetrabromobisphenol A dimethylether [37853-61-5]

No data has been retrieved on the use of Dimethylated TBBPA, neither globally, in Europe or in the Nordic countries. Di-Me-TBBPA is probably not produced and used specifically as a flame retardant but may be a primary but very minor degradation product of TBBPA in the environment, although results are inconclusive (Environment Agency, 2007).

4.3 Occurrence in the environment

By searching the open literature existing data on the occurrence of the substances included in this study in various environmental samples and compartments has been retrieved. The data include are simply listed as presented in corresponding references and no attempts have been made to evaluate the robustness of the individual data.

Table 9. Concentration of phenolic compounds in different environmental matrices/compartments (µg/L or µg/kg dw)

Name	Country/ location	STP influent	STP effluents	Landfill leachate	Recipient b/f/ma	STP sludge	Soil	Sediment b/f/m	Ref.
4-tBuP	Sweden	0.03-1.9	0.003-0.075		0.0003	4.6-210		1.5-28	3
	Sweden	0.028-0.14	0.003-0.075		0.0025-0.014	<1-210	0.6-1.4	<0.06-28	13
	Sweden	0.037-0.1	0.012-0.048			<DL-76		<0.1-8.9	25
2,6-di-tBuP	Sweden	0.001-0.02	0.0005-0.004		0.0002	2.5-240		0.34-9	3
	Sweden	<0.001-0.021	0,0005-004		0.0002-0.002	0.2-240	<0.1	<0.03-9	13
	Sweden	0.004-0.019	0.0005-0.0026			<DL-67		<0.1-9	25
4-tOP	Sweden	0.17-0.36	0.05-0.08						2
	Sweden	0.03-0.16	0.01-0.22		0.003-0.006	77-8,700	1-2	0.2-88	3
	Sweden	0.03-0.16	0.051-0.22		0.003-0.007	76-8700	0.8-2.1	0.17-88	13
	USA/Minnes.[i]	1.2	<1	<1-2.8	<1				17
	Spain	0.038-0.048	0.017-0.019						22
	Germany					77-201			29
OP	Germany				<0.01-0.19(f)				1
	USA/Canada				<0.005-0.084			<10-1.080(f)	1
	Japan				<0.02-0.09(f)				1
	??						50-180[a]		1
	UK/NL				<0.1-13(b)			2-340(b)	1
	USA/Minnes.[i]	1.6	<1	<1	<1-1.6				17
	Austria	0.118-0.68	n.d.-0.106						26
	Germany	0.19-4.28	0.02-2.41			6.2-13,300[m]			28
4-NP	Sweden							230-562	2
	Sweden	1-3.4	0.03-5.5		0.033-0.33	1.7-437[b]	11-60	7.3-7,700	3
	Sweden	0.99-3.4	0.028-5.5		0.047-0.26	1.7-437[b]	11-61	6-7,700	13
	USA/Minnes.[i]	56	5-13	7.2-10	<5				17
	Greece	<DL-0.09	<DL-0.07			110			23
	Germany					2,517-3,675			29
	Sweden					25-1,100[b]			30
NP	Faroe Islands							<0.1-3.3	7
	Germany							<50-260(f)	1
	Spain				<0.1-15(f)			22-645(f)	1
	USA/Canada				<0.01-0.92(f)			<3-7200(f)	1
	Japan				<0.02-0.3(f)				1
	??						2350-4610[a]		1
	Spain				0.15-4.1(m)			<10-1050(m)	1
	Adriatic Sea				<0.02-1.2(m)				1
	UK/NL				0.04-5.8(b)			30-9050(b)	1
	USA				0.08-0.42(m				1
	Denmark							<10-610	14
	Denmark					85-320[b]			18
	Denmark					16-42			19
	Japan		0.08-2.12		0.05-1.08(f)			0.03-13.0(f)	20
	Austria	1.28-4.03	0.28-0.487						26
	Spain					12.41-1433[b,m]			27
	Germany	0.4-11.6	0.06-7.89			0.75-559[b,m]			28
DDP	Sweden	<0.02-<0.1	<0.003-<0.06		<0.004-<0.01	<0.01-1.4	<2	<2-38	13
4-CP	USA/Minnes.[i]	<1	<1-1.2	<1	<1				17
BPA	Norway						7.06-371	6.1-623.4	11
	Sweden	24[c]	0.2[d]	0.1[d]		50-7000		50-300	3
	Denmark							<5-13(b)	14
	Sweden	0.87-2.30	0.10-0.38						12
	Norway				6.1-280(f)				4
	Norway				120-623(m)			0.01-305(m)	4
	USA/Minnes.[1]	<1	<1-8.7	6.7-26.1	<1				17
	Germany	0.15-7.22	0.03-2.52			75-32,100[m]			28
	Spain								22
	Greece	0.92-1.27	0.013-0.019						23
	Various	<DL-1.01	<DL-0.22	620					24
	Sweden			<DL-32,100[b]				<50	25
	Austria	0.35-2.4	0.11-0.23	<50-350					26
	Germany	0.72-2.376	0.026-1.53			70-770			29

Table 9 *cont'd*:

TBBPA	*Sweden*						*0.04-6.15*	*0.02-39.16*	*9*
	Sweden					*<3-180*		*50-2400*	*11*
	Norway			*0.3-320*			*1.9-44*	*50-2400*	*8*
	Norway	*<3.9-21.7*	*3.1-63*					*0.02-1.59(f)*	*4*
	??					*2-600*		*0.01-39.16(m)*	*4*
	Norway							*0.1-67(m)*	*6*
	Norway						*0.04-0.89[h]*	*1.92-44.4*	*8*
	Japan			*n.d.-0.62*					*16*
	Germany	*0.9-17.4*	*<0.2-18.8*		*<0.2-20.4*	*<0.2-34.5*		*<0.2-1.83*	*21*
	Sweden					*2.8-8.5*		*<1*	*25*
	Sweden					*<0.3-220*			*31*
di-Me-TBBPA	*Norway*						*<0.9-1.2[g]*	*0.00-1.23*	*4*
	Norway						*<0.0005[h]*	*0.11-1.23*	*8*
	Sweden							*24-1,500*	*15*
	Germany		*<0.2-0.52*						*21*
OP1EO	*Sweden*	*0.057-<2.3*	*<0.000-0.056*		*0.0023-0.001*	*<10-5000*	*<1*	*0.5-7.3*	*13*
	USA/Minnes.[i]	*<1*	*<1*	*<1-7*	*<1*				*17*
	Austria	*0.042-0.66*	*n.d.-0.470*						*26*
OPEO	*USA/Minnes.[i,j]*	*<1*	*<1-8.4*	*<1*	*<1*				*17*
NP1EO	*Faroe Islands*							*<1 - <70*	*7*
	Sweden	*0.89-<5.8*	*0.003-2.5*		*0.077-<0.1*	*1.6-160[b]*	*<14-<25*	*13-870*	*13*
	Spain				*<0.1-31(f)*				*1*
	USA/Canada				*<0.02-7.8(f)*			*<3-170(f)*	*1*
	Japan				*0.04-0.42(f)*				
	??						*70-1210[a]*		*1*
	Denmark							*<5-87(b)*	*14*
	Greece	*0.75-2.63*	*<DL-5.22*			*1,010*			*23*
	Spain					*4.61-268.1[b,m]*			*27*
	Sweden					*25-200[b]*			*30*
NPEO	*Spain*				*<0.2-11(m)*			*10-620(m)*	*1*
	Adriatic Sea				*<0.02-39(m)*				*1*
	UK/NL				*0.04-76(b)*			*40-3970(b)*	*1*
	USA				*0.16-0.94(m)*			*50-3000(m)*	*1*
	USA/Minnes.[i,k]	*<5*	*<5-42*	*<5*	*<5-34*				*17*
	Various					*<ND-559,300[b,l]*			*24*
	Austria	*4.06-7.30*	*n.d.-2.58*						*26*

Notes: b = brackish, f = freshwater, m = marine; [a]sludge-amended; [b]mg/kg dw; [c]average(n=55); [d]average (n=2); [g]waste deposit; [h]bog; [i]Minnesota, USA; [j]OP2EO; [k]NP2EO; [l]sum of OPEOs and NPEOs; [m]values for primary, secondary and dewatered sewage sludge;

1) M. Petrovic et a. (2004); 2) Darnerud (2002); 3) Naturvårdsverket (2005); 4) Norwegian study; 5) M. Cantero et al. (2006); 6) Morris et al. (2004); 7) Dam and Danielsen (2002).; 8) Schlabach et al. (2002); 9) Asplund et al. (2003); 11) Fjeld et al. (2004); 12) Naturvårdsverket (2006); 13) Remberger et al. (2003); 14) NERI, unpublished data; 15) Sellström and Jansson (1995); 16) Osako et al. (2004); 17) K.E. Lee et al. (2004); 18) Grüttner et al. (1996); 19) http://www.albertslund.dk/MiljoeOgForsyning/GroentRegnskab/GroentRegnskab2005/Spildevand/MiljoefremmedeStofferI-Spildevand.aspx; 20) Isobe et al. (2001); 21) Kuch et al. (2001); 22) Hernando et al. (2004); 23) Gatidou et al. (2007); 24) Harrison et al. (2006); 25) Nihl (2004); 26) Clara et al. (2005); 27) Aparicio et al. (2007); 28) Weltin et al. (2004); 29) Bolz et al. (2001): 30) Wahlberg et al. (1990); 31) Öberg et al. (2002).

Table 10. Concentration of selected phenols in various biota samples (µg/kg dw)

Name	*Country/ location*	*Mussel*	*Fish (fresh)*	*Fish (marine)*	*Egg*	*Mammal (marine)*	*Ref*
4-tBuP	*Sweden*		*<2[c]*	*<2[c]*			*5*
2,6-di-tBuP	*Sweden*		*<0.1[c]*	*<0.1[c]*			*5*
4-tOP	*Sweden*		*<0.3-1.3[c]*	*<0.3[c]*			*5*
OP	*Denmark*	*<1.5*	*<1.5*	*<1.5*			*6*
4-NP	*Sweden*		*<6-15[c]*	*<10[c]*			*5*
NP	*Faroe Islands*	*<2[b]*					*2*
	Denmark		*35-4635[d]*	*75-6925[d]*			*6*
	Denmark	*<1-1479[d]*	*<1-108*	*<1-5.3*			*6*
	Sweden	*200-400[d]*					*13*
DDP	*Sweden*		*<10[c]*	*<10[c]*			*5*
4-CP							
BPA	*Norway*		*1.0-13.7*	*1.9-<18*			*3*
	Sweden		*0.3-35*				*4*
	Denmark	*<2-2380[d]*	*<1-63.7[d]*	*<1-233[d]*			*6*
	Sweden		*10-23[c,h]*				*12*
TBBPA	*Norway*	*0.01-0.0.03*		*0.08-0.16*			*1*
	Norway		*0.01-0.18*	*0.05-<3.82*			*3*
	Norway			*0.5-2.5*			*9*
	Sweden		*210-450[c]*	*2-210*			*4*
	UK					*0.1-418[g]*	*10*
	UK					*<5-35[g]*	*11*
di-Me-TBBPA	*Norway*	*<0.1*		*<0.50[a]*			*1*
	Denmark				*0.1-940[e]*		*7*
	Japan	*5[f]*					*8*
OP1EO	*Sweden*		*<2[c]*	*<2[c]*			*5*
OPEO							
NP1EO	*Faroe Islands*	*<30[b]*					*2*
	Sweden		*<20[c]*	*<20[c]*			*5*
	Sweden	*80-280[d]*					*13*
NPEO	*Denmark*	*<2.5*	*<2.5*	*<2.5*			*6*

Notes: [a]liver; [b]snail (Nucella lapillus); [c]lipid weight; [d]wet weight; [e]Peregrine falcon egg, lipid weight; [f]average value, wet weight; [g]Porpoise blubber, lipid weight; [h]mg/kg;

Ref.: 1) Schlabach et al. (2002); 2) Dam and Danielsen (2002); 3) Fjeld et al. (2004); 4) Naturvårdsverket (2005); 5) Remberger et al. (2003); 6) NERI, unpublished data; 7) Vorkamp et al. (2005); 8) Watanabe et al. (1983); 9) de Wit et al. (2006); 10) Morris et al. (2004); 11) Law et al. (2006); 12) Nihl (2004); 13) Wahlberg et al. (1990);

5. Methods

5.1 Sampling

At the beginning of this project a sampling protocol was submitted to all the participating sampling institutions countries to ensure representative and comparable samples from all countries. A copy of this protocol is presented in Annex 2, and here only a brief description of the sampling guidelines is given.

5.1.1 Sample types

This screening project includes analysis of selected phenols in the following environmental sample types (matrices):

- Aqueous samples
  - influent/effluent water from STPs
  - surface runoff incl. leachate from landfills
  - recipient and background water (marine and lacustrine)
- Solid samples
  - sewage sludge from STPs
  - sediments (marine and lacustrine)
  - soil
- Biological samples
  - mussels (*Mytilus edulis*)
  - fish (liver samples)
  - seabird eggs
  - marine mammals (seal/pilot whale liver)

5.1.2 Selection of sampling sites

The specific selection sampling sites lies within the responsibility of the sampling institutes in the participating countries and are based on previous experiences with some of the substances selected for this project and the objectives to study specific environmental conditions. The same institutions are also responsible for proper storage and transportation of the collected samples to the analytical laboratory (NERI, DK), that has been assigned to this screening study. Sampling sites must be indicated on the sampling protocols as accurate as possible (preferably with latitude/longitude data and a map).

5.1.3 Sampling equipment

All utensils coming in contact with the samples should be solvent rinsed with 3 times acetone and 3 times dichloromethane (DCM) following the normal cleaning. Glass and metal utensils should eventually be heated for 2 hours at 450 °C; Teflon utensils should be heated for 12 hours at 200 °C.

Polymer materials based on phenolic resins pose a significant risk of contamination with phenols and equipment made of such material must be avoided when handling, storing or shipping samples. Generally, contact with polymer utensils should be kept at a minimum, and restricted to utensils made of Teflon and Nylon, the latter only in form of special sample bags as Rilsan® bags. Furthermore, detergents contain phenols and phenol ethoxylates and therefore all sampling equipment that has been washed should successively be carefully rinsed three times each with water, acetone and DCM. Samples should be collected in the same containers in which they are to be cooled/frozen, stored and shipped to the analysing laboratory to avoid losses due to adsorption and change of vessels.

Immediately after sampling, all samples (i.e. sample containers) must be carefully labelled to uniquely identify each sample and to avoid sample mixing. For unique identification each sample must be labelled with the following information using waterproof labels and ink:

- sample type (according to the sample types listed above)
- species (for biological samples)
- date and time of sampling
- position of sampling (latitude and longitude)
- name and affiliation of sample collector

5.1.4 Sample preservation and transportation

Generally, all collected samples are preserved by cooling to 0-5° C in dark immediately after sampling in the field; only water samples requires additional preservation. After returning to the laboratory, all samples except water samples are additionally preserved by freezing down to -18° C in the dark. This preservation technique is fast, uncomplicated and effective for short-term storage. However, to prevent degradation or other changes of the analytes, all samples must be transported to the analysing laboratory (NERI, DK) as soon as possible after being collected. During transportation it is mandatory that all samples are kept frozen (water: cooled below 5° C) and in the dark.

Samples should be uniquely labelled and transported in special cooling boxes that are capable of maintaining the required low temperatures and furthermore secured sufficiently to avoid breakage (water samples, eggs). Copies of the sampling protocols should be sent together with the

samples; the original sampling protocols should be send to NERI by separate mail (or e-mailed as PDF files).

5.1.5 Aqueous samples

Special cleaned and pre-treated sample containers (1 L Pyrex redcap bottles) will be provided by NERI prior to the sampling. Generally for this screening project, water samples are collected as grab (or dip) samples, and should preferably be collected in the middle of the stream of flowing water at the sampling location. The sample collector should move around carefully in the stream not to disturb the sampling site and avoid welling up material from the bottom. The sampling bottle is rinsed three times with the sampled water before the final 1 L sample is collected. After sampling, a small amount of the water is removed and replaced with an acidifying agent (H_2SO_4) to lower pH < 3 to preserve the sample; after preservation, the water sample should be stored in a cooling box kept at 0° C (use ice).

5.1.6 Solid samples

5.1.6.1 Sewage sludge samples

Sludge samples are collected either in Rilsan® (Nylon) or Teflon (Tedlar®) bags or cleaned and pre-treated glass jars, which will provided by NERI before the sampling period. Municipal sewage sludge should be fresh from the sewage plant, collected within one hour from final dewatering/stabilization, following a period of normal weather conditions. A composite sample should consist of 3-5 sub-samples collected at random from the stabilized sludge heap. Each sub-sample should consist of 100-150 g to add up to a final amount of approximately 500 g for the composite sample. After sampling, the sample bag should immediately be placed in the dark in a cool box kept below 5° C. After returning from the field to the laboratory, the samples should be frozen down to and stored at -18°C. During transportation to NERI the sludge samples should be kept frozen all the time.

5.1.6.2 Soil samples

Soil samples are also collected in Rilsan® (Nylon) or Teflon (Tedlar®) bags, which will provided by NERI before the sampling period. At each sampling location a composite sample consisting of 3-5 sub-samples is collected at equidistant (1-2 m) positions from the centre. Before collecting the sample, the surface layer (upper 0.5-1 cm) is removed. The subsample is then collected a depth of down to 5 cm. Before adding the subsample to the sampling bag, non-soily material like stones, root and leaves should be removed. Each sub-sample must include 20-25 g depending on the number of sub-samples collected. In total, about 100 g

must be collected. After pooling all sub-samples, the composite sample is mixed by carefully shaking the sample bag. After sampling, the sample bag should be labelled as required and tightly closed as described above. The bag is the immediately placed in the dark in a cool box kept at 0° C (use ice). After returning from the field to the laboratory, the soil samples should be frozen down to and stored at -18°C. During transportation to NERI the soil samples should be kept frozen all the time.

5.1.6.3 Sediment samples

Sediment samples should be collected using either a stainless steel "Haps" sampler or a stainless steel Kayak sampler and be stored in Rilsan® bags. Sediments are collected as composite samples consisting of 3-5 sub-samples. It is important that the bottom is as undisturbed as possible before taking the samples. Sub-samples are collected at equidistant (1-2 m) positions from the centre of the sampling spot. Only the upper 2 cm of the core is used. Stones and organic material is removed before pooling the sub-samples. Each sub-sample should contain 20-25 g depending on the number of sub-samples to add up to a total of approximately 100 g of composite sample.

5.1.7 Biological samples

5.1.7.1 Mussels

Mussel samples were collected as 30 – 40 preferably bottom-dwelling individuals at 40 – 60 mm length (and pooled in two size fractions: 40-50 and 50-60 mm) after the spawning season (in October). Only living mussels were sampled, and the shells were rinsed for sand etc. with water from the sampling environment. Eventually, the mussels were depurated in a carefully cleaned glass tank for 24 hours in fresh water from the sampling station. The soft tissue (incl. the adductor muscle) from all the mussels were pooled and frozen at - 20 °C.

5.1.7.2 Fish

Fish were sampled by using either a net or a fishing rod. Mussels were collected by hand or trawl. Details on how marine mammals are collected should be provided by the collecting institute.

Fish caught during the non-breeding season is preferred over fish from the breeding period. Immediately after being caught the fish are killed and its weight, length and sex (if possible) recorded.

5.1.7.3 Marine mammals

The liver samples from seals and pilot whales were transferred to a Rilsan® bag and were stored in a cooling box kept at 0° C (use ice). As soon as possible, the samples have been transported to the laboratory, where they were frozen below -18° C.

5.1.7.4 Birds egg

Bird eggs were collected from nesting colonies early in the breeding season (and should preferably not contain embryos). At least five eggs from individual nests of the same species have been collected from each colony.

5.2 Materials

All glassware are carefully washed, rinsed and heated to 450 °C for 4 hours before being used. All solvents used are of analytical grade or better (e.g. HPLC grade).

5.2.1 Analytical standards

The following list shows the isotopically marked compounds that have been used as recovery and injection standards.

5.2.1.1 Surrogate (recovery) standards

4-*tert*-Butyl-D9-phenol-D4	$C_{10}HD_{13}O$
4-n-Octyl-D17-phenol	$C_{14}H_5D_{17}O$
4-n-Nonylphenol-13C6	$^{12}C_9{}^{13}C_6H_{24}O$
Bisphenol A-D6	$C_{15}H_{10}D_6O_2$
Tetrabromobisphenol A-13C12	$^{12}C_3{}^{13}C_{12}H_{12}Br_4O_2$
4-n-Nonylphenol-13C6 monoethoxylate	$^{12}C_{11}{}^{13}C_6H_{28}O_2$

5.2.1.2 Injection standards

Naphthalene-D8	$C_{10}D_8$
Phenanthrene-D10	$C_{14}D_{10}$
Indeno(123-cd)pyrene-D12	$C_{22}D_{12}$

5.2.1.3 Calibration standards

4-*tert*-Butylphenol	$C_{10}H_{14}O$
2,6-di-*tert*-Butylphenol	$C_{14}H_{22}O$
4-*tert*-Octylphenol	$C_{14}H_{22}O$
4-n-Octylphenol	$C_{14}H_{22}O$
Nonylphenol mixture	$C_{15}H_{24}O$
4-n-Nonylphenol	$C_{15}H_{24}O$
4-Dodecylphenol	$C_{18}H_{30}O$
4-Cumylphenol	$C_{15}H_{16}O$
Bisphenol A	$C_{15}H_{16}O_2$
Tetrabromobisphenol A	$C_{15}H_{12}Br_4O_2$
Tetrabromobisphenol A, dimethylether	$C_{17}H_{16}Br_4O_2$
Octylphenol monoethoxylate	$C_{16}H_{26}O_2$
Nonylphenol monoethoxylate	$C_{17}H_{28}O_2$

5.3 Sample preparation

5.3.1 Extraction and clean-up

5.3.1.1 Water samples

Before extraction the water sample was equilibrated at room temperature. If containing particles or debris the water was filtered through pre-cleaned glass wool and transferred to a 2 L separating funnel before being spiked with 1 mL of mixture of recovery standards. The sample was then extracted by 3 x 50 mL dichloromethane (DCM). The combined extracts were dried over Na_2SO_4 and concentrated to 1 mL by rotary evaporation/gentle N_2 blowing. Before being analyzed the concentrated extract was derivatized using a silylating mixture (BSTFA-TMS, see 5.3.3).

5.3.1.2 Solid samples

After being thawed the sample (sludge, soil or sediment) was thoroughly homogenized before an aliquot of approximately 10 g was weighed and transferred to a pre-cleaned glass shaking flask and spiked with a 1 mL recovery standard. After 1 hr. 30-40 mL of DCM was added and the sample was extracted for 1 hr. at a shaking table (300 rpm). The solvent was decanted and another 30-40 mL of was added and the sample extracted for another 1 hr. at the shaking table. Again the solvent was decanted, and the combined extracts were filtered through pre-cleaned glass wool, dried over Na_2SO_4 and evaporated to 1 mL. The soil and sediment extracts were then derivatized directly. Sludge extracts were further cleaned-up using a SPE-SiO_2 column (2 g) conditioned with hexane and eluted with 20 mL hexane-acetone (1:1) and 10 mL DCM. The combined eluates were subsequently evaporated to 1 mL and derivatized with BSTFA-TMS (see 5.3.3).

5.3.1.3 Biological samples

Biological samples were thoroughly homogenized before an aliquot of 5-10 g were collected and thoroughly mixed with a sufficient amount of Hydromatrix to become a dry powder. The dried sample was quantitatively transferred to a pre-cleaned Soxhlet thimble and spiked with surrogate standards. After a couple of hours the sample was extracted for approximately 20 hrs. using a mixture of hexane-acetone-DCM (2:2:1). The extract was filtered through pre-cleaned glass-wool, dried over Na_2SO_4 and evaporated to 1 mL using a rotary evaporator and gentle N_2-blowing.

The concentrated extract was redissolved in 10 mL hexane and extracted with 2x25 mL acetonitril saturated with hexane. The combined acetonitril fractions are then concentrated and redissolved in hexane. following the procedure of Tsuda et al. (2000). Eventually, the biota extracts in hexane were further cleaned-up on a SPE-SiO_2 column (2 g).

Before being analyzed the extracts were derivatized using BSTFA-TMS (see 5.3.3).

5.3.3 Derivatization

100 µL of pre-cleaned extract was transferred to a GC-vial and mixed with 100 µL of BSTFA-TMS (N,O-bis(trimethylsilyl)trifluoroacetamide-trimethylchlorosilane, 9:1 mixture). After capping the vial, the sample was heated to 60 °C for 30 min. Silylation as a tool for derivatization in mass spectrometry has recently been reviewed by Halket & Zaikin (2003).

5.4 GC-MS analysis

5.4.1 GC parameters

All derivatized extracts are analysed using a Thermo Finnigan DSQ GC-MS instrument equipped with a PAL autosampler. GC-inlet: split/splitless injector operated at 280 °C at programmed flow (He) of 1-2.5 mL/min. with surge pressure (150 kPa for 0.7 min) during injection. Injection volume: 2 µL. Temperature programme: 90 °C for 1 min.; 90-240 °C @ 10 °C/min.; 240 °C for 4 min.; 240-270 °C @ 20 °C/min.; 270 °C for 18.5 min; total: 40 min.

5.4.2 MS parameters

The quadrupole is operated in single-ion-monitoring (SIM) mode at a source temperature of 200 °C and an ionising current of 70 eV. To detect selected compounds, recovery standards and injection standards, fragment ions are recorded in eight different windows with 3 to 8 ions in each according to Table 11.

Table 11. GC-retention times, MS-groups, dwell times and quantification ions used for detecting phenolic substances.

Compound	*MW (g/mole)*	*GC-Rt (min.)*	*MS-window*	*Dwell-time (msec.)*	*Quant. ion (m/z)*
Surrogate standards:					
*4-*tert*-Butyl-D9-phenol-D4*	*163.30*	*7.4*	*1*	*100/100*	*217/ 235*
4-n-Octyl-D17-phenol	*223.44*	*12.7*	*3*	*100*	*295*
4-n-Nonylphenol-13C6	*226.38*	*13.9*	*4*	*100*	*298*
Bisphenol A-D6	*234.33*	*16.8*	*6*	*100*	*378*
Tetrabromobisphenol A-13C12	*555.9*	*29.4*	*8*	*100*	*371*
4-n-Nonylphenol-13C6 monoethoxy-late	*270.43*	*17.0*	*6*	*100/100*	*185/342*
Injection standards:					
Naphthalene-D8	*136.22*	*5.6*	*1*	*50*	*136*
Phenanthrene-D10	*188.30*	*12.6*	*3*	*50*	*188*
Indeno(123-cd)pyrene-D12	*288.41*	*29.3*	*8*	*100*	*288*
Calibration standards/Quantified compounds:					
*4-*tert*-Butylphenol*	*150.22*	*7.5*	*1*	*300/300*	*151/222*
*2,6-di-*tert*-Butylphenol*	*206.33*	*8.6*	*2*	*300*	*191*
*4-*tert*-Octylphenol*	*206.33*	*11.0*	*2*	*300/300*	*179/278*
4-n-Octylphenol	*206.33*	*12.9*	*3*	*100/300*	*179/278*
Nonylphenol, mixture	*220.36*	*12.0-12.6*	*3*	*100/100/300*	*179/193/221*
4-n-Nonylphenol	*220.36*	*13.9*	*4*	*300/100*	*179/292*
Dodecylphenol, mixture	*262.44*	*14.1-14.9*	*4*	*100/400*	*193/221*
4-Cumylphenol	*212.29*	*13.7*	*4*	*300*	*269/284*
Bisphenol A	*228.29*	*16.8*	*6*	*200/100*	*357/372*
Tetrabromobisphenol A	*543.90*	*29.2*	*8*	*300/300/300*	*671/673/675*
Tetrabromobisphenol A, dimethyl-ether	*571.95*	*26.2*	*7*	*200/600/200*	*555/557/559*
Octylphenol monoethoxylate	*250.38*	*16.0*	*5*	*400/400*	*179/322*
Nonylphenol monoethoxylate	*264.41*	*17.0*	*6*	*200/100*	*179/336*

Notes: Parameters used with a Termo Finnigan DSQ GC-MS.

5.4.3 GC-MS chromatograms

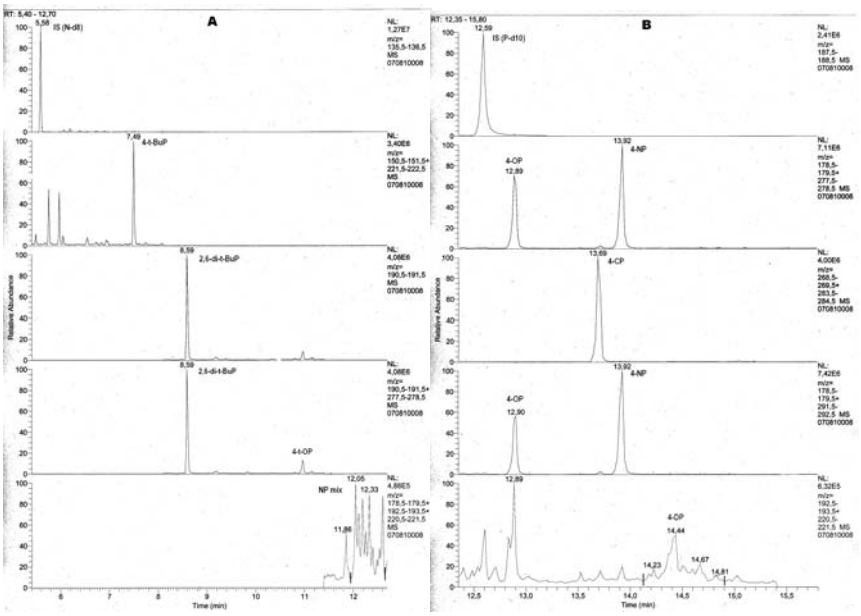


Figure 11. GC-MS chromatograms of selected phenols; A) and B) calibration and injections standards (IS).

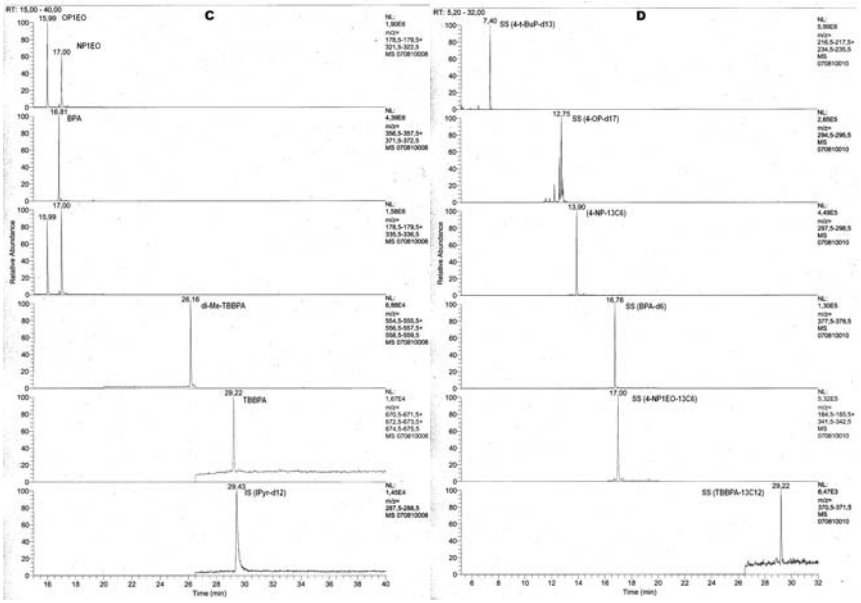


Figure 12. GC-MS chromatograms of selected phenols; C) calibration and injection standards (IS) and D) surrogate standards (SS).

5.5 Validation and control

5.5.1 Linearity

5.5.1.1 Calibration

Most of the calibration standards showed good linearity in the GC-MS analysis with R^2-values in the range of 0.993-0.999. 2,6-di-*tert*-Butylphenol showed a slightly inferior linearity with R^2-values in the range of 0.96-0.985. 2,6-di*tert*-Butylphenol is the only compound which is not readily derivatized. However, it appeared that during a GC-MS run the response-ratio of the signal of the calibration standard decreased steadily indicating that 2,6-di-*tert*-Butylphenol perhaps is very slowly derivatized.

5.5.2 Recoveries

The average recovery for the different matrices is shown in Table 12. Due to interference in the chromatograms it was not possible to use 4-n-Nonylphenol-$^{13}C_6$ monoethoxylate as a recovery standard except in sediments. All data have been corrected for recovery before reporting. For the biota samples, however, there were also some problems with TBBPA and bisphenol A, and for some samples it was not possible to quantify the recovery due to interferences.

Table 12. Average recoveries of surrogate standards.

Sample type	Water		Solid		Biota	
	average	typical range	average	typical range	average	typical range
4-*tert*-Butyl-D9-phenol-D4	52%	35-85%	78%	65-95%	76%	30-120%
4-n-Octyl-D17-phenol	78%	45-125%	102%	80-120%	71%	35-125%
4-n-Nonylphenol-13C6	103%	75-150%	100%	80-120%	100%	75-150%
Bisphenol A-D6	119%	85-175%	86%	55-120%	-	-
Tetrabromobisphenol A-13C12	75%	50-110%	67%	50-90%	-	-
4-n-Nonylphenol-13C6 mono-ethoxylate	-	-	96%	75-120%	-	-

5.3.3 Reproducibility and precision

5.3.3.1 Replicate analyses

Eight water samples were spiked with a mixture of the phenolic compounds. The concentration of the single compounds was determined in relation to their various detection limits. The results are shown in Table 13.

Table 13. Average and standard deviation of eight replicate analyses of a water.

Concentration (ng/L)	average	standard dev	%dev
4-tBuP	175,7	281,3	166,0
2.6-di-tBuP	45,2	21,7	48,2
4-tOP	63,6	12,0	18,9
4-OP	52,5	3,1	5,9
NP-mix	116,9	36,9	32,5
4-NP	15,6	1,4	8,5
DDP	641,6	86,7	13,7
4-CP	8,4	1,1	12,7
BPA	16,5	1,8	11,2
TBBPA	51,4	14,5	27,8
Me-TBBPA	50,0	7,3	14,4
OP1EO	11,2	2,2	19,3
NP1EO	31,6	2,8	8,8

The standard deviations are elevated for four compounds. There are different explanations for the different compounds. For 4-tBuP the problem is probably related to generally elevated blank values. For 2,6-di-tBuP it is probably due to a slow derivatization as mentioned above. Regarding the NP-mix this is quantified over a range of peaks which inherently increases the uncertainty, and for TBBPA it is most probably related to the low response the electron-impact GC-MS analysis. These explanations have to some degree been verified by the data in Table 14, where the same spiked water samples each were analyzed in triplicates in order to estimate the uncertainty from the GC-MS analysis.

Table 14. Average and standard deviation of triplicate analysis of the eight replicate water samples by GC-MS.

Concentration (ng/L)	average	standard dev	%dev
4-tBuP	4083,3	88,3	2,1
2.6-di-tBuP	47,5	4,9	10,5
4-tOP	63,6	5,7	9,0
4-OP	52,8	3,9	7,4
NP-mix	108,1	20,2	19,9
4-NP	18,9	2,8	14,7
DDP	926,7	87,0	9,4
4-CP	8,8	1,1	13,0
BPA	20,2	2,0	10,0
TBBPA	85,1	16,6	19,3
Me-TBBPA	50,0	11,0	22,0
OP1EO	11,9	1,2	10,4
NP1EO	31,8	2,5	7,9

5.3.3.2 Sample replicates

During the analysis of the collected samples approximately every tenth sample was analyzed in duplicate. It has been difficult to perform statistical analysis on the duplicates. Most of the duplicates were water samples, and for these samples a large number of measurements were below detection limits. For the sludge samples it turned out to be quite difficult to prepare homogeneous samples, and that increased the variation considerably. High variation between replicates was observed for some samples especially for NP-mix, DDP and in some cases also OP1EO and BPA, but generally the agreement between replicate analyses was satisfactory. Replicate analyses for the different types of samples are discussed in more details in Chapter 7.

5.3.3.3 Field replicates

Parallel field replicates or parallel samples were collected for most sample types, and they are described in more details in Chapter 7. Especially for wastewater, sludge and run-off samples high deviations between parallel samples were observed. This could be due to the fact that it is difficult to sample truly parallel samples in these matrices, and subsequently difficult to homogenize some of these sample types. As describe above, especially NP-mix, DDP and in some cases also BPA which showed higher deviations.

5.5.4 Detection limits

Detection limits were calculated as 5 times the signal-to-noise ratio. For 4-Dodecylphenol this approach was not possible due to interference from the column. In this case the lowest standard which indicated linearity was used as the detection limit.

5.5.5 Blanks

Laboratory blanks ware analyzed in all extraction batches. The values of the blanks were subtracted from the sample data before reporting the actual values.

Values for laboratory blanks were in generally low except for 4-tBuP, DDP and TBPPA. For 4-tBuP it has not been possible to find any obvious reasons for the elevated blank values. For DDP the elevated blanks are likely related to the interferences in the chromatograms i.e. probably column bleeding. For TBPPA the elevated blank values may be related to cleaning of the glassware. For some of the water analyses some of the glassware was rinsed with DCM after the normal cleaning procedure instead of heating it to 450 °C for four hrs. In the replicate experiment all glassware were heated to 450°C, and the blank values for these experiments were considerably lower, approximately 30 ng/L, than when the

glassware was just rinsed with DCM. So the cleaning procedure appears to be very important in connection to analysis of TBBPA.

In table 15 the average blind values for the different sample types are listed.

Table 15. Average values for laboratory blanks.

Sample type	Water	Solid	Biota
	ng/L	µg/kg	µg/kg
4-tBuP	650	190	85
2.6-di-tBuP	7	<0,5	<3
4-tOP	<1	<5	<6
4-OP	<1	<0,5	<1
NP-mix	28	10	40
4-NP	<1	<0,1	<1
DDP	130	50	150
4-CP	<1	<0,1	<1
BPA	3	2,5	2
TBBPA	110	35	<5
Me-TBBPA	0	<2	<10
OP1EO	1,5	<1	<1
NP1EO	3	<1	<2

5.6 Literature survey of relevant methodologies

In 2001 Petrovic and Barceló published a literature survey on the extraction and identification techniques used to analyze phenolic substances in environmental samples. The survey included phenolic endocrine disrupting compounds, and here it has been extended to include other phenolic substances included in this study. Another review on analytical methods for the determination of alkylphenolic surfactants and flame retardants in waste water and sewage sludge has recently been published by Scrimshaw et al. (2004).

Generally, analytes in aqueous samples are trapped on pre-packed SPE (mostly C18) and then recovered using a polar solvent like methanol (MeOH). If further clean-up is necessary this is typically accomplished by eluting the extract through a normal-phased column (e.g. silica gel, SiO2). The eventual analysis is mostly done by GC-MS or LC-MS.

Solid samples are extracted various techniques ranging from traditional shaking, ultrasonic and Soxhlet extraction to newer techniques like microwave assisted extraction (MWAE), pressurized liquid extraction/accelerated solvent extraction (PLE/ASE); supercritical fluid extraction (SFE) is also used occasionally. Subsequent clean-up is mostly obtained by eluting the extract through a reversed phased (e.g. C18) or a normal phased (e.g. SiO_2, Al_2O_3 or Florisil) column; the choice of technique of-

ten depends on the eventual analytical method, LC-MS or GC-MS, respectively.

Biological samples are either extracted by the same techniques used for solid samples or simply homogenized in an appropriate solvent (methanol, hexane-acetone). Depending on the lipid content various clean-up methods are used. Lipids can be destroyed by conc. sulphuric acid, either directly or on a SiO2 column saturated with conc. acid. The lipid can also be digested by boiling it with alkalized methanol. The lipid content may also be partitioned between hexane and acetonitrile or a first clean-up may be accomplished using gel permeation chromatography (GPC). Often a second clean-up is obtained by eluting the extract through a normal-phased column.

The extracted analytes are generally analysed either by LC-MS or GC-MS, occasionally also by LC/fluorescence or LC/UV. Liquid chromatography is probably more straightforward than GC-MS as the phenolic compounds can be well separated on a reversed-phased column (e.g. C18) and detected with good response using either fluorescence or mass spectrometry. With GC-MS it may be more problematic as the chromatographic performance of some free phenols is less satisfying. Consequently, phenols are often derivatized before being analysed by GC-MS to obtain better chromatographic performance and response. Often silylating agents like BSTFA (bistrimethylsilyltrifluoroacetamide) are used for derivatization of phenols.

Table 16. Literature survey of analytical methods applied for the determination of phenolic substances and alkylphenol ethoxylates in environmental samples.

Compound	Sample	Extraction	Clean-up	Identification	Ref.
BPA, OP	Fish	MWASE[a]	SPE-C18[b], SPE-NH2	LC/APCI-MS[c]	1
BPA	Sea water, spring water	LLE[d] (DCM[e])		GC-MS[f]	2
BPA	River/sea/ground water	Micro LLE (DCM)		GC-MS	3
BPA, OP, NP, NPEO, NPEC	Sewage sludge	Ultrasonic solvent extraction	SPE-C18	LC/(APCI/ESI[g])-MS	4
BPA	Riwer water	LLE (toluene)		LC/fluorescence + GC-MS	5
NP, OP, NPEO	Riwer water, sediment	LLE (DCM), Soxhlet (DCM)		GC-MS	6
NP, OP	Marine sediment	Soxhlet (DCM)		LC/fluorescence	7, 8
NP, OP, NPEO	Fish, sediment, water	LLE, steam distillilation (c-hexane)		GC-FID[h], GC-MS	9
NP, OP	Waste water effluents	SPE (Empore disk)		LC/fluorescence	10
NP, NPEC, OP, APEO	Waste/ground water	LLE (DCM)		LC/UV[i], GC-MS	11
NP, OP	Sewage sludge, sediment	SFE (CO2)[j]		GC-MS	12
NP, NPEO, NPEC	Waste water effluent	SPE-C18		LC/APCI-MS	13, 14
NP	River sediment	PLE[k]		GC-MS	15
NP, NPEO	Freshwater organisms	Steam distillation		LC/fluorescence	16
NP, OP, NPEO	Water, sediment, fish	Ultrasonic solvent extraction	SPE-C18	GC-MS	17
TBBPA	Sewage sludge, sediment	Shaking, sonication (DCM/MeOH[q])	SPE-C18	LC/ESI-MS/MS	18
4-tBuP, 2,6-di-tBuP, 4-OP, 4-tOP, 4-tOP1EO, 4-NP, 4-NP1EO, 4-DDP	Water, sludge, sediment, fish Waste water, sewage sludge	Water: Sludge/sediment: acetone, pentane/MTBE Fish: SPE-C18, SPE-NH2	SPE-ENV+SiO2[l]	GC-MS	19
NP, NPEO, BPA	Sludge, sediment, biota	Water: Solids: sonication (MeOH)	SPE-C18	GC-MS	20
HBCD, TBBPA	Sewage sludge	Soxhlet, homogenization (acetone-hexane)	GPC[m], SiO2	LC-MS	21
4-NP, BPA	Waste/surface water, sewage sludge, sediment, biota	Steam distillation, Soxhlet, SFE, PLE	Al2O3[n]	GC-MS	22
OP, NP, OPEO, NPEO	Leachate, sewage sludge, soil	SPE-C18, biota: MSPD[o]	Soxhlet Al2O3	LC/fluorescence, LC-MS	23
OP, NP, BPA, estrogens	Water, sediment, fish	SPE-C18, Soxhlet (MeOH)	GPC, SiO2	GC-MS	24
OP, NP, OPEO, NPEO	Water Sediment, biota	SPE-ENV+, PLE (acetone-hexane)	SPE-NH2	LC/fluorescence, GC-MS	25
TBBPA, BFRs		SPME[p]		GC-MS	26
4-tOP, 4-NP, 4-CP, BPA		MWE[a] (DCM, MeOH)	SPE-Envi Chrom P	GC-MS, LC-MS	27

Notes: [a]Microwave-assisted solvent extraction; [b]solid phase extraction with octadecylsilane (C18) or aminosilane(NH2); [c]LC, liquid chromatography; APCI, atmospheric pressure chemical ionization mass spectrometry; [d]liquid-liquid extraction; [e]Dichloromethane; [f]gas chromatography-mass spectrometry; [g]electrospray ionization; [h]gas chromatogratography-flame ionization detection; [i]ultraviolet detection; [j]supercritical fluid extraction with carbon dioxide; [k]pressurized liquid extraction; [l]silica gel column clean-up; [m]gel permeation chromatography; [n]alumina oxide column clean-up; [o]matrix solid phase dispersion; [p]solid-phase microextraction; [q]methanol;

Ref: 1) Pedersen & Lindholst (1999); 2) Olmo et al. (1997); 3) Gonzales-Casado et al. (1998); 4) Petrocic & Barceló (2000); 5) Markhan et al. (1998) ; 6) Bennie et al. (1997) ; 7) Khim et al. (1999a); 8) Khim et al. (1999b); 9) Lye et al. (1999); 10) Snyder et al. (1999); 11) Rudel et al. (1998); 12) Bennett & Metcalfe (1998); 13) Castillo & Barceló (1997); 14) Castillo et al. (1997); 15) Ding & Chen (2000); 16) Ahel et al. (2003); 17) Blackburn et al. (1999); 18) Saint-Louis & Pelletier (2004); 19) Remberger et al. (2003); 20) Gatidou et al. (2007); 21) Morris et al. (2004); 22) Meesters & Schröder (2002); 23) Voogt et al. (2000); 24) Weltin et al. (2004); 25) Rice et al. (2003); 26) Polo et al. (2006); 27) Stuart et al. (2005)

6. Sampling programme

6.1 Overall sampling schedule

For this screening project the steering group had decided that each of the six participating countries would provide 20 environmental samples (i.e. water, sludge, soil/sediment and biota). The sampling strategy regarding sample type and sampling sites was decided by the steering group based on known or assumed application and use of the phenolic substances. Following that, each participating country was responsible for collecting and shipping of samples to NERI for analysis and for providing the subsequent sampling data according to a general sampling protocol (Annex 1) distributed by NERI. In the table below an overview of all samples are listed, and in Annex 2 detailed sampling schemes for each country are listed. On the map below (Figure 13) the sampling positions for each country have been marked.

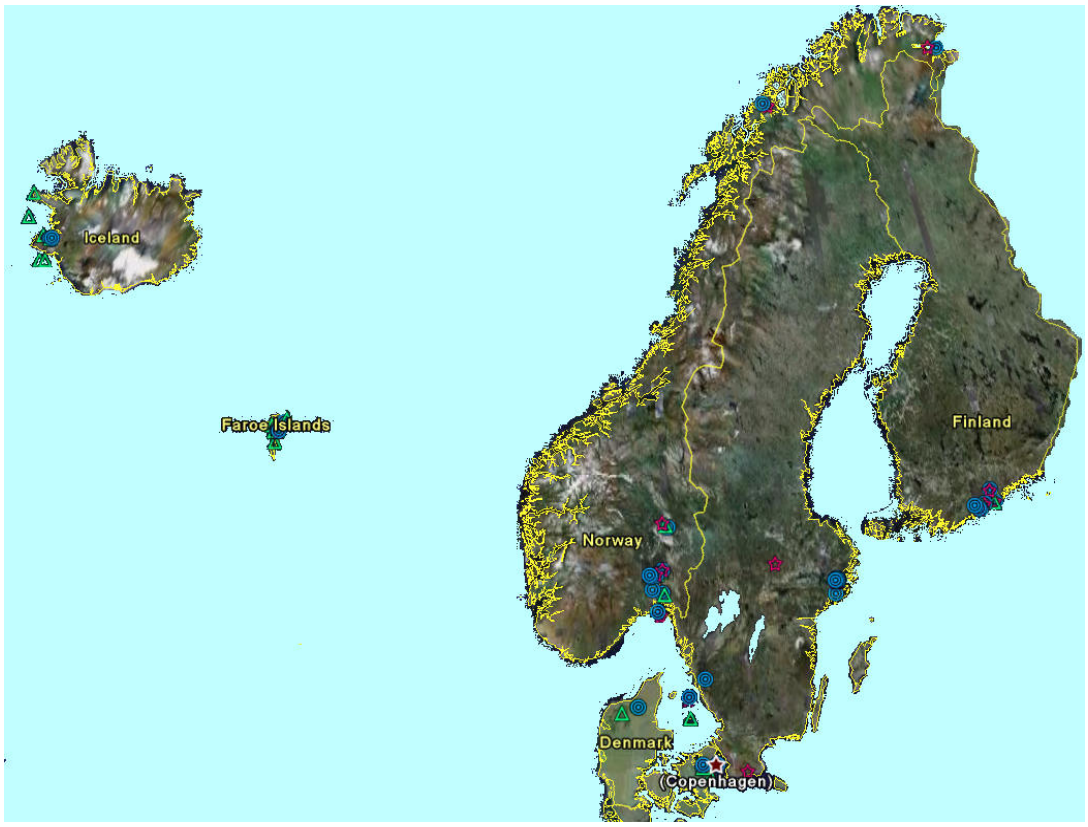


Figure 13. Sampling stations in the Nordic countries; colour codes: ◎ (blue), aqueous samples, ✯ (red), solid samples (sludge, soil, sediment), △ (green), biological samples (mussels, fish, eggs and marine mammals).

Table 17. List of number and types of samples provided by each country for the phenols screening project.

Sample type	*Aqueous samples*			*Solid samples*			*Biological samples*			
Country	*waste*[1]	*runoff*	*recipient*[2]	*sludge*	*sediment*[2]	*soil*	*Mussel*[3]	*Fish*[4]	*Egg*[5]	*mamm.*[6]
Denmark	*3*	*--*	*5*	*1*	*4*	*--*	*2*	*2*	*--*	*3*
Faroe Islands	*5*	*--*	*2*	*2*	*3*	*2*	*3*	*1*	*2*	*2*
Finland	*6*	*--*	*3*	*3*	*2*	*--*	*--*	*6*	*--*	*--*
Iceland	*4*	*--*	*4*	*4*	*--*	*--*	*--*	*6*	*--*	*--*
Norway[7]	*4*	*2*	*6*	*4*	*6*	*--*	*2*	*5*	*--*	*--*
Sweden	*--*	*6*	*5*	*4*	*6*	*--*	*--*	*--*	*--*	*--*
Total	*22*	*8*	*25*	*18*	*21*	*2*	*7*	*20*	*2*	*5*

Notes: [1]Includes both influent and effluent water from sewage treatment plants. [2]Includes samples from both lacustrine, brackish and marine environment. [3]Blue mussels. [4]Includes Atlantic cod (Iceland and Norway), European perch (Norway), Nothern pike (Finland), Sand goby (Denmark) and Trout (Norway); [5]Black guillemot (The Faroe Islands); [6]Includes liver from marine mammals: harbour seals (Denmark) and pilot whales (Faroe Islands). [7]Norway has made a special agreement to include 9 additional samples in their sampling programme.

6.2 National sampling programmes

In the following sections a brief description of the sampling programme and sample types and positions for each country is given. Further details are given in Appendix B.

6.2.1 Denmark

6.2.1.1 Waste water treatment plants (STP)

Samples in relation to two STPs were included in the programme. From Lynetten in Copenhagen (the biggest STP in Denmark) samples included one influent, one effluent and one recipient (Øresund) water sample. From the plant itself one sludge sample was included, while a sediment sample and one composite blue mussel sample from positions in Øresund close to the plant were included.

From Bjergmarken, another but much smaller STP in Roskilde (smaller town with some 50,000 inhabitants) one effluent and one recipient (Roskilde Fjord) water sample were included.

6.2.1.2 Hot spots

Due to its physical form, hydrodynamics (long narrow fiord with limited water exchange) and being a recipient for several smaller towns Roskilde Fjord (brackish) is considered a hot spot environment. Therefore, four samples were included from here: one recipient water, one sediment and two composite fish samples.

6.2.1.3 Background sites

Samples from three background sites were included. From Limfjorden (brackish environment) two recipient water samples and two sediment samples were included from a reference sampling site in the middle (west-east) of Limfjorden. From Blinderøn, a small sand bank in Løgstør

Bredning, the Western part of Limfjorden, a composite seal liver sample was included.

From another reference background site in Kattegat one recipient water sample and one sediment sample were included together with a composite seal liver sample from Anholt, a small island close to the reference station.

Finally, a composite seal liver sample was included from Køge Bugt, southern part of Øresund.

6.2.2 The Faroe Islands

6.2.2.1 Waste water treatment plants (STP)

Samples from two STPs were included. From the Torshavn area samples from both Sersjantvikin STP and Landssjúkrahúsið (hospital) STP were collected. From each STP one influent and one effluent water sample and one sludge sample were included.

6.2.2.2 Waste deposits (WD)

From Húsahagi WD one landfill leachate sample and one soil sample were included, and from Havnadalur WD one soil sample was included.

6.2.2.3 Hot spots

From Torshavn harbour one sediment sample, one composite fish sample and two composite blue mussel samples were included. From the Klaksvik (northern part of the islands) area one recipient water sample and one sediment sample were included. From the Vágsbotn and Gøtuvík areas one recipient water sample and one sediment sample, respectively, were included.

6.2.2.4 Background sites

Samples from background sites were included. From the Nólsoyar fjord area one composite blue mussel sample was collected. Two composite pilot whale liver samples were provided from the Hvannasund grind, and from each of the islands Koltur and Skúvoy one composite seabird egg (Black guillemot) sample were included.

6.2.3 Finland

6.2.3.1 Waste water treatment plants (STP)

Three municipal STPs were sampled. From both the Viikinmäki STP in Helsinki and the Suomenoja STP in Espoo three samples were included: one influent and one effluent water samples and as well as one sludge sample. From the more remote and small STP in Pornainen one effluent water and one sludge sample were included.

6.2.3.2 Waste deposits (WD)

From the Espoo WD one effluent (or runoff) water sample was included.

6.2.3.3 Hot spots

From the Helsinki city bay area near the port one recipient water sample, one sediment sample and four composite (pooled) fish (pikes) samples were included. The sampling area is in a brackish environment.

From the Espoo coastal bay area (brackish) another two composite fish (pikes) samples were collected.

6.2.3.4 Background sites

Samples from the Espoo coastal sea area (brackish) included two recipient water samples and one sediment sample. The outlet pipe for effluent waters from the Espoo City STP is located near the sampling area.

6.2.4 Iceland

6.2.4.1 Waste water treatment plants (STP)

Non-dehydrated and non-processed solid sludge samples were collected from two STPs in Reykjavík, Klettagarðar (samples KL-1 and KL-2) and Ánanaust (samples AN-1 and AN-2). These plants process sewage from different parts of Reykjavík and its suburban areas. Additionally, water samples were collected from two sewage streams in Mosfellbær, a suburban area of Reykjavík. One of the streams goes through a septic tank before being released at a nearby coast, and the sample MB-1 was collected upstream the septic tank. The second stream is part of the influent to a STP in Reykjavík (sample MB-2).

6.2.4.2 Landfills (LF)

Iceland also collected leachate from the Alfsnes landfill site in the nearby recipient stream (samples ALF-1 and ALF-2). The samples were diluted due to snow melting.

6.2.4.3 Hot spots

Water samples were collected in the harbour area just outside the Klettagarðar and Ánanaust STPs (samples HA-1 to HA-4). The area, however, does not serve recipient for the STPs, as the processed water is discharged much further out in the open sea. However, being collected in the harbour area they may represent a hot spot.

Five fish samples were caught near-coastal water not far from an old landfill site at Gufunes in Reykjavík (samples with the prefix GUF). Gufunes was used to store landfill waste from Reykjavík and neighbouring towns until 1991. Records on buried materials are not complete and seepage from this site is very likely. The site is also of general interest as it is located close Reykjavík.

6.2.4.4 Background sites

Five fish samples were collected at two open sea positions, one close to Faxaflói bay west of Iceland and one south of Reykjanes (samples FS115, FS116, F28, F31 and F38).

6.2.5 Norway

6.2.5.1 Waste water treatment plants (STP)

One influent and one effluent water sample were included together with two sludge samples from the VEAS STP in the south-western part of Oslo. From the Bekkelaget, central Oslo area, four samples from Bekkelaget STP also included one influent and one effluent water sample together with two sludge samples.

6.2.5.2 Hot spots

Samples from five hot spot areas were included. From the inner Oslo Fiord one recipient water sample, one sediment, three composite fish samples and composite blue mussel sample were included. From Lake Mjøsa near Lillehammer one recipient water sample, one sediment sample and one composite fish sample were included. From Vanemfjorden and Storfjorden, both inland waters east of Oslo Fjord, one recipient water sample plus one sediment sample and one composite fish sample, respectively, were included. Finally, from the Lier area north of Oslo two run-off water samples from plastic covered greenhouses were included.

6.2.5.3 Background sites

Two backgrounds stations were included; from the outer Oslo Fjord one recipient water sample, one sediment sample and one composite blue mussel sample were included. Finally, from northern Norway one recipient water sample and one sediment sample were included from both the Tromsø and the Varangerfjord areas.

6.2.6 Sweden

6.2.6.1 Waste water treatment plants (STP)

Samples from STP included two sludge samples from Henriksdal and Hammarby Sjöstad STPs, respectively, both in the Stockholm area. Henriksdal is the biggest STP in Sweden, while the one in Hammarby Sjöstad is a much smaller one serving mainly a new urban resident area.

6.2.6.2 Hot spots

Samples from hot spots included urban areas. From both old and new parts of Stockholm one recipient water and two surface runoff water samples together with one sediment sample were included. From a newer

urban area in Stockholm (Hammarby Sjöstad) two recipient water samples and two sediment samples were included.

6.2.6.3 Background sites

Samples from two inland lakes, Övre Skärsjön in the middle of Sweden and Lilla Öresjön in south-western Sweden, included a recipient water sample and a sediment sample.

7. Results

In this section the results of the screening study is presented. The data are listed for each country and according to the environmental compartments where the samples have been collected.

For about 10 % of all samples replicate analyses have been made, and the average values of the replicates are reported. Similarly, some samples have been collected as two or more parallel samples, and here average values are also reported. In those cases where values are below detection limits (< DL) a value of DL/2 has been substituted for the missing value when estimating the average value.

Occasionally, for some substances the determined concentrations were outside the calibration range, and in such cases the reported value is a best estimate. Especially, dodecylphenol was measured in relatively high concentrations in most samples; these values, however, are somewhat uncertain, as most blanks values also had high DDP values, and despite that all reported values have been corrected for blank values, this increases the uncertainty.

7.1 Aqueous samples

The water samples have been split up in five individual groups according to where in the sewage process stream they belong. Hence, the following groups are listed: STP influents, STP effluents, landfill leachates, surface runoff/surface water and water from background sites.

Generally, contamination problems prevented the detection of 4-*tert*-butylphenol in most water samples. Calibration and blank runs, however, did not indicate that this problem was related to specific laboratory procedure, and it is not clear what caused the problem. For some samples, especially nonylphenol, bisphenol A and nonylphenol ethoxylate, were detected in very high concentration; some of these concentrations were outside the calibration range, and therefore the reported values are only best estimates.

7.1.1 Influents from waste water treatment plants (STPs)

Ten water samples from STP influents have been provided by all countries except Sweden. The Faroe Islands, Finland and Norway delivered samples from two different STPs, Denmark from one (two parallel samples), while Iceland collected two samples from local sewage streams in a suburban area (Mosfellsbær) of Reykjavík. One of these streams is actu-

ally not a STP influent, but it disposes the sewage to the sea through a septic tank.

4-tOP was detected in most samples in relatively low concentrations ranging from < 10 to about 70 ng/L. Nonylphenol isomers (NP-mix) were detected in all samples with concentrations ranging from about 130 ng/L (MB-1, Reykjavík) to about 5,700 ng/L (Viikinmäki, Helsinki), but also samples from Copenhagen and Espoo had high levels > 3,000 ng/L. Also DDP and BPA were detected in most samples and in high concentrations, DDP in samples from Torshavn (hospital E-1 and Sersjantvikin) and Helsinki (Viikinmäki) from about 3,300 to 4,100 ng/L, and BPA in samples from Finland (Suomenoja and Viikinmäki) from about 7,800 to 9,900 ng/L, respectively. Nonylphenol monoethoxylates (NP1EO) were also detected in most samples ranging from about 1,140 ng/L (hospital-E1, Torshavn) to about 4,900 ng/L (Sersjantvikin, Torshavn); also samples from Espoo and Helsinki (Finland) showed high levels of NP1EO, about 3,300 to 4,700 ng/L.

As the water samples were analyzed in different batches with varying GC-MS instrumental performance, and as the samples differed widely in both concentration ranges and particle content, the detection limits could vary from batch to batch and sometimes from sample to sample. For the two parallel samples from Lynetten, Copenhagen, the variation for e.g. NP-mix and BPA was < 20 %, while it was up to 50 % or more for some of the other substances in lower concentrations.

Table 18. Concentration of phenolic substances in STP influents and sewage in Nordic countries in 2006/2007 (ng/L).

Country	DK	FO		FI		IS		NO	
Location	Copenhagen	Torshavn		Espoo	Helsinki	Reykjavík		Oslo	
Site	Lynetten	Hospital-E1	Sersjantvikin	Suomenoja	Viikinmäki	MB-1[1]	MB-2[2]	Bekkelaget	VEAS
Sample no.	778-779	1416	1420	719	716	1474	1475	675	678
Compound:	[7]		[5]		[5]				
4-tBuP	N/A[3]	N/A[3]	N/A[3]	N/A[3]	N/A[3]	N/A[3]	<10	N/A[3]	N/A[3]
2.6-di-tBuP	<10	9.0	<5	<10	<10	<15	<25	<10	<10
4-tOP	43.0	8.5	20.3	16.1	40.8	N/A	72.8	<10	<10
4-OP	12,3	60.6	5.8	66.6	22.5	<2	<1	4.9	8.3
NP-mix	3,550[4]	923	969	3,146[4]	5,688[4]	133	1,520	266	1,108
4-NP	2.3	18.7[6]	54.3	38.8	19.3	<1	14.6	<1	11.9
DDP	693	4,096[4]	3,422[4]	182	3,291[3]	<125	501	2,154[4]	1,356
4-CP	1.0	<1	<1	3.9	10.9	<1	2.2	61.1	7.9
BPA	2,138[4]	232	1,016	9,828[4]	7,766[4]	N/A[3]	204	765	1,236
TBBPA	<15	<15	<15	N/A[3]	N/A[3]	N/A[3]	<25	N/A[3]	N/A
Me-TBBPA	<5	<2	<2	<10	<10	<5	N/A[3]	<10	<10
OP1EO	77.5	157	56.8	22.3	129	13.5	68.8	68.3	65.9
NP1EO	2,897[4]	1,142	4,896[4]	3,300[4]	4,743[4]	N/A[3]	N/A[3]	1,148	2,757[4]

Notes: [1]Sewage sample from Mosfellsbær, near horse stable; [2]Sewage sample from Mosfellsbær, Arnarhöfdi; [3]Data not available; either do to contamination or other analytical problems; [4]Estimate, outside calibration range; [5]Recoveries were generally low for this sample and values are uncertain; [6]High uncertain due to low recovery; [7]average of two parallel samples.

7.1.2 Effluents from waste water treatment plants

Denmark, the Faroe Islands and Norway all collected effluent samples from two STPs, while Finland collected samples from three different

STP; in total 11 samples were collected and analyzed. Both in Denmark and Finland the STPs are of different size as they receive sewage from towns of different sizes. Lynetten in Copenhagen serve as STP for the metropolitan area (> 750,000 people) while Bjergmarken in Roskilde only processes sludge from a smaller provincial town (some 50,000 people); two parallel samples were collected from Lynetten STP. In Finland, Pornaninen covers a small town of 1,000 people, Suomenoja in Espoo covers about 400,000 people, and Viikinmäki in Helsinki about 1,000,000 people. No specific information about the STPs in Torshavn is available, but both the hospital and the town STP in Torshavn are supposed to be relative small; Sersjantvikin STP process predominantly household waste. Regarding Norway, the VEAS and Bekkelaget STPs in the Oslo area covers approximately 700,000 and 350,000 people, respectively.

4-tOP was detected in most samples, but for samples from Bjergmarken, Roskilde, and Bekkelaget, Oslo, levels were below detection limits (DL). For the other samples levels ranged from about 55 to 2,100 ng/L, highest in effluents from STPs in Finland. NP-mix and BPA were detected in all samples with a couple of results being below DL. Levels were ranging from < DL to about 2,200 ng/L for NP-mix and from <DL to about 560 ng/L for BPA. Generally, effluent levels were lower than the corresponding influent levels. This trend is also observed for the ethoxlates, OP1EO and NP1EO, which were both reduced considerably, and for several samples levels below DL.

The variation between the two parallel samples from Lynetten STP in Copenhagen was higher than for the influent samples and for most substances >50 %.

Table 19. Concentration of phenolic substances in STP effluents in Nordic countries in 2006/2007 (ng/L).

Country	*DK*			*FO*		*FI*			*NO*	
Location	*Copenhag.[1]*	*Roskilde*		*Torshavn*		*Pornainen*	*Espoo*	*Helsinki*	*Oslo*	
Site	*Lynetten*	*Bjergmarken*		*Hospital-E2*	*Sersjantvik.[3]*	*Pornainen*	*Suomenoja*	*Viikinmäki*	*Bekkelag.[4]*	*VEAS STP*
Sample no.	*780-781*	*1009*	*1633*	*1417*	*1418*	*724*	*720*	*717*	*676*	*679*
Compound:	[2]	[5]	[5]	[8]						
4-tBuP	*N/A[6]*	*<10*	*N/A[6]*	*N/A[6]*	*N/A[6]*	*N/A[6]*	*N/A[6]*	*N/A[6]*	*N/A[6]*	*N/A[6]*
2.6-di-tBuP	*<30*	*<20*	*<10*	*<30*	*<30*	*<30*	*<45*	*<45*	*<10*	*<45*
4-tOP	*490*	*<5*	*<5*	*N/A[6]*	*55.1*	*628*	*2,099[7]*	*1,086*	*<10*	*67.1*
4-OP	*<5*	*<1*	*1.4*	*<5*	*16.9*	*42.6*	*<5*	*<5*	*<1*	*<5*
NP-mix	*116*	*<15*	*51.3*	*2,173[7]*	*169*	*64.6*	*189*	*374*	*189*	*105*
4-NP	*2.9*	*2.0*	*<1*	*71.8*	*16.9*	*2.6*	*13.9*	*7.0*	*2.3*	*2.0*
DDP	*154*	*<100*	*297*	*N/A[6]*	*N/A[6]*	*1,115*	*2,206[7]*	*2,065[7]*	*N/A[6]*	*1,294*
4-CP	*1.4*	*<1*	*<1*	*<1*	*4.6*	*6.6*	*<1*	*7.7*	*<1*	*1.8*
BPA	*8.5*	*8.1*	*58.5*	*<1*	*561*	*223*	*200*	*467*	*69.3*	*96.9*
TBBPA	*<10*	*<20*	*58.5*	*<10*	*<10*	*<10*	*<10*	*<10*	*<10*	*<10*
Me-TBBPA	*<3*	*<5*	*<10*	*<3*	*<3*	*<3*	*<3*	*<2*	*<10*	*<3*
OP1EO	*<1*	*2.6*	*7.1*	*<1*	*<1*	*147*	*165*	*239*	*<1*	*33.7*
NP1EO	*<2*	*<2*	*13.4*	*N/A[6]*	*1,585*	*2.4*	*<2*	*<2*	*<1*	*<2*

Notes: [1]Copenhagen; [2]Average of two parallel samples; [3]Sersjantvikin STP; [4]Bekkelaget STP. [5]Average of replicate analyses; [6]Data not available due to contamination or other laboratory problems; [7]Estimate, outside calibration range; [8]not corrected for recovery due to contamination problems;

7.1.3 Effluents form landfills/waste dumps (WDs)

The Faroe Islands, Finland and Iceland have collected effluent/leachate water samples from landfills (waste dumps). In the Faroe Islands the landfill of Husahagi receives no household waste, while both in Finland and Iceland the landfills probably serve as waste dumps for both industry and households. The Ämmässuo landfill is the biggest in Finland. Iceland collected two parallel samples from their landfill (ALF), and the samples were collected where the effluents run into a nearby riwer. An average variation was observed between the two parallel samples from the landfill in Iceland, except for BPA that varied more than 100 % between the two samples; the concentration of BPA in both samples were very high and fell outside the calibration range.

Samples from landfill effluents were in some cases very high in concentrations for both 4-tOP, NP-mix, DDP and BPA, especially in the samples from Espoo (Ämmässuo) and Reykjavík (ALF). As mentioned earlier, some of the measured values were outside the calibration range, and must therefore only be considered as best estimates.

Table 20. Concentration of phenolic substances in landfill effluents in Nordic countries in 2006/2007 (ng/L).

Country	***FO***	***FI***	***IS***
Location	*Torshavn*	*Espoo*	*Reykjavík*
Site	*Husahagi*	*Ämmässuo*	*ALF*[1]
Sample no.	*1421*	*718*	*1476-1477*
Compound\(Sample no)			[2]
4-tBuP	*N/A*[3]	*N/A*[3]	*834*
2.6-di-tBuP	*<30*	*<45*	*254*
4-tOP	*<10*	*2,372*	*487*
4-OP	*5.9*	*N/A*[3]	*3.6*
NP-mix	*27.2*	*16,997*[4]	*4,866*[4]
4-NP	*5.9*	*<1*	*71.1*
DDP	*241*	*4,844*	*4,902*
4-CP	*8.3*	*988*	*40.8*
BPA	*711*	*N/A*[3]	*5,910*[4,5]
TBBPA	*<10*	*<10*	*<20*
Me-TBBPA	*<3*	*<3*	*<5*
OP1EO	*<1*	*413*	*81.2*
NP1EO	*<2*	*<2*	*84.9*

Notes: [1]Site unknown; [2]Average of two parallel samples. [3]Data not available due to contamination or other laboratory problems; [4]Estimate, outside calibration range; [5]The recovery of BPA value in sample 2007-1477 was very low, and the value has been excluded

7.1.4 Recipient waters

All countries except Sweden collected recipient water samples from STPs and other recipient areas, both freshwater/lacustrine, brackish and marine

environments. In Denmark, recipient water was collected close to both Lynetten (two parallel samples) and Bjergmarken STPs, while a third sample was collected in Limfjorden, which may be considered a background area but at the same time Limfjorden also serves as a recipient environment for several smaller towns along its coast.

The Faroe Islands collected two water samples from the harbours of Tórshavn and Klaksvik, both hot spot areas.

In Finland, water samples were collected in the coastal bay area outside Espoo and the city bay of Helsinki, where the discharge from the STPs were let out.

In Reykjavík four water samples (2x2 parallel samples) were collected close to the STPs; however, they are not considered real recipient samples, as the STPs discharge their processed water much further out at open sea.

In Norway recipient water was collected in the inner part of Oslo Fjord and from two freshwater lakes (Lake Mjøsa and Vanemfjord).

Recipient water samples generally had low levels for all measured substances with only NP above DL in most samples. One sample from Tórshavn (Vagsbotn) had high concentrations of NP-mix and detectable concentrations of several phenolic substances.

Table 21. Concentration of phenolic substances in recipient waters in Nordic countries in 2006/2007 (ng/L).

Country	**DK**			**FO**		**FI**			**IS**		**NO**		
Environment	*Marine*	*Brackish*		*Marine*		*Brackish*			*Marine*		*Marine*	*Lacustrine*	
Location	*Copenh.*[1]	*Ros. Fj.*[2]	*Limfjo.*[3]	*Klaksv.*[4]	*Torsha.*[5]	*Helsink.*[6]	*Espoo*		*Reykjavík*		*Oslo Fj.*[7]	*Hamar*	*Vansjø*
Site	*Øresund*	*St.60*[9]	*MSS3*[9]	*Marina*	*Vagsb.*[10]	*H1*[10]	*E1*[12]	*E2*[13]	*HA-1*[14]	*HA-2*[14]	*St.30B*	*Mjøsa*	*Vanem.*[15]
Sample no.	*691-692*	*1029*	*711*	*1422*	*1419*	*721*	*722*	*723*	*766-767*	*768-769*	*1077*	*677*	*1076*
Compound:	[8]		[9]						[8]				
4-tBuP	*<10*	*<10*	*N/A*[17]	*N/A*[17]	*N/A*[17]	*N/A*[17]	*N/A*[17]	*N/A*[17]	*N/A*[17]	*N/A*[17]	*N/A*[17]	*N/A*[17]	*N/A*[17]
2.6-di-tBuP	*<25*	*<20*	*<15*	*<5*	*64.9*	*<1*	*<1*	*<1*	*<25*	*<25*	*<1*	*<1*	*<1*
4-tOP	*<1*	*<5*	*<10*	*<5*	*<1*	*2.8*	*<1*	*<1*	*<1*	*<1*	*<1*	*<1*	*<1*
4-OP	*<1*	*<1*	*<2*	*<1*	*<1*	*<1*	*<1*	*<1*	*<1*	*<1*	*<1*	*<1*	*<1*
NP-mix	*18.8*	*17.9*	*<10*	*<15*	*4,199*[16]	*93.6*	*20.4*	*47.9*	*38.8*	*35.0*	*<20*	*22.6*	*46.5*
4-NP	*<1*	*<1*	*<1*	*<1*	*287*	*<1*	*<1*	*<1*	*<1*	*<1*	*<1*	*6.8*	*<1*
DDP	*<100*	*<100*	*<125*	*<110*	*<100*	*<50*	*<50*	*<50*	*N/A*[17]	*N/A*[17]	*N/A*[17]	*N/A*[17]	*N/A*[17]
4-CP	*<1*	*<1*	*2.9*	*<1*	*454*	*<1*	*<1*	*<1*	*<1*	*<1*	*<1*	*<1*	*<1*
BPA	*<5*	*<2*	*3.0*	*<1*	*22.3*	*10.9*	*1.1*	*4.0*	*15.4*	*14.1*	*11.5*	*3.9*	*1.7*
TBBPA	*<25*	*<10*	*<10*	*<15*	*<25*	*<10*	*<10*	*<10*	*<25*	*<25*	*<10*	*<10*	*<10*
Me-TBBPA	*<5*	*<5*	*<5*	*<2*	*<5*	*<10*	*<10*	*<10*	*<5*	*<5*	*<10*	*<10*	*<10*
OP1EO	*5.6*	*2.2*	*3.7*	*<1*	*118*	*1.8*	*<1*	*<1*	*<1*	*<1*	*<1*	*<1*	*<1*
NP1EO	*<5*	*<2*	*<1*	*<2*	*60.8*	*<1*	*<1*	*<1*	*<5*	*<5*	*<1*	*<1*	*<1*

Notes: [1]Copenhagen; [2]Roskilde Fjord; [3]Limfjorden; [4]Klaksvik; [5]Torshavn; [6]Helsinki; [7]Oslo Fjord – inner; [8]Average of two parallel samples; [9]Average of replicate measurements; [10]Vagsbotn; [11]Near shipping port; [12]Near pipeline outlet, 1 m depth; [13]Near pipeline outlet, 16 m depth; [14]Site unknown; [15]Vanemfjorden. [16]BPA used for estimating recovery; [17]Data not available due to contamination or other laboratory problems;

7.1.5 Surface runoffs

Water samples collected by Sweden all consisted of urban runoff (storm water) or surface water, either point or diffuse sources, from the Stockholm area. These samples were collected either in the old part of Stockholm or in newer urban districts. In total 11 samples were collected, and from Hammarby Sjöstad and Stora Essingen two parallel samples were collected. Another set of two parallel samples were collected from Sveavägen in Stockholm, but one of the samples was lost during transportation to NERI.

In Lier, west of Oslo (Norway), runoff samples were collected in a recipient stream at two positions downstream from greenhouses with plastic covering.

For the surface runoff samples from Lier in Norway (greenhouses) none of the substances were measured in detectable amounts, and generally, only samples from urban point sources in Stockholm, i.e. predominantly streets in the older part of the city, e.g. Båtbyggargatan, Lugnets Alle and Sveavägen, showed detectable amounts for both 4-tOP, NP, 4-NP, DDP, 4-CP, BPA, OP1EO and NP1EO with values from <DL up to a few hundred ng/L, while TBBPA only was detected above DL in two samples.

Table 22. Concentration of phenolic substances in surface runoff water in Nordic countries in 2006/2007 (ng/L).

Country	**NO**		**SE**								
Location	Lier		Stockholm								
Type	Surface point source		Storm water point source				Storm water diffuse source		Surface point source		Surface diffuse
Site	St.1	St.2	Båtbygg.[1]	Lugnets[2]	Sveaväg.[3]	Styrmans.[4]	Lill-Jans.[5]	Årstafält.[6]	Hamm.[7]	Riddarfjä.[8]	St. Essi.[9]
Sample no.	1079	1078	1454	1455	1456	1457	1458	1459	1462-1463	1464	1460-1461
Compound:									[10]		[10]
4-tBuP	N/A	N/A	N/A	N/A	N/A	N/A	<10	32.0	N/A	N/A	<10
2.6-di-tBuP	<30	<30	3.4	8.4	<30	<15	<25	<25	<30	<30	<20
4-tOP	<10	<10	233	197	379	240	<1	<1	<10	<10	<5
4-OP	<5	<5	1.9	1.3	<5	<2	1.0	<1	<5	<5	<1
NP-mix	<15	<15	272	235	359	186	<20	41.8	74.1	<15	45.4
4-NP	<1	<1	18.2	12.9	10.1	12.6	1.2	5.7	<1	<1	<1
DDP	<150	<150	1,106	552	4,280[11]	702	<100	<100	<50	<150	<100
4-CP	<1	<1	8.1	109	154	2.6	3.6	2.5	<1	1.2	<1
BPA	<1	<1	1,319	1,513	2,398[11]	1,180	14.5	54.9	17.0	1.6	2.4
TBBPA	<10	<10	15.8	15.9	<10	<10	<25	<25	<10	<10	<15
Me-TBBPA	<3	<3	<10	<10	<3	<5	<5	<5	<10	<3	<5
OP1EO	<1	<1	8.0	7.8	30.8	4.8	1.0	<1	1.9	<1	2.0
NP1EO	<2	<2	2.1	2.8	102	<1	<5	<5	<1	<2	<2

Notes: [1]Båtbyggargatan; [2]Lugnets Allé; [3]Sveavägen; [4]Styrmansgatan; [5]Lill-Jansskogan; [6]Årstafältet; [7]Hammarby Sjöstad; [8]Riddarfjärden; [9]Stora Essingen; [10]Average of two parallel samples; [11]estimate, outside calibration range.

For the two sets of parallel samples from the Stockholm area levels were generally low, but for those substances detected in both samples the variation was about 50 %

7.1.6 Background environments

Both Denmark, Norway and Sweden collected water samples from background environments. In Denmark, two samples (at different times and not exactly parallel) together with five additional (extra) parallel samples were collected from a reference station in Kattegat (St. 905).
Norway collected background samples from the outer part of Oslo Fjord and from the Northern part of the country, Malangen at Tromsø and in the Varangerfjord.

Sweden, on their part, collected two freshwater background samples from the lacustrine environments of Tärnan (a freshwater lake south of Stockholm) and Lille Öresjön near Gothenburg.

For all background water samples, only NP-mix and BPA were measured in low but detectable amounts, while other substances were below detection limits. For both substances highest levels were recorded in samples form the two Swedish freshwater lakes, Tärnan and Lille Öresjön.

For the parallel samples and extra samples collected at St. 905 in Kattegat (DK) the average variation for NP-mix and BPA was about 60 %.

Table 23. Concentration of phenolic substances in water samples from background sites in Nordic countries in 2006/2007 (ng/L).

Environment			***Marine***			***Lacustrine***	
Country	***DK***		***NO***			***SE***	
Location	*Kattegat*		*Oslo Fjord*	*Tromsø*	*Varangerfjord*	*Stockholm*	*Gothenburg*
Site	*St.905-1*	*St.905-2*	*St.36*	*St.42*	*St.10*	*Tärnan*	*Lille Öresjön*
Sample no.	*694-698*	*801-802*	*1081*	*1080*	*1082*	*1465*	*1466*
Compound:	[1]	[2]					
4-tBuP	*N/A*[3]	*N/A*[3]	*N/A*[3]	*N/A*[3]	*N/A*[3]	*N/A*[3]	*N/A*[3]
2.6-di-tBuP	*<15*	*<15*	*<1*	*<1*	*<1*	*<1*	*<1*
4-tOP	*<10*	*<10*	*<1*	*<1*	*<1*	*<1*	*<1*
4-OP	*<2*	*<2*	*<1*	*<1*	*<1*	*<1*	*<1*
NP-mix	*42.1*	*22.2*	*<20*	*<20*	*<20*	*68.3*	*107*
4-NP	*<1*	*<1*	*<1*	*<1*	*<1*	*<1*	*1.5*
DDP	*<125*	*<125*	*<50*	*<50*	*<50*	*<50*	*88.8*
4-CP	*<1*	*<1*	*<1*	*<1*	*<1*	*<1*	*<1*
BPA	*1.4*	*4.8*	*8.7*	*<1*	*<1*	*5.4*	*10.8*
TBBPA	*<10*	*<10*	*<10*	*<10*	*<10*	*<10*	*<10*
Me-TBBPA	*<5*	*<10*	*<10*	*<10*	*<10*	*<10*	*<10*
OP1EO	*<1*	*<1*	*<1*	*<1*	*<1*	*<1*	*2.4*
NP1EO	*<1*	*<1*	*<1*	*<1*	*<1*	*<1*	*<1*

Notes: [1]Average of five parallel samples; [2]Average of two parallel samples. [3]Data not available due to contamination or other laboratory problems.

7.2 Solid samples

Three types of solid samples including sewage sludge collected at STPs, sediments from both lacustrine/fresh water and marine environments and two soil samples from landfills at the Faroe Islands were part of this study.

All countries collected sewage sludge samples, and in all countries samples were collected at two different types of STPs, typically a major STP serving a large urban/capitol area and a smaller STP serving a much smaller population.

Sediment was also collected by all countries and included both samples from recipient areas and from more remote/background sites in both marine and lacustrine/fresh water environments.

7.2.1 Sludge from waste water treatment plants

24 sewage sludge samples from STPs were collected in all six participating countries, and they covered both very large, medium size and small STPs. In Denmark two STPs were included: Lynetten in Copenhagen (750,000 peq) and Bjermarken in Roskilde (50,000 peq). In Tórshavn, the Faroe Islands, sewage sludge was collected from two relative small STPs, the hospital and Sersjantvikin STP (processing mostly domestic waste). In Finland sewage sludge was collected from three different STPs: Viikinmäki in Helsinki (1,000,000 peq), Suomenoja in Espoo (500,000 peq) and in Pornainen with only about 1,000 peq. Iceland collected sewage sludge from two STPs in Reykjavík, Klettargadar and Ánanaust, but the size of these two STPs is unknown.

Norway collected sewage sludge from two STPs in the Oslo area, Bekkelaget (250,000 peq) and VEAS (500,000 peq). From Bekkelaget six samples were collected: three from the inlet (wet sludge) and three from the outlet (stabilized dry sludge); one of the sludge samples from the inlet (682) was lost in the laboratory and no data could be reported for that sample. From VEAS two samples were collected: one from the inlet (wet sludge) and one from the silo (dry sludge).

Also Sweden collected parallel samples from two STPs in Stockholm: two from Henriksdal, which is the biggest STP in Sweden, and two from Hammarby Sjöstad STP, which is a new but much smaller STP processing mainly domestic waste from a new urban settlement.

Concentration levels were generally high for all sewage sludge sample, and several compounds, e.g. NP-mix and DDP, ranged well above the calibration range. However, 4-NP, TBBPA and di-Me-TBBPA, were undetected in most samples.

For several samples (1435, 683 and 684) replicate analyses were performed with variations between 50-100 % for all compounds. Also for the parallel samples significant variations were observed. For the two samples from the inlet at Bekkelaget the average variation was about 50 %, while it was between 50 and 100 % for the three samples from the outlet at Bekkelaget. Sample inhomogeneity may explain much of the observed variation.

NP-mix and DDP were measured in highest concentration in all samples, and levels ranged from about 1,460 to 28,400 µg/kg dw for NP-mix and from about 1,330 to 47,400 µg/kg dw for DDP (Table 25). Highest levels for NP-mix were measured in sludge from Suomenoja STP in Finland, while DDP had highest levels in wet sludge from Bekkelaget and VEAS STPs in Norway.

Due to the detrimental effect some of the sludge samples had on the performance of the GC-MS system two sets of detection limits, DL1 and DL2 were used (*cf.* Table 24).

Table 24. Detection limits (DL1 and DL2) for phenolic substances in sewage sludge (µg/kg ww).

4-tOP	2,6-di-tOP	4-tOP	4-OP	NP-mix	4-NP	DDP	4-CP	BPA	TBBPA	di-Me-TBBPA	NP1EO	OP1EO
5.0	**0.1**	**3.5**	**0.1**	**2.0**	**0.1**	**50**	**0.1**	**0.4**	**5.0**	**20**	**1.0**	**1.0**
5.0	**2.0**	**7.5**	**0.5**	**8.0**	**0.6**	**100**	**0.5**	**0.4**	**10**	**5.0**	**1.0**	**1.0**

Notes: DL1, upper row; DL2, lower row

Table 25. Concentration of phenolic substances in sewage sludge from STPs in Nordic countries in 2006/2007 (µg/kg dw).

Country	***DK***		***FO***		***FI***			***IS***		***NO***				***SE***	
Location	*Copen.*[1]	*Rosk.*[2]	*Torshavn*		*Pornai.*[3]	*Espoo*	*Helsin.*[4]	*Reykjavík*		*Bekkelaget*		*Oslo VEAS*		*Stockholm*	
Site/type	*Lynett.*[5]	*Bjerg.*[6]	*Hosp.*[7]	*Sersja.*[8]	*Pornai.*[3]	*Suome.*[9]	*Viikin.*[10]	*Kletta.*[11]	*Anan.*[12]	*wet*	*dry*	*silo*	*wet*	*Hen.*[13]	*Ham.*[14]
DW (%)[17]	*20.3*	*28.4*	*13.7*	*18.0*	*15.0*	*13.5*	*49.9*	*32.5*	*23.2*	*4.3*	*88.2*	*58.2*	*6.2*	*28.0*	*15.1*
Sample no.	*782-783*	*1634*	*1435*	*1436*	*732*	*733*	*734*	*770-771*	*772-773*	*681/683*	*684-686*	*688*	*689*	*1450-1451*	*1452-1453*
Compound:	[15]		[15]					[15]	[15]	[16]	[16]			[15]	[15]
4-tBuP	*210*	*1,314*[18]	*515*[18]	*348*[18]	*4,474*[18]	*1,843*[18]	*391*	*1,447*[18]	*466*[18]	*<DL1*	*80.4*	*141*	*691*[18]	*<DL1*	*86.0*
2.6-di-tBuP	*46.3*	*5.6*	*<DL2*	*17.3*	*96.1*	*23.2*	*50.5*	*23.2*	*104*	*55.4*	*9.2*	*5.4*	*27.1*	*61.6*	*143*
4-tOP	*595*[18]	*812*[18]	*155*	*N/A*	*<DL1*	*1,386*[18]	*778*	*N/A*	*70.1*	*372*	*378*	*261*	*422*	*448*[18]	*712*[18]
4-OP	*2.9*	*14.1*	*11.2*	*8.4*	*14.6*	*3.4*	*5.3*	*N/A*	*<DL1*	*23.6*	*6.9*	*4.6*	*44.0*	*13,4*	*6.2*
NP-mix	*4,878*[18]	*3,658*[18]	*1,460*[18]	*2,388*[18]	*8,932*[18]	*28,360*[18]	*14,583*[18]	*N/A*	*2,413*[18]	*3,556*[18]	*4,078*[18]	*9,697*[18]	*3,005*[18]	*7,570*[18]	*14,328*[18]
4-NP	*<DL1*	*<DL1*	*<DL2*	*N/A*	*N/A*	*<DL*	*<DL2*	*N/A*	*<DL2*	*<DL1*	*4.2*	*<DL2*	*<DL1*	*5.6*	*<DL1*
DDP	*10,044*[18]	*8,463*[18]	*N/A*	*N/A*	*N/A*	*N/A*	*26,485*[18]	*N/A*	*N/A*	*47,396*[18]	*17,492*[18]	*11,334*[18]	*47,021*[18]	*11,104*[18]	*29,509*[18]
4-CP	*10.3*	*7.4*	*24.5*	*9.2*	*<DL1*	*<DL*	*<DL2*	*N/A*	*N/A*	*64.3*	*16.1*	*21.5*	*115*	*12.1*	*<DL1*
BPA	*271*	*410*	*<DL2*	*451*	*<DL1*	*1,914*[18]	*217*	*N/A*	*637*	*539*	*41.3*	*290*	*<DL1*	*96.7*	*444*
TBBPA	*<DL1*	*<DL1*	*<DL2*	*56.7*	*<DL1*	*<DL1*	*<DL2*	*38.8*	*<DL2*	*1,138*	*<DL1*	*<DL2*	*602*	*<DL1*	*179*
Me-TBBPA	*<DL2*	*<DL1*	*<DL1*	*<DL2*	*<DL1*	*<DL2*	*<DL2*	*8.5*	*>DL2*	*<DL1*	*<DL1*	*<DL2*	*<DL1*	*<DL1*	*<DL1*
OP1EO	*42.4*	*46.5*	*71.0*	*336*	*51.3*	*14.0*	*25.5*	*N/A*	*96.9*	*115*	*24.1*	*<DL2*	*<DL2*	*15.7*	*22.6*
NP1EO	*70.3*	*320*	*N/A*	*N/A*	*N/A*	*11.4*	*363*	*N/A*	*N/A*	*N/A*	*182*	*104*	*N/A*	*N/A*	*163*

Notes: [1]Copenhagen; [2]Roskilde; [3]Pornainen; [4]Helsinki; [5]Lynetten; [6]Bjergmarken; [7]Hospital; [8]Sersjantvikin; [9]Suomenoja; [10]Viikinmäki; [11]Klettagardar; [12]Ánanaust; [13]Henriksdal; [14]Hammarby Sjöstad; [15]average of two parallel samples; [16]average of three parallel samples; [17]Dry weight (%); [18]estimate, outside calibration range.

7.2.2 Soil samples from landfills

The soil sample from the active landfill of Torshavn, Húsahagi, showed detectable amounts of most substances while 4-tBuP, 2,6-di-tBuP, 4-NP, DDP and TBBPA were below DLs. 4-tOP and NP-mix were observed in highest amounts, about 23 and 47 µg/kg dw, respectively. The observed value of 57 µg/kg dw for di-Me-TBBPA is rather unusual as this compound is only rarely detected in environmental samples (cf. Table 9); hence it should be considered cautiously as it might be due to an artefact. For the soil sample from the old landfill at Havnadalur only 4-tOP, 4-CP and NP1EO were above DLs (cf. Table 27), and levels were significantly lower than for the Húsahagi landfill sample, only a few µg/kg dw. The detection limits regarding soil samples are listed below (Table 26).

Compared to literature values (cf. Table 9) Sweden has previously reported 4-tOP, 4-NP in soil in the range of 1-2 and 11-60 µg/kg dw, respectively (Remberger et al., 2003; Naturvårdsverket, 2005). Norway (Fjeld et al., 2004a; Schlabach et al., 2002) has reported levels of BPA, TBBPA and di-Me-TBBPA in the range 7-370, 2-44 and up to 1 µg/kg dw, respectively.

Table 26. Detection limits (DL) for phenolic substances in soil samples (µg/kg ww).

4-tOP	2,6-di-tOP	4-tOP	4-OP	NP-mix	4-NP	DDP	4-CP	BPA	TBBPA	di-Me-TBBPA	NP1EO	OP1EO
2.0	**5.0**	**1.0**	**0.2**	**3.5**	**0.1**	**25**	**0.1**	**0.1**	**1.0**	**5.0**	**0.1**	**0.2**

Table 27. Concentrations of phenolic substances in soil samples from two landfills, the Faroe Islands, 2006 (µg/kg dw).

Location	***Torshavn***	
Site	*Húsahagi*	*Havnadalur[1]*
DW (%)[2]	*44.3*	*63.0*
Sample no.	*1433*	*1434*
Compound:		
4-tBuP	*N/A*	*N/A*
2.6-di-tBuP	*<DL*	*<DL*
4-tOP	*23.2*	*3.5*
4-OP	*1.1*	*<DL*
NP-mix	*47.0*	*<DL*
4-NP	*<DL*	*<DL*
DDP	*<DL*	*<DL*
4-CP	*7.5*	*0.6*
BPA	*2.8*	*<DL*
TBBPA	*<DL*	*<DL*
Me-TBBPA	*56.8*	*<DL*
OP1EO	*0.4*	*<DL*
NP1EO	*2.3*	*0.9*

Notes: [1]Old waste deposit; [2]Dry weight (%)

7.2.3 Sediment samples

7.2.3.1 Sediment from recipient environments

16 sediment samples from marine, brackish and lacustrine/freshwater environments were analysed. From Stora Essingen and Hammarby Sjöstad, Stockholm, two samples were collected in parallel, and here results are given as average values. Variation between parallel samples was significant, especially for the samples from Hammarby Sjöstad (above 100 %); for the samples from Stora Essingen the variation was generally below 50 %.

For another two samples, one from Copenhagen (693) and one Helsinki (736), replicate analyses were performed, and here the variation was generally below 20 %.

As for the corresponding water samples, some substances were detected in almost all samples, e.g. NP, 4-NP, 4-CP, BPA and NP1EO, while other substances were only detected in some samples. Generally, highest concentrations were detected in samples from Torshavn harbour (FO), a hot spot area, the coastal sea are outside Espoo (FI) and in Stockholm (SE). For NP concentrations ranged from <DL to about 480 µg/kg dw, while 4-CP ranged from <DL to about 180 µg/kg dw. BPA ranged from <DL to about 70 µg/kg dw, while TBBPA went undetected in all of the sediment samples. OP1EO and NP1EO levels were generally low, except for a couple of samples from Espoo coastal bay and Årstaviken in Stockholm, where NP1EO was about 65 µg/kg dw.

All data have been determined on the basis of wet weight (ww) and subsequently converted to dry weight (dw) basis using the reported dry weight (DW %) values. Due to the relatively low DW (%) for some samples, the conversion factor is often a factor 5 or more; this introduces more uncertainty on the results. For the same reason the detection limits have not been converted to dry weight basis, and in those cases where determined values (in ww) were below the detection limit, it has been reported as <DL (below detection limits) in stead of converting this to an actual number. The obtained detection limits (ww) are given here:

Table 28. Detection limits (DL) for phenolic substances in sediment (µg/kg ww).

4-tOP	2,6-di-tOP	4-tOP	4-OP	NP-mix	4-NP	DDP	4-CP	BPA	TBBPA	di-Me-TBBPA	OP1EO	NP1EO
2.0	5.0	1.0	0.2	3.5	0.1	25	0.1	0.1	1.0	5.0	0.2	0.1

Table 29. Concentration of phenolic substances in sediment from recipient environments in Nordic countries in 2006/2007 (µg/kg dw).

Country	DK			FO		FI		NO			SE			
Environment	Brackish			Marine		Brackish		Marine	Lacustrine		Brackish			
Location	Copen.[1]	Rosk.[2]	Klaksv.[3]	Götuv.[4]	Torsh.[5]	Espoo	Helsink.[6]	Oslo	Hamar	Vansjø				Stockholm
Site	Øresund	Ros. F.[7]	Pollur.[8]	Bekka.[9]	Harbour	C. sea[16]	City bay	Inner[10]	Mjøsa	Vane.[11]	St. Es.[12]	Årstav.[13]	Hamm.[14]	Riddar.[15]
DW (%)[19]	82.1	15.9	46.1	59.3	32.5	4.8	38.2	33.9	10.0	20.1	17.8	13.5	26.2	33.5
Sample no.	693	1030	1428	1429	1432	735	736	1086	687	1468	1442-1443	1444	1445-1446	1447
Compound:	[17]						[17]				[18]		[18]	
4-tBuP	N/A	N/A	N/A	N/A	79.8	N/A	N/A	N/A	N/A	N/A	134	N/A	40.0	N/A
2.6-di-tBuP	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
4-tOP	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	9.2	<DL
4-OP	<DL	1.5	<DL	<DL	24.8	<DL	24.8	0.9	<DL	<DL	3.1	8.6	<DL	12.0
NP-mix	<DL	85.6	15.0	13.6	340	440	390	<DL	43.4	21.4	449	342	485	257
4-NP	0.1	<DL	0.3	0.4	3.1	2.2	1.8	<DL	<DL	0.5	1.4	<DL	0.6	<DL
DDP	<DL	<DL	<DL	<DL	529	<DL	<DL	<DL	<DL	<DL	137	216	<DL	179
4-CP	0.5	<DL	0.7	1.7	180	49.4	115	0.7	3.7	2.1	7.9	10.5	4.9	35.1
BPA	<DL	2.6	<DL	<DL	74.0	5.4	39.7	0.3	<DL	<DL	11.8	15.2	11.8	16.5
TBBPA	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Me-TBBPA	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
OP1EO	<DL	0.6	<DL	<DL	1.5	<DL	1.3	0.7	<DL	1.2	0.6	<DL	<DL	<DL
NP1EO	0.3	<DL	<DL	<DL	1.4	66.9	2.3	<DL	7.4	2.3	1.5	64.3	1.7	<DL

Notes: [1]Copenhagen; [2]Roskilde; [3]Klaksvik; [4]Götuvik; [5]Torshavn; [6]Helsinki; [7]Roskilde Fjord; [8]Pollurin; [9]Bekkafrost; [10]Oslo Fjord – inner; [11]Vanemfjord; [12]Stora Essingen; [13]Årstaviken; [14]Hammarby Sjöstad; [15]Riddarfjärden; [16]Coastal sea; [17]average of replicate analyses; [18]average of two parallel samples; [19]Dry weight (%)

7.2.3.2 Sediment from background environments

Nine sediment samples were analysed from background environments in Denmark, Norway and Sweden. Samples from Kattegat (St. 905, DK) and northern Norway (St. 42, Tromsø and St. 10, Vanrangerfjord) were collected as two parallel samples, and here average values have been reported as mentioned earlier. As the levels are low and <DL for most compounds, if not in both samples then in one of them, no attempts have been made to estimate the variation for replicate analyses.

Apart from one sample from Krageholmssjöen in Sweden (1149) where levels generally were higher than in other samples, all other samples had low values with only NP-mix being detected in concentrations well above DL, 9 to 249 µg/kg dw. Apart from that 4-CP, BPA, OP1EO and NP1EO were detected in a few samples at levels of 1-2 µg/kg dw.

Table 30. Concentration of phenolic substances in sediments from background environ-ments in Nordic countries in 2006/2007 (µg/kg dw).

Country	DK	NO			SE	
Type	Marine				Lacustrine	
Location	Kattegat	Oslo Fjord	Tromsø	Varangerfjord	Västman.[1]	Skåne
Site	St.905	St.360	St.42	St.10	Ö. Skärsjön[2]	Krageholm.[3]
DW (%)[5]	37.5	25.5	34.1	33.8	15.6	11.1
Sample no.	699/803	680	1083/1087	1084-1085	1448	1449
Compound:	[4]		[4]	[4]		
4-tBuP	N/A	N/A	N/A	N/A	N/A	N/A
2.6-di-tBuP	<DL	<DL	<DL	<DL	<DL	54.0
4-tOP	<DL	<DL	<DL	<DL	<DL	18.8
4-OP	<DL	<DL	<DL	<DL	<DL	2.6
NP-mix	9.2	23.7	<DL	<DL	54.3	249
4-NP	0.2	<DL	<DL	<DL	<DL	5.2
DDP	<DL	<DL	<DL	<DL	<DL	289
4-CP	1.8	3.0	<DL	<DL	1.3	108
BPA	0.4	0.9	<DL	0.4	<DL	<DL
TBBPA	<DL	<DL	<DL	<DL	<DL	<DL
Me-TBBPA	<DL	<DL	<DL	<DL	<DL	<DL
OP1EO	<DL	1.1	0.2	<DL	0.7	<DL
NP1EO	0.7	<DL	<DL	<DL	2.0	70.4

Notes: [1]Västmanmands Län; [2]Övre Skärsjön; [3]Krageholmssjön; [4]average of two parallel samples; [5]Dry weight (%); *viviparus*), three individuals pooled; [h]soluble fat not fully removed by clean-up; [i]estimate, outside calibration range.

7.3 Biological samples

The study included four types of biological samples: mussels, fish liver, liver from marine mammals and bird eggs. Mussels (*Mytilus edulis*) were collected from brackish and marine environments in Denmark, the Faroe Islands and Norway. Fish liver included samples from various types of fish from both brackish, fresh water/lacustrine and marine environments in all countries except Sweden. Liver from marine mammals included samples from harbour seals (*Phoca vitulina*) from Denmark and pilot

whales (*Globicephala melas*) from the Faroe Islands. The Faroe Islands also collected two egg samples from fish feeding sea birds (black guillemot, *Cepphus grylle*).

7.3.1 Fish from brackish and lacustrine/fresh water environments

Denmark and Finland collected fish from brackish environments. In Denmark sand gobys (*Pomatoschistus minutus*) and eelpouts (*Zoarces viviparus*) were caught in Roskilde Fjord relatively close to the local STP, Bjergmarken; liver from 14 and 3 individuals, respectively, were pooled to make up two composite liver samples.

In Finland, 15 Northern pikes (*Esox lucius*) were caught in two areas; 10 in the city bay of Helsinki and five in the coastal bay of Espoo, both brackish environments. For the pikes from the Helsinki area livers from 3 x 3 females were pooled to make three composite samples, while the liver from a single male pike was processed as one sample. From the Espoo area, livers from three females and two males were pooled to make two composite samples, respectively.

From Norway two composite fish samples (liver) were collected from freshwater environments. Livers from five trouts (*Salmo trutta*) from Lake Mjøsa were pooled to make one composite sample, and from Storfjorden livers from five European perch (*Perca fluviatillis*) were pooled to make a second composite sample.

For some of the samples it did not seem possible to obtain a satisfactory clean-up, and for these samples the analyses had to be discarded. A general trend for all liver samples from fish caught in brackish/freshwater environments is the elevated levels of 2,6-di-tBuP. Very high concentrations of OP and NP ethoxylates were measured in eelpouts from Roskilde Fjord (DK). Otherwise, highest concentrations of most substances were observed in fish from Norwegian freshwater environments.

Table 31. Concentrations of phenolic substances in fish (liver samples) from brackish/lacustrine environments in Nordic countries in 2006/2007 (µg/kg ww).

Country	DK		FI						NO	
Type	Brackish		Brackish						Lacustrine	
Location	Roskilde Fjord		City bay, Helsinki				Coastal bay, Espoo		Lake Mjøsa	Storfjorden
Sample no.	1159[a,h]	1161[g,h]	1014-1016[b]	1017-1019[b]	1020-1022[b,h]	1023[c]	1024-1026[b]	1027-1028[d]	1467[e,h]	1469[f]
Compounds:										
4-tBuP	<10	<10	N/A	N/A	<10	449	N/A	<4	<10	N/A
2.6-di-tBuP	5,081[i]	91,5	318	2,912[i]	452	69,3	49.4	12.1	413	73.2
4-tOP	N/A	225	355	294	N/A	13,2	165	N/A	134	229
4-OP	N/A	7	N/A	<1	8,4	4,5	N/A	N/A	<1	<1
NP-mix	N/A	N/A	62.2	N/A	989	N/A	43.7	338	75,7	318
4-NP	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	9.6
DDP	N/A	N/A	<100	N/A	N/A	N/A	N/A	N/A	N/A	253
4-CP	N/A	5,7	<1	<1	15,6	N/A	5.9	1.3	N/A	5.3
BPA	N/A	<5	N/A	N/A	56,8	N/A	<1	<1	11	N/A
TBBPA	N/A	N/A	<10	N/A	N/A	N/A	<10	<10	N/A	<10
Me-TBBPA	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
OP1EO	N/A	2,499[i]	N/A	4,035	N/A	N/A	N/A	N/A	N/A	18.1
NP1EO	N/A	18,821[i]	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A

Notes: [a]Sand goby (*Pomatoschistus minutus*), 14-16 individuals were pooled; [b]Nothern pike (*Esox lucius*), three females were pooled; [c] Northern pike (*Esox lucius*), one male; [d]Northern pike (*Esox lucius*), two males were pooled; [e]Trout (*Salmo trutta*), five individuals were pooled; [f]European perch (*Perca fluviatillis*), five individuals were pooled; [g]Eelpout (*Zoarces*

7.3.2 Fish from marine environments

The Faroe Islands, Iceland and Norway collected fish from marine environments; all fish were Atlantic cod (*Gadus morhua*). From the Faroe Islands livers from fish caught in the harbour of Tórshavn were pooled to make one composite sample. At Iceland, livers from fish caught at open sea south and west of Iceland were pooled to make five composite samples. In Norway 15 fish were caught in Oslo Fjord at St. 30B, and livers from groups of five individuals were pooled to make three parallel composite samples.

For several of the marine fish liver samples the analysis results had to be discarded as unsatisfactory clean-up of the extracts rendered the results unusable. The samples analysed of cod liver from Iceland also showed high concentrations of 2,6-di-tBuP as was observed for the freshwater liver samples, just as a couple of samples had very high concentrations of OP1EO.

Table 32. Concentrations of phenolic substances in fish (liver samples) from marine environments in Nordic countries in 2006/2007 (µg/kg ww).

Country	FO	IS					NO		
Location	Torshavn	Open sea - West of Iceland			Open sea – South of Ice[a]		Oslo Fjord - inner		
Site	Bursatanga	F28	F31	F38	FS115	FS116	St. 30B	St. 30B	St. 30B
Sample no.	1437[b]	1671[c]	1672[c]	1673[c,g]	1674[c,f]	1675[c]	1045[d]	1046[d]	1047[d]
Compound:	[e]					[e]	[e]	[e]	
4-tBuP		<20	1,079	38.5	<10				<10
2.6-di-tBuP		80.8	570	153	4,064[h]				291
4-tOP		<12	N/A	N/A	N/A				N/A
4-OP		<2	N/A	N/A	N/A				N/A
NP-mix		165	1,085	N/A	N/A				N/A
4-NP		44.3	N/A	N/A	N/A				<1
DDP		N/A	N/A	N/A	N/A				N/A
4-CP		<2	N/A	29.7	N/A				N/A
BPA		<10	N/A	N/A	N/A				N/A
TBBPA		N/A	N/A	N/A	N/A				N/A
Me-TBBPA		<10	<5	<5	<5				<5
OP1EO		<10	4,529[h]	<5	31,697[h]				N/A
NP1EO		N/A	N/A	N/A	N/A				N/A

Notes: aOpen sea – South of Iceland; [b]Atlantic cod (*Gadus morhua*), seven individuals pooled; [c]Atlantic cod (Gadus morhua); [d]Atlantic cod (Gadus morhua), five individuals pooled; [e]analytical results discarded due to problems with insufficient clean-up of the extracts; [f]bad performance and sensitivity of GC-MS instrument; [g]soluble fat not fully removed by clean-up; [h]estimate, outside calibration range

7.3.3 Mussels

Denmark, the Faroe Islands and Norway collected blue mussels from marine environments for this project; all mussels were of the same type, blue mussels (*Mytilus edulis*). In Denmark, the mussels were collected in Øresund close to the Lynetten STP and in Limfjorden at a reference station (MSS 3); more than 20 individuals (30-40 mm) were pooled to make the composite samples.

At the Faroe Islands mussels that had been held in cages for 6 weeks both in Torshavn harbour and at a reference site outside the harbour area were collected for the screening study. The mussels from the harbour were divided and pooled into two size fraction, 30-40 mm and 60-70 mm, and included 33 and 13 individuals, respectively.

In Norway mussels were collected in Oslo Fjord at St. 30A and St. 36A (Færder); 20 individuals (30-50 mm) were pooled from each station to make composite samples.

Generally, 2,6-di-tBuP, 4-tOP, NP-mix and OP1EO were measured in mussels with 4-tOP in very high concentrations (up to about 7 mg/kg ww).

Table 33. Concentration of phenolic substances in blue mussels[a] from marine environments in the Nordic countries in 2006/2007 (µg/kg ww).

Country	DK		FO			NO	
Location	Copenha.[b]	Limfjorden	Torshavn			Oslo Fjord	
Site	Lynetten	MSS3	harbour	harbour	Ref. site	St. 30A	St. 36A
Sample no.	702[j]	712[c,j]	1423[e]	1424[f]	1425[g]	1089[h]	1088[h]
Compounds:							
4-tBuP	204	<10	N/A	N/A	N/A	86	424
2.6-di-tBuP	92	21	4.5	21.9	17.3	<2.5	14
4-tOP	7,319[d]	1,980[d]	<13	19.2	2,428[d]	<3	7,362[d]
4-OP	<1	<1	3.8	<1	<1	<1	<1
NP-mix	509	N/A	11.4	49.0	908	<5	214
4-NP	37	6	<1	4.6	8.4	13	18
DDP	N/A	N/A	<100	<100	181	N/A	N/A
4-CP	<1	2	<1	<1	2.8	<1	<0.5
BPA	<5	<5	3.3	<1	<1	<5	<2.5
TBBPA	N/A	N/A	<5	<5	<5	N/A	N/A
Me-TBBPA	<5	<5	<5	<5	<5	<2.5	<5
OP1EO	<5	18	22.1	25.5	28.1	15	<5
NP1EO	<5	39	N/A	N/A	N/A	33	N/A

Notes: [a]*Mytilus edulis* [b]Copenhagen; [c]collected at 1,5 m depth; [d]estimate, outside calibration range; [e]33 individuals pooled, size 30-40 mm; [f]13 individuals pooled, size 60-70 mm; [g]12 individuals pooled, size 60-70 mm; [h]20 individuals pooled, size 30-50 mm; [i]more than 20 individuals pooled; size 30-40 mm.

7.3.4 Bird eggs

The Faroe Islands collected eggs from two colonies of black guillemots (*Cepphus grylle*), a common seabird at the Faroe Islands. Two composite samples were made of five eggs pooled from each colony at the small islands of Koltur and Skúvoy, respectively.

Generally, concentration levels were very low for the egg samples with several substances below detection limits. Highest concentration was observed for 4-tOP (up to 27 µg/kg ww).

7.3.5 Marine mammals

Liver samples from marine mammals were also collected for this project. Denmark delivered liver samples from harbour seals (*Phoca vitulina*) collected at three different locations: Limfjorden (Blinderøn), Anholt in Kattegat and in Køge Bugt south of Copenhagen. From each location livers from three individuals were pooled to make a composite sample; in Limfjorden, livers from one male and two females were pooled; at Anholt, livers from two males and one female were pooled, and in Køge Bugt, livers from three females were pooled.

The Faroe Islands delivered two composite liver samples from pilot whales (*Globicephala melas*) caught in Hvannasund; one composite sample comprised liver samples from six females, while the other comprised liver samples from six males.Seal liver samples mostly showed detectable concentrations of 2,6-di-tBuP and 4-tOP, while NP-mix and OP1EO also were detected in pilot whale liver samples.

Table 34. Concentration of phenolic substances in marine mammals (liver samples) and seabird eggs collected in the Nordic countries in 2006/2007 (µg/kg ww

Country	DK			FO			
Sample type	Harbour seal[a]			Pilot whale[b]		Black guillemot[c]	
Location	Limfjorden[d]	Kattegat[e]	Køge Bugt[f]	Hvannasund		Koltur	Skúvoy
Sample no.	1676-1678[e]	1679-1681[g]	1682-1684[h]	1430[i]	1431[j]	1426[k]	1427[k,l]
Compounds:							
4-tBuP	29	N/A	190	100	N/A	<10	N/A
2.6-di-tBuP	45	60.9	677	47	27.2	<5	2.8
4-tOP	241	<25	472	N/A	<25	15	26.9
4-OP	4.0	<1	<1	3.0	1.5	<1	<1
NP-mix	97	<6	N/A	52	197	16	9.9
4-NP	N/A	<1	N/A	<1	2.2	<1	<1
DDP	<100	N/A	N/A	N/A	<100	N/A	<100
4-CP	N/A	N/A	<1	3.0	6.7	3.0	<1
BPA	N/A	N/A	N/A	N/A	N/A	6.0	9.0
TBBPA	N/A	<10	N/A	N/A	<10	N/A	<10
Me-TBBPA	<5	N/A	<5	<5	<5	<5	<5
OP1EO	N/A	<1	N/A	356	36.4	8.0	7.3
NP1EO	N/A	N/A	N/A	N/A	N/A	<5	N/A

Notes: [a]*Phoca vitulina;* [b]*Globicephala melas*; [c]*Cepphus grylle*; [d]Blinderøn; [e]1 male + 2 females, 3-4 years; [f]Anholt; [g]2 males + 1 female, approx. 2 years; [h]3 females, 1-4 years; [i]6 females; [j]6 males; [k]composite of 5 eggs; [l]average of replicate analyses.

8. Discussion

8.1 Water samples

8.1.1 Influents from STPs and sewage streams

Nine water samples from STP influents and sewage streams have been measured. Apart from 4-tBuP, which has not been determined due to contamination problems, and di-Me-TBBPA, that was undetected, all other substances were recorded in most samples. All samples generally show highest concentration of NP-mix, BPA and NP1EO, but NP-mix range from 265 to 5,688 ng/L, BPA ranged from 204 to 9,828 ng/L and NP1EO ranged from 1,142 to 4,896 ng/L. Some of the highest values were outside the calibration range, and, therefore, are estimates with higher uncertainty. Also Dodecylphenol (DDP) showed rather high values, but also these values are somewhat uncertain due to interferences in the chromatograms. Highest concentrations were detected in the STPs in Finland, both regarding NP-mix and BPA, but also the influent sample from Lynetten in Copenhagen showed high values. Also for NP1EO did the Finnish STPs have high values together with the sample from the Sersjantvikin STP in Tórshavn (FO). See Figure 14 for a graphical de-

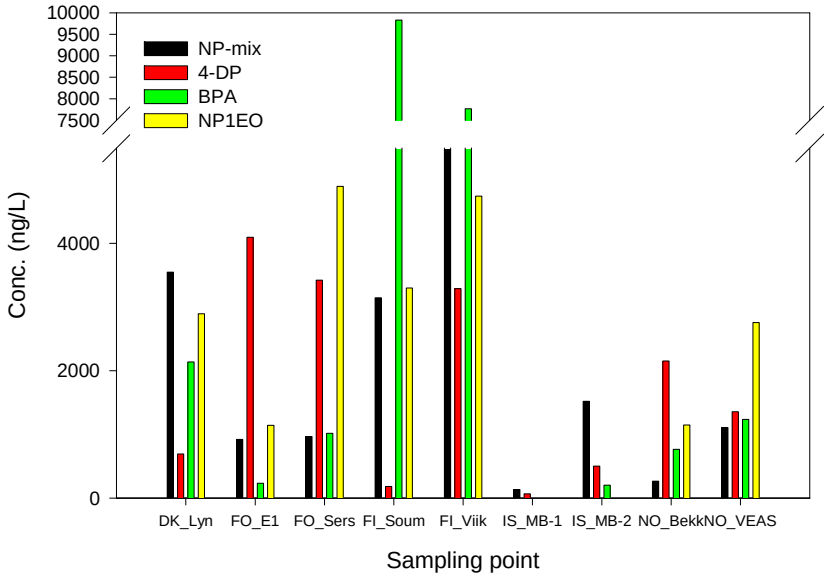


Figure 14. Concentration of selected phenolic compounds measured in influent waste water streams at STPs in Nordic countries. See Table 18 for a description of the sampling points.

When comparing the detected amounts with the latest reports on the use of the substances in the Nordic countries we find that Denmark had the highest use of nonylphenol ethoxylates while it was considerably lower in Finland during 2000-2005. Also NP was used in highest amount in Denmark during 2000-2005, but again influents to Finnish STPs generally had higher concentrations. Apart from 2002, where Norway has reported a very high consumption of BPA, the highest use during 2000-2005 has been in Finland, and this seems to be reflected in highest concentrations in inlet streams.

Regarding the two samples from local sewage streams in Reykjavík (MB-1 and MB-2) we find relatively high concentrations of NP-mix, and generally MB-2 has the higher concentrations of all detected substances. The exact origin of these local sewage streams is not know, but they are supposed to be of mainly domestic origin and thus probably reflects the general contribution from consumer products.

Comparing the reported results with literature values as listed in Table 9 is seems obvious that octylphenols (4-tOP and 4-OP) are at lower concentrations than was recently reported for Sweden by e.g. Naturvårdsverket (2005). For NP-mix the results are comparable to other recent studies, e.g. in Germany (Clara et al., 2005) and Austria (Weltin et al., 2004). For BPA the results obtained here are lower than average results reported by Naturvårdsveket (2005) in Sweden, but higher than those in another report from Naturvårdsverket (2006). Compared to the German results reported by Weltin et al. (2004), the BPA levels in this study are comparable. Also for the ethoxylates (OP1EO and NP1EO) the results in this study seem to be lower than or at the same level as those reported in the studies as referred to above for both Sweden and Germany.

8.1.2 Effluents from STPs and landfills

Eleven water samples from STP effluent streams and four leachate samples from landfills have been analysed. Compared to the influent samples the effluents have much lower concentrations for both NP-mix, BPA and NP1EO. NP1EO concentrations are below detection limit in all samples except the one from Sersjantvikin STP in Torshavn; this seems to demonstrate an effective removal of the ethoxylates from the waste stream as reported by Zhang et al. (2008).

For other substances, however, effluents from the Finnish STPs showed the highest concentrations; especially interesting is the fact, that both the effluents from Finnish STPs and Lynetten in Copenhagen have relative high concentrations of 4-tOP, a substance that was detected in much lower concentrations in the respective influent samples, and it does not seem obvious that the increase alone stems from the degradation of octylphenol ethoxylates that are not used in very high amounts. See Figure 15 for a graphical illustrations of these features.

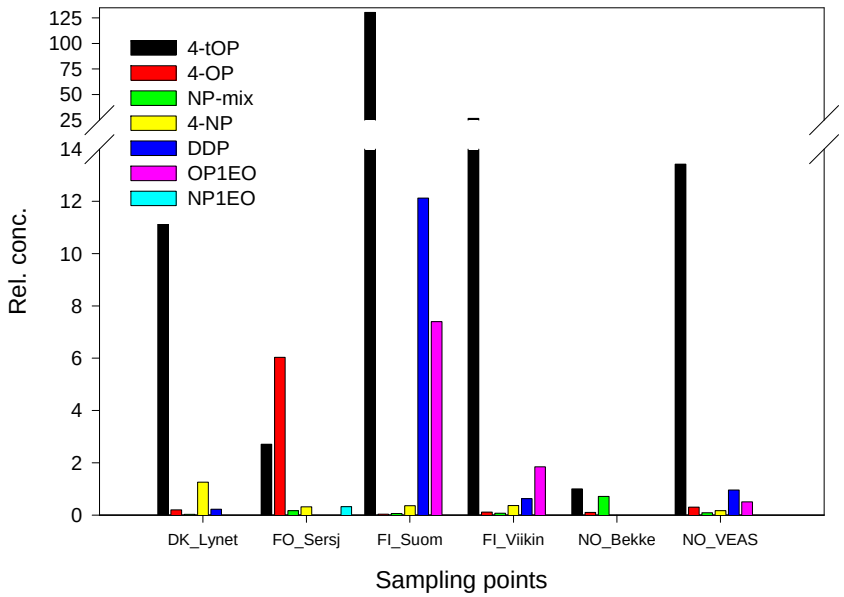


Figure 15. Ratios between selected phenolic compounds measured in effluent and influent (Effl/Infl) waste water streams at STPs in Nordic countries. See Table 19 for a description of the sampling points.

Also OP1EO seems to occur in the effluents samples in higher concentration than in the respective influents, but here increase could very well come from the degradation of nonylphenol ethoxylates that are produced and used in high amounts. As for the influents we also detected high concentrations of DDP in the effluents. Again this may be due the co-elution of other substances, and when comparing with the reported low use of DDP in the Nordic countries it does not seem reasonable that the environmental concentrations should be that high.

When comparing concentrations in effluents with those in corresponding influent samples, i.e. corresponding samples collected at the same STP within a short time span, a few general trends can be observed. The ethoxylates (OP1EO and NP1EO) are dramatically reduced and are below DLs for several samples. Only at the Finnish STPs is there an increase in the observed OP1EO concentration in the effluent compared to the influent; this could be caused by the possible breakdown of higher ethoxylates to mono-ethoxylates. Parallel to that an increase is observed in the alkylphenol concentrations, especially for 4-tOP, where concentrations are increased by 2.7 to 130; this trend is different for 4-OP where there is generally no increase in the concentration. However, the results stem from one-time spot samples, and fluctuations in rapidly changing flow systems may also be the cause of the observed trends. For comparison we refer to a recent study of Céspedes et al. (2006), who observed that on the average, the levels of alkylphenols and their ethxoylates were 10 times lower in effluents than in influents from STPs along a Spanish river.

Comparing the values observed here with literature values (*cf*. Table 9) a few trends seem obvious. Concentrations of 4-tOP are generally higher by up to a factor 10 than values reported for Sweden (Remberger et al. 2003; Naturvårdsverket, 2005), while they generally are lower for NP-mix (e.g. compared to Austrian data by Clara et al., 2005), a little higher or comparable for BPA compared to Swedish data (Naturvårdsverket, 2006), but lower than data from e.g. Germany (Bolz et al., 2001; Weltin et al., 2004), and lower for NP1EO (e.g. Remberger et al., 2003).

Regarding the leachate/runoff samples from waste deposits and landfills we find that the samples from Finland and Iceland have high concentrations of 4-tOP, NP-mix, BPA and to some degree of OP1EO; the sample from the Ämmässuo landfill in Finland had very high estimated concentration of NP-mix (almost 17 µg/L).

8.1.3 Recipient waters

Sixteen recipient water samples have been analysed from locations close to STPs; other samples are from other recipient areas not in direct connection with STPs.

Generally, concentrations for all substances were low, and in most cases below detection limits. Only NP-mix was detected in most of the samples in concentrations ranging from < DL to about 100 ng/L when excluding the values from one sample from Tórshavn harbour (1419), that had a very high value of NP-mix close to 4,200 ng/L. The same sample also had detectable amounts of 2,6-di-tBuP, 4-CP, OP1EO and NP1EO. BPA was also detected in several samples with concentrations ranging from DL to about 15 ng/L, and 22 ng/L in the sample form Tórshavn harbour.

The low concentrations generally detected in the recipient samples seem to reflect the relatively low concentrations measured in the effluent streams. The even lower concentrations detected in the recipient samples is probably an effect of further dilution, degradation and partitioning to particles and sediment.

Compared to literature values, especially for NP-mix, BPA and OP1EO, the concentrations observed in this study are generally lower to much lower, see e.g. the overview compiled by Petrovic et al. (2004) and the values listed in Table 9, except for the aforementioned Tórshavn harbour sample, where the observed NP-mix concentration was very high (~ 4,200 ng/L).

When evaluating the observed concentrations for 4-tOP, NP-mix, BPA and NP1EO with the effect concentrations listed in Table 8 they all seem to be consistently lower. For 4-tOP, NP (mixture of isomers), BPA and NP1EO the listed NOEC values for fish are 77, 240, 16 and 19 µg/L in 96-hr tests, respectively. Compared to the EQS (environmental quality standards) values listed for OP and NP in the proposal for a directive of

the EU regarding the Water Framework Directive (WDF) the values determined here are also below the AA-EQS (annual average) values for OP and NP of 10 and 300 ng/L for marine waters, respectively (EU Commission, 2006).

8.1.4 Surface runoffs

Eleven water samples from urban runoffs and two from greenhouses with plastic covering have been analysed. The two samples collected in the recipient stream downstream from the greenhouses in Lier in Norway both had concentrations below detection limits for all substances. Hence the use of plastic covers for greenhouses does not seem to give to elevated levels of the substances studied here.

The storm water runoffs from the older part of Stockholm all had detectable amounts of several substances including 4-tOP, NP-mix, DDP, BPA, TBBPA, OP1EO and NP1EO with 4-tBuP, NP-mix, DDP and BPA in highest concentrations. The samples were collected in Båtbyggargatam, Lugnets Alle, Sveavägen and Styrmansgatan, and all four samples are relatively comparable with slightly higher concentrations measured in the sample from Sveavägen, right in the centre of Stockholm. Compared to the samples from the other areas in Stockholm including some newer districts we find that the concentrations here are much lower, and only NP-mix, BPA and OP1EO are detected in concentrations above the detection limit. These trends are illustrated in Figure 16.

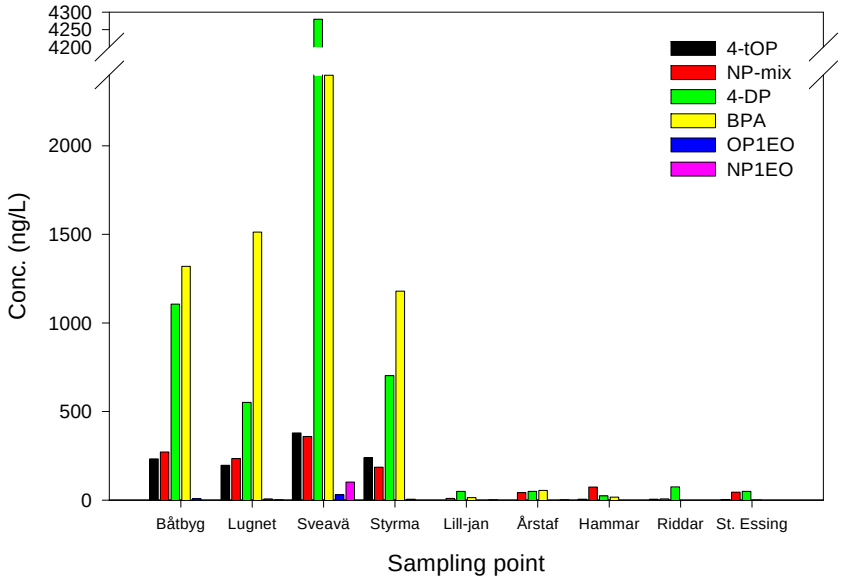


Figure 16. Concentration of selected phenolic compounds measured in storm water runoff from different sampling points in Stockholm (SE), old part of the city (high concentrations) and newer parts of the city (low concentrations). See Table 22 for a description of the sampling points.

A thorough discussion on how pollutants are transported and spread with storm water into the recipient environment has recently been the subject of a PhD-project at Luleå University of Technology (Karlsson et al., 2006).

8.1.5 Background

Samples from seven background locations have been analysed, most of them from marine environments; two samples were from lacustrine environments in Sweden. The same pattern as observed for all other water samples are also observed here: NP-mix and BPA are detected in highest concentrations. NP was detected in water samples from Kattegat in Denmark (about 30 ng/L) and in both lakes in Sweden (about 80 ng/L), while NP-mix was not detected in the background marine samples from Norway (outer Oslo Fjord and northern Norway). A similar trend was observed for BPA.

As was discussed for the recipient water samples the concentrations observed for the background water samples are lower than relevant literature values (*cf.* Table 9), just as they are below NOEC values for fish (*cf.* Table 8) and the proposed EU AA-EQS values (EU Commission, 2006).

8.2 Sewage sludge from STPs

The recorded data for the analysed sewage sludge samples are presented in Table 25. They show that apart from 4-NP, TBBPA and di-Me-TBBPA all other screened substances were detected in almost all samples and in relatively high concentrations. Especially NP-mix and DDP were detected in very high concentrations up to several mg/kg dw. Most of these high values, however, were outside the calibration range and should therefore be regarded as best estimates and not absolute and qualified values. It should be mentioned, however, that most of the sludge samples were very inhomogenous and that no complete homogenization could be obtained for all samples. The inhomogeneity of the analysed samples added significantly to the variations between samples, between parallel samples and replicate analyses.

When comparing the values for samples from the different STPs it seems like the Finnish STPs have highest concentrations (9-28 mg/kg dw) of NP-mix while they are lowest in Torshavn (1.4-2.4 mg/kg dw). Levels of DDP were also very high from about 11.3 to 47.4 mg/kg dw at VEAS and Bekkelaget STPs, respectively.

Sewage sludge samples were collected at both large, medium and small STPs, but no clear conclusions can be made regarding the influence of the size of the STP on the actual concentrations. Comparing e.g. levels of NP-mix it is lower at the smaller at Bjergmarken in Roskilde compared

to the bigger Lynetten in Copenhagen, but in Stockholm the bigger Henriksdal STP had lower levels than the smaller Hammarby Sjöstad STP. Thus influent composition and not size (and processing) may be the determining factor.

Looking at the data from both Bekkelaget and VEAS in Oslo it seems like concentration levels of e.g. NP-mix and NP1EO is higher in dry sludge than in wet (i.e. inlet vs. outlet). This could indicate that alkylphenols and monoethoxylates are generated in the STP by breakdown of higher ethoxylates. This, however, does not correspond to the observations made for the corresponding waste waters, where higher concentrations of alkylphenols and monoethoxylates were observed in influents than in effluents. The difference between concentration of selected phenolic compounds in wet and dry (stabilized) sludge is illustrated in Figure 17.

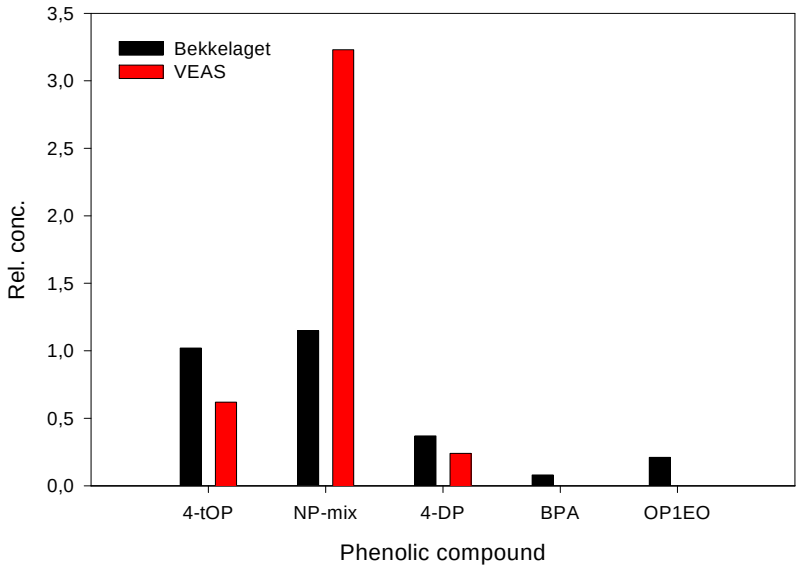


Figure 17. Ratios between concentrations of selected phenolic compounds measured in dry and wet (dry/wet) sludge from Bekkelaget and VEAS STPs (NO).

For BPA, NP-mix and NP1EO the concentration levels are comparable to values from other studies listed in Table 9, e.g. data from Naturvårdsverket (2005). The observed levels may also be compared the actual accept criteria for amending treated sewage sludge to agricultural fields; in Denmark these criteria are 10 mg/kg dw for NPE, which is the sum of NP, NP1EO and NP2EO. Thus the levels observed for sewage sludge from both Lynetten (Copenhagen) and Bjergmarken (Roskilde) seems to comply with these criteria.

8.3 Soil samples from landfills

The concentration recorded for the two soil samples from landfills at the Faroe Islands show higher levels for the active site than for the old landfill. Levels range from about 1 µg/kg dw for 4-OP and the ethoxylates (OP1EO and NP1EO) up to 47 µg/kg dw for NP-mix. The differences observed between the active and the abandoned landfill probably reflects that the old landfill initially had lower levels, but also that the phenolic compounds have been degraded and washed out.

Comparing with literature values (*cf*. Table 9) Sweden has previously reported 4-tOP, 4-NP in soil in the range of 1-2 and 11-60 µg/kg dw, respectively (Remberger et al., 2003; Naturvårdsverket, 2005). Norway (Fjeld et al., 2004a; Schlabach et al., 2002) has reported levels of BPA, TBBPA and di-Me-TBBPA in the range 7-370, 2-44 and up to 1 µg/kg dw, respectively. However, ordinary soil samples are probably not directly comparable to the soil samples hot spot areas like landfills.

8.3 Sediments

8.3.1 Sediment from recipient environments

The results listed in Table 29 indicate that only a few compounds are found in detectable amounts. NP-mix range from about 14 to 485 µg/kg dw, 4-CP from about 1 to 180 µg/kg dw, BPA from < 1 to 74 µg/kg dw and NP1EO from < 1 to about 67 µg/kg dw and 4-OP from about 1 to 25 µg/kg dw. Highest levels were generally recorded for the sample from Torshavn harbour (1432), a typical hot spot area. Inputs may come from various sources including effluents from the two STPs, but also from surface runoffs and spills from ferries and fishing vessels.

When comparing the levels in the sediment sample from Torshavn harbour with the corresponding water sample from the harbour (1419) relatively high levels of the same compounds (i.e. NP-mix, 4-CP BPA, OP1EO and NP1EO) were also detected. This observation seems to support the partitioning from water to sediment estimated in Chapter 3 (Table 5) using the PBT Profiler. The values observed for NP-mix in sediment from the harbour seems to be lower than in another recent study reported by Dam & Danielsen (2002), where the NP level at this particular site was found to be 3,300 µg/kg dw.

Also sediments from the Stockholm area (Stora Essingen, Årstaviken, Hammarby Sjöstad and Riddarfjärden) showed relative high levels of especially NP-mix (257 to 485 µg/kg dw); 4-CP ranged from about 8 to 35 µg/kg dw and BPA from 12 to about 16 µg/kg dw. Compared with the levels detected in the run-off water samples from the areas it is again observed that the same compounds are detected in highest levels in water

as in sediments. This also seems to be the case for the Tórshavn harbour samples, except for DDP, which was undetected in the water phase but detected in high concentrations in sediment.

Other studies of sediments (*cf.* Table 9) reveal much higher variations than observed in this study. Levels typically vary between <1 to several mg/kg dw for e.g. NP. Also data reported by Naturvårdsverket (2005) show higher variations than observed here for e.g. NP and BPA.

8.3.2 Sediment from background environments

The data for sediments from background areas (both marine and freshwater) listed in Table 30 generally show much lower concentrations than was observed for sediments from recipients areas except for the sample from Krageholmssjöen in Sweden. NP-mix was detected in highest concentration from about 10 to 54 µg/kg dw, while both 4-CP, BPA OP1EO and NP1EO were about unity. Krageholmssjöen had a factor 10-50 higher levels for all detected substances than the marine sediments. This seems to illustrate that a relatively small freshwater lake, probably serving as a recipient environment and with limited water exchange, preserves a larger part of the added pollutants than the marine areas, where dilution and transportation may play an important role. Thus, in sediments from Northern Norway (Tromsø and Varangerfjord) almost all substances screened in this study were < DL.

8.4 Biological samples

8.4.1 Fish from brackish/freshwater environments

Liver samples from brackish/freshwater fish showed considerable amounts of 2,6-di-tBuP ranging from about 10 up to more than 5,000 µg/kg ww; the very high levels were only observed in a couple of samples from Roskilde Fjord (1159) and Helsinki city bay (1017-1019). For the other samples levels ranged from about 12 to 413 µg/kg ww. Such relatively high concentrations of 2,6-di-tBuP do not correspond to literature values observed elsewhere (cf. Table 10), and the values observed here may not represent realistic levels. Thus, a recent Swedish study also reported low levels of 2,6-di-tBuP < 0.1 µg/kg lipid weight (Remberger et al., 2003). The usage of 2,6-di-tBuP is below 100 tonnes/year in most countries (cf. Figure 3), and according to the PBT Profiler estimates it has a log K_{ow} of 4.8 and hence should not be very bioaccumulative. Most probably, the high levels are due to unexplained analytical artifacts (*cf.* Section 8.4.6).

Also 4-tOP and NP-mix were detected at relatively high levels from less than 100 up to about 355 and 990 µg/kg, respectively. BPA was only

detected in two samples (11 and 57 µg/kg ww). OP1EO was detected in very high levels in the same two samples from Roskilde and Helsinki - 2,500 and 4,035 µg/kg ww, respectively - where also 2,6-di-tBuP was found in high concentrations. In the Roskilde sample NP1EO was also detected in very high concentration (> 18 mg/kg ww). According to the PBTprofiler estimates (*cf*. Table 7) neither OP1EO nor NP1EO should be particularly bioaccumulative and persistent, and the high values are rather extraordinary.

For the fish from the Norwegian freshwater environments the results presented here may be compared with other recent studies in both Norway (e.g. Fjeld et al., 2004), and in Sweden (e.g. Remberger et al., 2003).

8.4.2 Fish from marine environments

Compared to the results obtained for fish samples from brackish/freshwater environments the results for fish from marine environments appear to be somewhat similar. Compared to the other compounds, 2,6-di-tBuP was again detected in relatively high concentrations; especially in one cod liver sample (1674) from the open sea south of Iceland (about 4 mg/kg ww). This sample also had an unusual high value of OP1EO (about 32 mg/kg ww). Similarly, another sample of cod liver from the open sea west of Iceland also showed elevated concentrations of NP-mix (> 1 mg/kg ww) and OP1EO (> 4.5 mg/kg ww). On the other hand, the cod liver sample from the inner Oslo Fjord (1047) only showed a detectable amount of 2,6-di-tBuP (0.3 mg/kg ww). As discussed in Section 8.4.6 no definite explanation can be given for the observed trends.

With four of the composite cod liver samples the clean-up was unsuccessful, and the resulting GC-MS results were useless, and no results are reported for these four samples. This corresponds to PCB analyses of cod samples, where the clean-up seems to be more troublesome than for other fish samples (NERI, unpublished results).

8.4.3 Mussels from marine environments

In contrast to the fish samples discussed above, the mussel show another unusual trend. 2,6-di-tBuP are detected but in much lower concentrations than in fish; on the contrary, 4-tOP are detected in very high concentrations in most samples – from below DL up to more than 7 mg/kg ww. The concentrations observed for NP-mix in mussels (from DL up to about 900 µg/kg ww) seem to be a little higher or comparable to the concentrations in fish liver. Concentrations of OP1EO, however, seem to be lower in mussels (from DL to about 30 µg/kg ww) than in fish. One explanation regarding 4-tOP could be that mussels do not have the appropriate enzyme system to metabolize it, or that it partition into the mussel's lipid tissues.

Regarding NP-mix the observed concentrations are comparable to values reported by both Denmark (NERI, unpublished data) and Sweden (Wahlberg et al., 1990). For NP1EO the concentrations observed here are in the same range as those recently reported by Dam & Danielsen (2002), while older data reported for Sweden have higher values (Wahlberg et al., 1990).

8.4.4 Eggs from black guillemots, the Faroe Islands

The two composite egg samples collected at two small Faroese islands (Koltur and Skúvoy) only showed low concentrations of most substances. 2,6-di-tBuP, 4-tOP, NP-mix, BPA and OP1EO were observed in detectable amounts from about 3 to 27 µg/kg ww; 4-tOP was detected in highest concentrations.

8.4.5 Marine mammals

Composite liver samples from harbour seals collected in Denmark only showed detectable concentrations of 2,6-di-tBuP (45 to 677 µg/kg ww), 4-tOP (< DL to 472 µg/kg ww) and NP-mix (up to 97 µg/kg ww). Again the relatively high levels of 2,6-di-tBuP seem hard to explain.

The pilot whale liver samples from the Faroe Islands had detectable concentrations of more compounds. Thus, 2,6-di-tBuP, NP-mix, 4-CP and OP1EO were detected in ranges from 27 to 47, 52 to 197, 3 to 7 and 36 to 356 µg/kg ww, respectively.

8.4.6 Detection of 2,6-di-tBuP in biological samples

In most biota samples analysed in this study relatively high, compared to literature values, concentrations of 2,6-di-tBuP have been detected. The presence of such high concentrations does not correspond to the application pattern and the bioaccumulating tendency of 2,6-di-tBuP (estimated BCF = 430). As laboratory blanks (< 3 µg/kg) do not indicate a serious laboratory contamination problem, other analytical problems may have caused the detection of high concentrations. One problem could be the very slow reaction with the silylating agent which might result in varying and different responses of 2,6-di-tBuP in standards and real samples. Another explanation could be co-elution of some unknown compound(s) present in biological matrices. As none of these potential problems have been pursued in details, it is not possible to conclude which one, if any, is the most likely explanation to the observed data. One way or the other, the observed concentrations of 2,6-di-tBuP should be regarded with reasonable care before definite conclusions regarding this compound are made.

Conclusions

In total about 130 samples have been analysed including additional 9 nine samples from Norway. The samples included water, solids such as sludge, sediments and soil and biological samples.

Generally, wastewater samples had the highest concentration of especially NP-mix, DDP, BPA and NP1EO. Typically, influent waste water had higher concentration than effluent samples. At some STPs, however, higher concentrations are observed in effluent samples than in the corresponding influent samples. In particular, this observed for 4-tOP, where the increase in concentration could be linked to a preceding degradation of 4-tOP ethoxylates. Recipient and background water samples were generally low in concentrations, and they all were below NOEC values for fish and the proposals for EU EQS criteria, except for some samples from Tórshavn harbour.

Of the solid samples sewage sludge were high in concentrations of especially NP-mix and low in ethoxylates which again demonstrates the degradation of the latter during the sludge processing. The concentrations in sediment samples were also generally low, but freshwater sediments for some Swedish lakes had higher levels than the marine sediments. This is probably an effect of reduced dilution in the constrained lacustrine environment.

Of the biological samples highest concentration were measured in fish liver, especially of 2,6-di-tBuP, 4-tOP, NP-mix and OP1EO. The reason for that is not quite clear as none of the substances are expected to bioaccumulate extensively. A similar picture was observed for mussels. Due to unexplained analytical “artifacts” regarding the quantification of 2,6-di-tert-BuP the data for this compounds must be evaluated carefully before being applied in risk assessments and similar studies.

Regarding the marine mammals more compounds were detected (i.e. > DL) in the pilot whales than in harbour seals. 2,6-di-tBuP was detected in higher concentration in harbour seals while NP-mix was detected in higher concentration in pilot whales, but generally concentrations in these mammals were low.

Acknowledgements

NERI/AU

Laboratory technicians Charlotte Dahl Schøidt, Ellen Christiansen, Gitte H. Jensen, Inge Merete Worsøe and Nina Wiese Thomsen are greatly acknowledged for skilful technical assistance during sample preparation and analysis, for lots of energy and devotion, and for always keeping a high spirit.

Denmark

Thanks to Jan Rasmussen, Københavns Miljøkontrol, Jane Brøns Hansen, Københavns Amt, Bruno Hansen og Søren Hedal, Roskilde Amt, Lone Reersø Hansen, Frederiksborg Amt, Christen Jensen, Nordjyllands Amt, Lene Vig, Lynette Fællesskabet A/S, Lotte Larsen and Stella Sørensen at Roskilde kommune and Rune Dietz at the National Environmental Research Institute at University of Aarhus (NERI) for providing samples for this project. Thanks to Martin Larsen (NERI) for co-ordinating the sampling programs.

Faroe Islands

Thanks to Katrin Hoydal, for lending a hand with the sampling and sample preparation, and to the staff of Tórshavn Kommune and at the Landssjúkrahúsið hospital for assistance during the sampling visits.

Finland

Finnish Environment Institute (Research Programme for Contaminants and Risks) organized the sampling work. We will thank the personnel for all help in the sewage treatment plants of Helsinki City (Mrs. Heli Lindberg), Espoo City (Mrs. Maija Jäppinen) and Pornainen Commune (Mr. Jukka Pietilä and Mr. Timo Anttila). The Northern pikes were collected by Mr. Matti Mielonen and Mr. Mikko Karvonen, who are controlling and monitoring fish in the Helsinki coastal area. Discharge water from the Ämmässuo landfill was collected in collaboration with the Helsinki Metropolitan Area Council (YTV/Mr. Pertti Ruuskanen).

Iceland

Thanks to the staff at Klettagarðar and Ánanaust sewage treating plants for their help in collecting samples. Thanks also to the department of biology at the University of Iceland for their help in catching fish for use as samples, also thanks to Matis ohf. for their help in providing marine fish samples. Kind regards must also go to the staff at “Áhaldahús” in Mos-

fellsbær for their help in collecting sewage water samples with such a short notice.

Norway

We want to thank Arne Haar at Vestfjorden Avløpsselskap (VEAS) for collecting samples of influent water, effluent water and sludge from VEAS sewage treatment plant. For collecting all the other Norwegian samples we will thank John Arthur Berge, Anne Marie Bomo, Norman Green, Jarle Håvardstun and Merethe Schøyen at Norwegian Institute of Water Research (NIVA).

Sweden

Samples of traffic storm water were kindly provided by Jan Stenlycke, Stockholm Vatten AB.

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Sammenfatning

Dette projekter omhandler screening af udvalgte fenolstoffer i det nordiske miljø og er initieret af Kemikaliegruppen under Nordisk Ministerråd.

Alle seks nordiske lande (Danmark, Finland, Færøerne, Island, Norge og Sverige) har deltaget i projektet, som har inkluderet indsamling og analyse af 129 prøver fra forskellige udvalgte miljømatricer. Undersøgelsen har omfattet analyse af 13 forskellige fenolstoffer fra alkylfenoler (4-*tert*-butylfenol, 2,6-di-*tert*-butylfenol, oktyl-, nonyl- og dodecylfenoler) over 4-cumylfenol til bisfenoler (bisfenol A, tetrabrombisfenol A og dennes dimethylæter) samt oktyl- og nonylfenol monoetoxylater. Forskellige miljøinstitutter og -institutioner i medlemslandene har haft ansvaret for at indsamle og fremsende prøverne til analyse ved Danmarks Miljøundersøgelser ved Århus Universitet i Danmark, som var udvalgt til at udføre projektet.

Der indgik tre typer af prøver i projektet: vandprøver, faste prøver og biologiske prøver. Vandprøverne omfattede spildevand fra rensningsanlæg (influent og effluent) og perkolat fra lossepladser; desuden indgik også afløbsvand fra gader og veje og overfladevand fra såvel ferskvands-/brakvandsområder som marine områder. De faste prøver omfattede slam fra rensningsanlæg (både vådt og tørt), jord fra lossepladser/deponier og sediment fra både ferskvands-/braksvandsområder og marine områder. Endelig omfattede de biologiske prøver blåmuslinger fra marine områder, lever fra fisk fanget i ferskvands- (søer)/braksvandsområder og i marine områder, lever fra havpattedyr (spættet sæl og grindehval) samt æg fra havfugle (tejst).

For vandprøverne blev NP-mix (forskellige nonylfenol isomerer), dodecylfenol (DDP), bisfenol A (BPA), 4-*tert*-oktylfenol (4-tOP) og nonylfenol monoetoxylat (NP1EO) fundet i de højeste koncentration i spildevandsprøver, især i prøver af influent. Til gengæld var de fundne koncentrationer for de fleste fenolstoffer generelt lave i prøver fra recipienter og baggrundsstationer; NP-mix, DDP, BPA og NP1EO blev dog målt over detektionsgrænsen, og i en prøve fra Tórshavn havn blev der estimeret den højeste målte værdi af NP-mix.

For de faste prøver blev de højeste værdier målt i spildevandsslam, og som for prøver af spildevand blev NP-mix og DDP målt i de højeste koncentrationer, mens niveauerne for etoxylater var væsentligt reducerede. Til sammenligning var de målte koncentrationer i de andre faste prøver, jord og sediment, lave for de fleste af de målte fenolstoffer.

I modsætning til de andre prøvetyper blev der i de biologiske prøver målt relativt høje værdier af 4-*tert*-butylfenol (4-tBuP) og 2,6-di-*tert*-butylfenol (2,6-di-tBuP), men årsagen hertil er ikke kendt. Desuden blev

der målt 4-tOP, NP-mix, DDP og oktyl- og nonylfenol monoetoxylater i muslinger og fiskelever, mens niveauerne af disse stoffer var lave i prøver af både fugleæg og sællever. Med hensyn til NP-mix og OP1EO blev der målt højere koncentrationer i prøver af lever fra grindehvaler end fra sæler.

Udover de omtalte analyseresultater sammenstiller rapporten også fysisk-kemiske data for de undersøgte fenolstoffer tillige med estimerede og eksperimentelle data for stoffernes spredning og forekomst i miljøet, deres persistens/nedbrydelighed og toksicitet overfor forskellige test organismer.

Appendix A

Abbreviation list

AA	Annual average
AP	Alkylphenol
APEO	Alkylphenol ethoxylate
ASE	Accelerated solvent extraction
BCF	Bioconcentration factor
Bp	Boiling point (in °C)
BPA	Bisphenol A
BSTFA	N,O-bis(trimethylsilyl)trifluoroacetamide
BuP	Butylphenol
CHRIP	Chemical Risk Information Platform: Information on Biodegradation and Bioconcentration of Existing Chemical Substances in the Chemical Risk Information Platform
ChV	Chronic no-effect concentration (same as NEC) used in PBT Profiler
CP	Cumylphenol
DL	Detection limit
DDP	Dodecylphenol
dw	dry weight
ECB	European Chemicals Bureau
EC50	Concentration of a t that gives rise to non-lethal adverse effects in 50 % of the test organisms
EQS	Environmental quality standard
EUSES	European Union System for the Evaluation of Substances
ESIS	European Chemical Substances Information System
GC-MS	Gas chromatography-mass spectrometry
HPVC	High Production Volume Chemicals
HPVIS	High Production Volume Information System (US EPA)
INCHEM	Chemical Safety Information from Intergovernmental Organizations (Internal programme on Chemical Safety, IPCS)
IUCLID	International Uniform Chemical Information Database for HPVCs
K_{ow}	Octanol-water partition coefficient
LC-MS	Liquid chromatography-mass spectrometry
LC50	Concentration of test substance that is lethal to 50 % of the test organisms
LOEC	Lowest observable effect concentration; i.e. the lowest concentration of a test substance that is statistically different in adverse effect on a specific population of test organisms from that observed in controls
LPVC	Low Production Volume Chemicals
MATC	Geometric mean of the maximum allowable toxicant concentration, i.e. the geometric mean of LOEC and NOEC
Me-	Methyl group
Mp	Melting point (in °C)
MW	Molecular weight
MWE	Microwave extraction
NEC	Chronic no-effect concentration (the same as MATC)

NITE	National Institute of Technology and Evaluation (Japan)
NOEC	No-effect concentration; the highest concentration of a test substance that shows no statistical difference in adverse effect on a specific population of test organisms from that observed in controls
NP	Nonylphenol
NPEO	Nonylphenol ethoxylates
NP1EO	Nonylphenol monoethoxylate
OECD	Organization for Economic Cooperation and Development
OECD HPV	OECD Integrated HPV Database (OECD)
OP	Octylphenol
OPEO	Octylphenol ethoxylates
OP1EO	Octylphenol monoethoxylate
OSPAR	Oslo-Paris Commission for the Protection of the Marine Environment of North-East Atlantic
PBT	Persistence-Bioaccumulation-Toxicity
peq	person equivalent
PLE	Pressurized liquid extraction
PNEC	Predicted no-effect concentration (at specified endpoint)
SIDS	Screening Information Data Sets
SPE	Solid phase extraction
STP	Sewage treatment plant
TBBPA	Tetrabromobisphenol A
UN-ECE	United Nations Economiv Comission for Europe
UNEP	United Nations Environment Programme
US-EPA	US Environmental Protection Agency
Vp	Vapour pressure (in Pa)
WD	Waste deposit
WFD	Water Framework Directive
Wsol	Water solubility (in mg/L)
ww	wet weight

Appendix B

Detailed information on samples and sampling sites

Table 35. Number, type, location and position of samples collected in Denmark, 2006-2007.

Sample type	Sample no.	Sample name	Sampling date	Location	Sampling site	Latitude	Longitude	Remarks
Water								
STP influent	*2006-778*	*Ni-indløb*	*17-10-2007*	*Copenhagen*	*Lynetten STP*	*55°41.75' N*[1]	*012°37.0' E*[1]	
STP influent	*2006-779*	*Ni-indløb*	*17-10-2007*	*Copenhagen*	*Lynetten STP*	*55°41.75' N*[1]	*012°37.0' E*[1]	*replicate*
STP effluent	*2006-780*	*STA-afløb*	*17-10-2007*	*Copenhagen*	*Lynetten STP*	*55°41.75' N*[1]	*012°37.0' E*[1]	
STP effluent	*2006-781*	*STA-afløb*	*17-10-2007*	*Copenhagen*	*Lynetten STP*	*55°41.75' N*[1]	*012°37.0' E*[1]	*replicate*
STP effluent	*2006-1009*	*Bjergmark-udl.*	*13-11-2006*	*Roskilde*	*Bjergmarken STP*	*55°38.95' N*[1]	*012°03.43' E*[1]	
STP effluent	*2007-1633*	*Bjergmark-udl.*	*15-02-2007*	*Roskilde*	*Bjergmarken STP*	*55°38.95' N*[1]	*012°03.43' E*[1]	
Recipient[2]	*2006-691*	*Lynetten-1*	*04-10-2006*	*Copenhagen*	*Lynetten STP*	*??*	*??*	
Recipient[2]	*2006-692*	*Lynetten-2*	*04-10-2006*	*Copenhagen*	*Lynetten STP*	*??*	*??*	*replicate*
Recipient[2]	*2006-1029*	*St. 60*	*14-11-2006*	*Roskilde Fjord*	*Station 60*	*55°42.78' N*	*012°04.00' E*	*Depth: 1 m*
Recipient[2]	*2006-711*	*MSS3*	*03-10-2006*	*Nibe Bredning*	*MSS 3*	*57°00.58' N*	*009°39.45' E*	*Depth: <2 m*
Background[3]	*2006-694*	*Togt 238*	*21-09-2006*	*Kattegat*	*Station 905*	*57°11.06' N*	*011°39.62' E*	
Background[3]	*2006-801*	*Togt 238*	*18-10-2006*	*Kattegat*	*Station 905*	*57°11.06' N*	*011°39.62' E*	
Background[3]	*2006-802*	*Togt 238*	*18-10-2006*	*Kattegat*	*Station 905*	*57°11.06' N*	*011°39.62' E*	*replicate*
Solid								
STP sludge	*2006-782*	*kageslam*	*17-10-2007*	*Copenhagen*	*Lynetten STP*	*55°41.75' N*[1]	*012°37.0' E*[1]	
STP sludge	*2006-783*	*kageslam*	*17-10-2007*	*Copenhagen*	*Lynetten STP*	*55°41.75' N*[1]	*012°37.0' E*[1]	*replicate*
STP sludge	*2007-1634*	*slam fra centri.*[4]	*15-02-2007*	*Roskilde*	*Bjergmarken STP*	*55°38.95' N*[1]	*012°03.43' E*[1]	
Sediment[2]	*2006-693*	*Lynetten*	*04-10-2006*	*Copenhagen*	*Lynetten STP*	*??*	*??*	
Sediment[2]	*2006-1030*	*St. 60*	*14-11-2006*	*Roskilde Fjord*	*Station 60*	*55°42.78' N*	*012°04.00' E*	*Depth: 5.5 m*
Background[3]	*2006-699*	*Togt 238*	*21-09-2006*	*Kattegat*	*Station 905*	*57°11.06' N*	*011°39.62' E*	
Biological								
Mussels[2,5]	*2006-712*	*MSS3*	*03-10-2006*	*Nibe Bredning*	*MSS3*	*57°00.58' N*	*009°39.45' E*	*Depth: <2 m*
Fish liver[2,6]	*2006-1159*	*Kutling*	*29-10-2006*	*Roskilde Fjord*	*Inner fjord*	*??*	*??*	*Pool: 14*
Fish liver[2,6]	*2006-1160*	*Kutling*	*15-11-2006*	*Roskilde Fjord*	*Inner fjord*	*??*	*??*	*Pool: 18*
Seal liver[3,7]	*1676-1678*	*Blinderøn*	*??*	*Limfjorden*	*Blinderøn*	*56°54.0' N*[1]	*009°00.7' E*[1]	*Pool: 3*[8]
Seal liver[3,7]	*1679-1681*	*Anholt*	*??*	*Kattegat*	*Anholt*	*56°44' N*[1]	*011°39' E*[1]	*Pool: 3*[9]
Seal liver[3,7]	*1682-1684*	*Køge Bugt*	*??*	*Øresund*	*Køge Bugt*	*??*	*??*	*Pool: 3*[10]

*Notes: [1]Estimated; [2]Brackish environment; [3]Marine environment; [4]sludge from centrifuge; [5]Blue mussel (*Mytilus edulis*); [6]Sand goby (* Pomatoschistus minutus*); [7]Harbour seal (*Phoca vitulina*); [8]1 male + 2 females, 3-4 years; [9]2 males + 1 female, 2 years; 3 females, 1-4 years;*

Table 36. Number, type, location and position of samples collected at the Faroe Islands, 2006-2007.

Sample type	Sample no.	Sample name	Sampling date	Location	Sampling site	Latitude	Longitude	Remarks
Water								
STP influent	*2007-1416*	*E-1*	*12-11-2006*	*Torshavn*	*Hospital STP*	*62°00,103' N*	*006°46,526' W*	
STP influent	*2007-1420*	*E-3*	*29-12-2006*	*Torshavn*	*Sersjantvikin STP*	*62°00,508' N*	*006°45,697' W*	*household*
STP effluent	*2007-1417*	*E-2*	*12-11-2006*	*Torshavn*	*Hospital STP*	*62°00,103' N*	*006°46,526' W*	
STP effluent	*2007-1418*	*E-4*	*29-12-2006*	*Torshavn*	*Sersjantvikin STP*	*62°00,508' N*	*006°45,697' W*	
Landfill effluent	*2007-1421*	*E-5*	*29-12-2006*	*Torshavn*	*Húsahagi*	*62°01,711' N*	*006°48,307' W*	
Recipient[2]	*2007-1422*	*RES-1*	*12-01-2007*	*Klaksvik*	*Marina*	*62°13,707' N*	*006°35,221' W*	*oilslick*
Recipient[2]	*2007-1419*	*RES-2*	*12-01-2007*	*Vágsbotn*	*Vágsbotn*	*62°00,501' N*	*006°46,347' W*	*oilslick*
Solids								
STP sludge	*2007-1435*	*SL-1*	*12-01-2007*	*Torshavn*	*Hospital STP*	*62°00,103' N*	*006°46,526' W*	
STP sludge	*2007-1436*	*SL-2*	*29-12-2006*	*Torshavn*	*Sersjantvikin STP*	*62°00,508' N*	*006°45,697' W*	
Soil	*2007-1433*	*SO-1*	*29-12-2006*	*Torshavn*	*Húsahagi*	*62°01,711' N*	*006°48,307' W*	*landfill*
Soil	*2007-1434*	*SO-2*	*29-12-2006*	*Torshavn*	*Havnadalur*	*62°01,066' N*	*006°49,069' W*	*landfill, old*
Sediment[2]	*2007-1428*	*SE-1*	*15-06-2006*	*Klaksvik*	*Pollurin, St. 7*	*62°14' N*[1]	*006°36' W*[1]	*hot spot*
Sediment[2]	*2007-1429*	*SE-2*	*15-06-2006*	*Götuvik*	*Bakkafrost, St. 16*	*62°11' N*[1]	*006°44' W*[1]	*hot spot*
Sediment[2]	*2007-1432*	*SE-3*	*12-01-2007*	*Torshavn*	*Harbour (BA)*	*62°00,430' N*	*006°46,434' W*	*hot spot*
Biological								
Mussels[3]	*2007-1423*	*NE-06*	*12-01-2007*	*Torshavn*	*Harbour*	*62°01' N*[1]	*006°46' W*[1]	*hot spot*
Mussels[3]	*2007-1424*	*NE-06*	*12-01-2007*	*Torshavn*	*Harbour*	*62°01' N*[1]	*006°46' W*[1]	*hot spot*
Mussels[3]	*2007-1425*	*NE-05*	*30-10-2006*	*Giljanes*		*62°06.06' N*[1]	*007°08.74' W*[1]	*Ref. site*
Fish liver[4]	*2007-1437*	*COD-T*	*13-01-2007*	*Torshavn*	*Bursatanga*	*62°01' N*[1]	*006°46' W*[1]	*Pool: 7*
Birds egg[5]	*2007-1426*	*CG-KOL*	*June-2006*	*Koltur*		*61°59.7' N*[1]	*006°58.5' W*[1]	*Pool: 10*
Birds egg[5]	*2007-1427*	*CG-SKU*	*June-2006*	*Skúvoy*		*61°46.3' N*[1]	*006°49.4' W*[1]	*Pool:10*
Whale liver[6]	*2007-1430*	*PW-1*	*28-08-2006*	*Hvannasund*		*62°18' N*[1]	*006°30' W*[1]	*Pool: 6*[7]
Whale liver[6]	*2007-1431*	*PW-2*	*28-08-2006*	*Hvannasund*		*62°18' N*[1]	*006°30' W*[1]	*Pool: 6*[8]

*Notes: [1]Estimated coordinate; [2]Marine environment; [3]Blue mussel (*Mytilus edulis*); [4]Atlantic cod (*Gadus morhua*); [5]Black guillemot (*Cepphus grylle*); [6]Pilot whale (*Globicephala melas*); [7]6 females; [8]6 males;*

Table 37. Number, type, location and position of samples collected in Finland, 2006-2007.

Sample type	Sample no.	Sample name	Sampling date	Location	Sampling site	Latitude	Longitude	Remarks
Water								
STP influent	*2006-719*	*SO STP*	*04-10-2006*	*Espoo*	*Suomenoja STP*	*60°09.4' N[1]*	*024°42.5' E[1]*	*270,000[2]*
STP influent	*2006-716*	*VM STP*	*04-10-2006*	*Helsinki*	*Viikinmäki STP*	*60°13.7' N[1]*	*025°01.0' E[1]*	*1,000,000[2]*
STP effluent	*2006-724*	*P STP*	*04-10-2006*	*Pornainen*	*Pornainen STP*	*60°28.6' N[1]*	*025°22.5' E[1]*	*< 1000[2]*
STP effluent	*2006-720*	*SO ST*	*04-10-2006*	*Espoo*	*Suomenoja STP*	*60°09.4' N[1]*	*024°42.5' E[1]*	*270,000[2]*
STP effluent	*2006-717*	*VM STP*	*04-10-2006*	*Helsinki*	*Viikinmäki STP*	*60°13.7' N[1]*	*025°01.0' E[1]*	*1,000,000[2]*
Landfill effluent	*2006-718*	*AM LF*	*04-10-2006*	*Espoo*	*Ämmässuo*	*60°14.5' N[1]*	*024°32.5' E[1]*	*Largest in F.[7]*
Recipient[3]	*2006-721*	*H1 SI*	*03-10-2006*	*Heslsinki*	*Near ship port*	*60°11.72' N*	*025°29.87' E*	*Depth: 1 m*
Recipient[3]	*2006-722*	*H2 SI*	*03-10-2006*	*Espoo*	*Coastal sea*	*60°06.8' N[1]*	*024°46.07' E[1]*	*Depth: 1 m*
Recipient[3]	*2006-723*	*H3*	*03-10-2006*	*Espoo*	*Coastal sea*	*60°06.8' N[1]*	*024°46.07' E[1]*	*Depth: 16 m*
Solids								
STP sludge	*2006-732*	*P STP*	*04-10-2006*	*Pornainen*	*Pornainen STP*	*60°28.6' N[1]*	*025°22.5' E[1]*	*< 1000[2]*
STP sludge	*2006-733*	*SO STP*	*04-10-2006*	*Espoo*	*Suomenoja STP*	*60°09.4' N[1]*	*024°42.5' E[1]*	*270,000[2]*
STP sludge	*2006-734*	*VM STP*	*04-10-2006*	*Helsinki*	*Viikinmäki STP*	*60°13.7' N[1]*	*025°01.0' E[1]*	*1,000,000[2]*
Sediment[3]	*2006-735*	*E1 SED*	*03-10-2006*	*Espoo*	*Coastal sea*	*60°06.8' N*	*024°46.07' E*	*Depth: 17 m*
Sediment[3]	*2006-736*	*H1 SED*	*03-10-2006*	*Helsinki*	*City bay*	*60°11.72' N*	*025°29.87' E*	*Near port*
Biological								
Fish liver[3,4]	*1014-1016*	*PIKE-VaKaLa*	*20-10-2006*	*Helsinki*	*City bay*	*60°11.72' N*	*025°29.87' E*	*Pool: 3[5]*
Fish liver[3,4]	*1017-1019*	*PIKE-VaKaLa*	*20-10-2006*	*Helsinki*	*City bay*	*60°11.72' N*	*025°29.87' E*	*Pool: 3[5]*
Fish liver[3,4]	*1020-1022*	*PIKE-VaKaLa*	*22-10-2006*	*Helsinki*	*City bay*	*60°11.72' N*	*025°29.87' E*	*Pool: 3[5]*
Fish liver[3,4]	*2006-1023*	*PIKE-VaKaLa*	*22-10-2006*	*Helsinki*	*City bay*	*60°11.72' N*	*025°29.87' E*	*male*
Fish liver[3,4]	*1024-1026*	*PIKE-LaLa*	*02-11-2006*	*Espoo*	*Coastal bay*	*60°11.80' N*	*024°51.50' E*	*Pool: 3[5]*
Fish liver[3,4]	*1027-1028*	*PIKE-LaLa*	*02-11-2006*	*Espoo*	*Coastal bay*	*60°11.80' N*	*024°51.50' E*	*Pool: 2[6]*

*Notes: [1]Estimated coordinate; [2]Estimated population; [3]Brackish environment; [4]Nothern pike (*Esox lucius*); [5]3 females pooled; [6]2 males pooled; [7]Largest landfill in Finland*

Table 38. Number, type, location and position of samples collected at Iceland, 2006-2007.

Sample type	Sample no.	Sample name	Sampling date	Location	Sampling site	Latitude	Longitude	Remarks
Water								
STP influent	*2007-1474*	*MB-1*	*23-01-2007*	*Reykjavík area*	*Mosfellsbær*	*64°10.36' N*	*021°41.91' W*	*Sewage*
STP influent	*2007-1475*	*MB-2*	*23-01-2007*	*Reykjavík area*	*Mosfellsbær*	*64°10.14' N*	*021°43.59' W*	*Sewage*
Landfill effluent	*2007-1476*	*ALF-1*	*23-01-2007*	*Reykjavík area*	*Álfsnes landfill*	*64°11.20' N*	*021°45.27' W*	
Landfill effluent	*2007-1477*	*ALF-2*	*23-01-2007*	*Reykjavík area*	*Álfsnes landfill*	*64°11.20' N*	*021°45.27' W*	
Recipient[2]	*2006-766*	*HA-1*	*11-10-2006*	*Reykjavík area*	*Ánanaust, coast*	*64°09.19' N*	*021°57.39' W*	*Surf. water*
Recipient[2]	*2006-767*	*HA-2*	*11-10-2006*	*Reykjavík area*	*Ánanaust, coast*	*64°09.19' N*	*021°57.39' W*	*Surf. water*
Recipient[2]	*2006-768*	*HA-3*	*11-10-2006*	*Reykjavík area*	*Klettagar., coast*	*64°09.36' N*	*021°52.44' W*	*Surf. water*
Recipient[2]	*2006-769*	*HA-4*	*11-10-2006*	*Reykjavík area*	*Klettagar., coast*	*64°09.36' N*	*021°52.44' W*	*Surf. water*
Solids								
STP sludge[1]	*2006-770*	*KL-1*	*10-10-2006*	*Reykjavík area*	*Klettagarðar STP*	*64°09.33' N*	*021°52.41' W*	
STP sludge[1]	*2006-771*	*Kl-2*	*10-10-2006*	*Reykjavík area*	*Klettagarðar STP*	*64°09.33' N*	*021°52.41' W*	
STP sludge[1]	*2006-772*	*AN-1*	*10-10-2006*	*Reykjavík area*	*Ánanaust STP*	*64°09.18' N*	*021°57.33' W*	
STP sludge[1]	*2006-773*	*AN-2*	*10-10-2006*	*Reykjavík area*	*Ánanaust STP*	*64°09.18' N*	*021°57.33' W*	
Biological								
Fish liver[2,3,6]	*2007-1479*	*GUF3Hip*	*01-11-2006*	*Reykjavík area*	*Outside Gufunes*	*64°09.60' N*[8]	*021°49.38' W*[8]	*Depth: 6 m*
Fish liver[2,3,6]	*2007-1480*	*GUF4Hip*	*01-11-2006*	*Reykjavík area*	*Outside Gufunes*	*64°09.60' N*[8]	*021°49.38' W*[8]	*Depth: 6 m*
Fish liver[2,3,6]	*2007-1482*	*GUF5Hip*	*01-11-2006*	*Reykjavík area*	*Outside Gufunes*	*64°09.60' N*[8]	*021°49.38' W*[8]	*Depth: 6 m*
Fish liver[2,4,6]	*2007-1478*	*GUF1Lim*	*29-10-2006*	*Reykjavík area*	*Outside Gufunes*	*64°09.60' N*[8]	*021°49.38' W*[8]	*Depth: 6 m*
Fish liver[2,5,6]	*2007-1481*	*GUF2Ple*	*29-10-2006*	*Reykjavík area*	*Outside Gufunes*	*64°09.60' N*[8]	*021°49.38' W*[8]	*Depth: 6 m*
Fish liver[2,4]	*2007-1674*	*FS115*	*12-03-2006*	*S. of Reykjanes*	*Open sea*	*63°37.83' N*	*021°51.81' W*	
Fish liver[2,4]	*2007-1675*	*FS116*	*12-03-2006*	*S. of Reykjanes*	*Open sea*	*63°41.51' N*	*021°33.62' W*	
Fish liver[2,7]	*2007-1671*	*F28*	*06-03-2006*	*Near Snæfellsn.*	*Open sea*	*64°52.87' N*	*024°04.03' W*	
Fish liver[2,7]	*2007-1672*	*F31*	*07-03-2006*	*Faxaflói*	*Open sea*	*64°09.30' N*	*022°18.38' W*	
Fish liver[2,7]	*2007-1673*	*F38*	*08-03-2006*	*Faxaflói*	*Open sea*	*64°21.09' N*	*022°38.57' W*	

*Notes: [1]Non-processed and non-dehydrated; [2]Marine environment; [3]American plaice (*Hippoglossoides platessoides*); [4]Dab (*Limanda limanda*); [5]European plaice (*Pleuronectes platessa*); [6]the liver sample was too small to be analysed ; [7]Atlantic cod (*Gadus morhua*); [8]Estimated coordinate.*

Table 39. Number, type, location and position of samples collected in Norway, 2006-2007.

Sample type	Sample no.	Sample name	Sampling date	Location	Sampling site	Latitude	Longitude	Remarks
Water samples								
STP influent	*2006-675*	*Bekkelaget*	*06-09-2006*	*Oslo*	*Oslo, inner*	*59.882° N*	*010.767° E*	
STP influent	*2006-678*	*VEAS*	*13-09-2006*	*Oslo*	*Oslo, outer*	*59.789° N*	*010.496° E*	
STP effluent	*2006-676*	*Bekkelaget*	*06-09-2006*	*Oslo*	*Oslo, inner*	*59.882° N*	*010.767° E*	
STP effluent	*2006-679*	*VEAS*	*13-09-2006*	*Oslo*	*Oslo, outer*	*59.789° N*	*010.496° E*	
Recipient[1]	*2006-1077*	*St. 30B*	*25-10-2006*	*Oslo*	*Oslo Fj., St. 30B*	*59.49° N*	*010.33° E*	
Recipient[1]	*2006-677*	*Mjøsa*	*11-09-2006*	*Hamar*	*Lake Mjøsa*	*60.82° N*	*010.98° E*	
Recipient[1]	*2006-1076*	*Vanemfjord*	*19-10-2006*	*Vansjø*	*Vanemfjord*	*59°24.7' N*[3]	*010°44.7' E*	
Surface runoff	*2006-1079*	*Lier-St. 1*	*27-10-2006*	*Lier*	*St. 1*	*59°47.594' N*	*010°14.275' E*[3]	*Greenhouse*
Surface runoff	*2006-1078*	*Lier-St. 2*	*27-10-2006*	*Lier*	*St. 2*	*59°45.943' N*	*010°16.882' E*	*Greenhouse*
Background[1]	*2006-1081*	*St. 36A*	*08-11-2006*	*Oslo*	*Oslo Fj., St. 36A*	*59°01.63' N*	*010°31.53' E*	
Background[1]	*2006-1082*	*St. 10S*	*07-09-2006*	*Northern Norway*	*Varangerfjord*	*69°56.156' N*	*030°06.67' E*	
Background[1]	*2006-1083*	*St. 42S*	*30-08-2006*	*Tromsø*	*Malangen,St. 42S*	*69°30.443' N*	*018°07.09' E*	
Solid samples								
STP sludge	*2006-681*	*Bekkelaget-inl.*	*07-09-2006*	*Oslo*	*Bekkelaget STP*	*59.882° N*	*010.767° E*	*wet*
STP sludge	*2006-682*	*Bekkelaget-inl.*	*07-09-2006*	*Oslo*	*Bekkelaget STP*	*59.882° N*	*010.767° E*	*wet*
STP sludge	*2006-638*	*Bekkelaget-inl.*	*07-09-2006*	*Oslo*	*Bekkelaget STP*	*59.882° N*	*010.767° E*	*replicate*
STP sludge	*2006-684*	*Bekkelaget-outl.*	*07-09-2006*	*Oslo*	*Bekkelaget STP*	*59.882° N*	*010.767° E*	*dry*
STP sludge	*2006-685*	*Bekkelaget-outl.*	*07-09-2006*	*Oslo*	*Bekkelaget STP*	*59.882° N*	*010.767° E*	*dry*
STP sludge	*2006-686*	*Bekkelaget-outl.*	*07-09-2006*	*Oslo*	*Bekkelaget STP*	*59.882° N*	*010.767° E*	*replicate*
STP sludge	*2006-6868*	*VEAS*	*13-09-2006*	*Oslo*	*VEAS STP*	*59.789° N*	*010.496° E*	*silo*
STP sludge	*2006-689*	*VEAS*	*13-09-2006*	*Oslo*	*VEAS STP*	*59.789° N*	*010.496° E*	*wet*
Sediment[1]	*2006-1086*	*St. 30S*	*25-10-2006*	*Oslo*	*Steilene, St. 30S*	*59°49.10' N*	*010°33.80' E*	
Sediment[2]	*2006-687*	*Mjøsa*	*11-09-2006*	*Hamar*	*Lake Mjøsa*	*60.82° N*	*010.98° E*	*Depth: 200 m*
Sediment[2]	*2007-1468*	*Vanemfjord*	*19-10-2006*	*Vansjø*	*Vanemfjord*	*59°24.7' N*[3]	*010°44.7' E*	
Sediment[3]	*2006-680*	*St. 360A*	*14-06-2006*	*Oslo Fjord*	*Færder, St. 360A*	*58°56.78' N*	*011°38.34' E*	*Depth: 356 m*
Sediment[3]	*2006-1083*	*St. 42S*	*30-08-2006*	*Tromsø*	*Malangen, St.42S*	*69°30.44' N*	*018°07.09' E*	
Sediment[3]	*2006-1087*	*St. 42S*	*30-08-2006*	*Tromsø*	*Malangen, St.42S*	*69°30.44' N*	*018°07.09' E*	*replicate*
Sediment[3]	*2006-1084*	*St. 10S*	*07-09-2006*	*Northern Norway*	*Varangerfjord*	*69°56.16' N*	*030°06.67' E*	
Sediment[3]	*2006-1085*	*St. 10S*	*07-09-2006*	*Northern Norway*	*Varangerfjord*	*69°56.16' N*	*030°06.67' E*	*replicate*
Biota samples								
Mussels[1,4]	*2006-1089*	*St. 30A*	*30-10-2006*	*Oslo*	*Oslo Fj., St. 30A*	*59°52.5' N*	*010°43.0' E*	*Pool: 20*
Fish liver[1,5]	*2006-1045*	*St. 30B-1*	*??*	*Oslo*	*Oslo Fj. St. 30B*	*59°49.00' N*	*010°33.00' E*	*Pool: 5*
Fish liver[1,5]	*2006-1046*	*St. 30B-2*	*??*	*Oslo*	*Oslo Fj. St. 30B*	*59°49.00' N*	*010°33.00' E*	*Pool: 5*
Fish liver[1,5]	*2006-1047*	*St. 30B-3*	*??*	*Oslo*	*Oslo Fj. St. 30B*	*59°49.00' N*	*010°33.00' E*	*Pool: 5*
Fish liver[1,6]	*2007-1467*	*Mjøsa*	*Autumn 2006*	*Hamar*	*Lake Mjøsa*	*60.82° N*	*010.98° E*	*Pool: 5*
Fish liver[1,7]	*2007-1469*	*Storfjorden*	*03-11-2006*	*Vansjø*	*Storfjorden*	*59°23.1' N*	*010°50.8' E*	*Pool: 5*

*Notes: [1]Marine environment; [2]Lacustrine environment; [3]Estimated coordinate; [4]Blue mussel (*Mytilus edulis*); [5]Atlantic cod (*Gadus morhua*); [6]Trout (*Salmo trutta*) ; [7]European perch (*Perca fluviatillis*)*

Table 40. Number, type, location and position of samples collected in Sweden, 2006-2007.

Sample type	Sample no.	Sample name	Sampling date	Location	Sampling site	Latitude	Longitude	Remarks
Water samples								
Urban runoff[1]	*2007-1454*	*5281*	*06-12-2006*	*Stockholm*	*Båtbyggargatan*	*59°18.4' N*[2]	*018°06.7' E*[2]	*Storm water*
Urban runoff[1]	*2007-1455*	*5282*	*06-12-2006*	*Stockholm*	*Lugnets Allé*	*59°18.2' N*[2]	*018°06.3' E*[2]	*Storm water*
Urban runoff[1]	*2007-1456*	*5283*	*06-12-2006*	*Stockholm*	*Sveavägen*	*59°20.6' N*[2]	*018°03.4' E*[2]	*Storm water*
Urban runoff[1]	*2007-1457*	*5284*	*06-12-2006*	*Stockholm*	*Styrmansgatan*	*59°19.9' N*[2]	*018°05.2' E*[2]	*Storm water*
Urban runoff[1]	*2007-1458*	*5388*	*16-01-2007*	*Stockholm*	*Lill-Jansskogen*	*59°21.2' N*[2]	*018°04.3' E*[2]	*Storm water*
Urban runoff[1]	*2007-1459*	*5389*	*16-01-2007*	*Stockholm*	*Årstafältet*	*59°17.4' N*[2]	*018°02.8' E*[2]	*Storm water*
Urban runoff[1]	*2007-1462*	*5292a*	*06-12-2006*	*Stockholm*	*Hammarby Sjö.*[4]	*59°19.4' N*[2]	*018°05.5' E*[2]	*Surf. water*
Urban runoff[1]	*2007-1463*	*5292b*	*06-12-2006*	*Stockholm*	*Hammarby Sjö.*[4]	*59°19.4' N*[2]	*018°05.5' E*[2]	*replicate*
Urban runoff[1]	*2007-1464*	*5293b*	*06-12-2006*	*Stockholm*	*Riddarfjärden*	*59°19.4' N*[2]	*018°02.9' E*[2]	*Surf. water*
Recipient[1]	*2007-1460*	*5290a*	*05-12-2006*	*Stockholm*	*Stora Essingen*	*59°19.2' N*[2]	*017°59.4' E*[2]	*Surf. water*
Recipient[1]	*2007-1461*	*5290b*	*05-12-2006*	*Stockholm*	*Stora Essingen*	*59°19.2' N*[2]	*017°59.4' E*[2]	*replicate*
Background[3]	*2007-1465*	*4368*	*19-11-2006*	*Stockholm*	*Lake Tärnan*	*59°02.6' N*[2]	*017°55.8' E*[2]	*Surf. water*
Background[3]	*2007-1466*	*4483*	*13-01-2006*	*Gothenburg*	*Lilla Öresjön*	*57°33.0' N*[2]	*012°19.4' E*[2]	*Surf. water*
Solid samples								
STP sludge	*2007-1450*	*5075*	*18-10-2006*	*Stockholm*	*Henriksdal STP*	*59°18.629' N*	*018°06.501' E*	
STP sludge	*2007-1451*	*5285*	*06-12-2006*	*Stockholm*	*Henriksdal STP*	*59°18.629' N*	*018°06.501' E*	
STP sludge	*2007-1452*	*5078*	*18-10-2006*	*Stockholm*	*Hammarby*[4] *STP*	*59°18.629' N*	*018°06.501' E*	
STP sludge	*2007-1453*	*5286*	*06-12-2006*	*Stockholm*	*Hammarby*[4] *STP*	*59°18.629' N*	*018°06.501' E*	
Sediment[1]	*2007-1442*	*5287a*	*05-12-2006*	*Stockholm*	*Stora Essingen*	*59°19.2' N*[2]	*018°00.2' E*[2]	*Depth:27.7 m*
Sediment[1]	*2007-1443*	*5287b*	*05-12-2006*	*Stockholm*	*Stora Essingen*	*59°19.2' N*[2]	*018°00.2' E*[2]	*replicate*
Sediment[1]	*2007-1444*	*5288*	*05-12-2006*	*Stockholm*	*Årstaviken*	*59°18.3' N*[2]	*018°03.1' E*[2]	*Depth: 7.6m*
Sediment[1]	*2007-1445*	*5289a*	*05-12-2006*	*Stockholm*	*Hammarby Sjö.*[4]	*59°18.4' N*[2]	*018°06.0' E*[2]	*Depth: 3.6 m*
Sediment[1]	*2007-1446*	*5289b*	*05-12-2006*	*Stockholm*	*Hammarby Sjö.*[4]	*59°18.4' N*[2]	*018°06.0' E*[2]	*replicate*
Sediment[1]	*2007-1447*	*5296*	*05-12-2006*	*Stockholm*	*Riddarfjärden*	*59°19.4' N*[2]	*018°02.7' E*[2]	*Depth:19.2 m*
Sediment[3]	*2007-1448*	*5240*	*05-12-2006*	*Västmanland*	*Övre Skärsjön*	*59°50.8' N*[2]	*015°32.8' E*[2]	*Background*
Sediment[3]	*2007-1449*	*5242*	*23-11-2006*	*Skåne*	*Krageholmssjön*	*55°30.0' N*[2]	*013°44.9' E*[2]	*Background*

Notes: [1]Brackish environment; [2]Estimated coordinate; [3]Lacustrine environment; [4]Hammarby Sjöstad

Appendix C: Sampling Guideline

Introduction and objectives of the study

This guideline concerns the sampling, sample handling and shipping of water, sludge, soil, sediment, and a variety of biota samples for trace analysis of organic contaminants. The guideline is intended for a suite of phenolic substances. To obtain representative and comparable samples from all countries, this sampling guideline should be followed as precisely as possible, and any deviations from the guideline must be reported in the sampling protocols.
The purpose of this study is a first quantitative screening of selected phenolic compounds including Bisphenol A (CAS no 80-05-7), Tetrabromobisphenol A (CAS no 79-94-7), n-Octylphenol (CAS no 1806-26-4), Octylphenol ethoxylate (CAS no 9063-89-2), n-Nonylphenol (CAS no 104-40-5), Nonylphenol ethoxylate (CAS no 9016-45-9), Dodecylphenol (CAS no 27193-86-8/121158-58-5), 4-Cumylphenol (CAS no 599-64-5), 4-*tert*-Butylphenol (CAS no 98-54-4), 4-*tert*-Octylphenol (CAS no 140-66-9), 4-Nonylphenol, branched (CAS no 84852-15-3), 2,6-di(*tert*-butyl)phenol (CAS no 129-39-2) and methylated TBBPA (CAS no 37853-61-5) in various environmental matrices (se below) throughout the Nordic countries (i.e. Denmark, the Faeroe Islands, Finland, Iceland, Norway and Sweden). This will allow the assessment of existing levels of contamination, possibly indicate regional differences and provide information about the ubiquity of the studied phenolic substances in the Nordic countries.

Phenolic substances/Alkylphenols

Usage

Alkylphenols such as nonylphenol and octylphenol are mainly used to make alkylphenol ethoxylate (APE) surfactants (detergents), though alkylphenols themselves can be used as plasticisers in plastics; alkylphenol phosphites can be used as UV stabilisers in plastics, while the more “bulky” alkylphenols (like t-butylphenols) are used as stabilizers in other formulations. In Europe, alkyl-phenol ethoxylates are mainly used as detergents, industrial processes and in some pesticide formulations. Tetrabromobisphenol A (TBBPA) is the largest volume brominated flame

retardant (BFR) in production and is mainly used in electrical and electronical equipment.

Environmental fate

APEs do not break down effectively in sewage treatment plants or in the environment. They tend to loose some of their ethoxylate groups quite easily, which prevents them acting as detergents - this is called 'primary biodegradability'. This leaves alkylphenols, alkylphenols with one or two ethoxylate groups and alkylphenoxy carboxylic acids (APEC), which persist for longer. Alkylphenols accumulate where there is inadequate oxygen, e.g. in sediments, whilst APEC persist in rivers and effluents.
Alkylphenolic compounds are concentrated by organisms such as fish and birds, leading to contamination in their internal organs between ten and several thousand times greater than in the surrounding environment.
TBBPA is predicted to partition to soil and sediment if released to the environment. The majority would be reacted in sediment and soil (approx. 85%) with only approx. 15% of the total undergoing advection. TBBPA is expected to be essentially immobile in soil, where it can undergo degradation. It may also undergo photolytic degradation with a short half-life. Hydrolysis is not expected to be a significant environmental process due to its low water solubility. TBBPA is not expected to undergo long range transport and is not expected to volatilize from water based on its air-water partition coefficient and its river and lake volatilization half lives, and is expected to partition to biomass.
While not expected to undergo biodegradation during sewage treatment, TBBPA is expected to be removed from the effluent during passage through a wastewater treatment plant. However, observation of methylated derivatives of TBBPA is suspected to arise from microbial methylation, and reductive debromination has been observed in sediments.

Sample types

This screening project includes analysis of selected phenols in the following environmental sample types (matrices):

- Water, incl.
  - effluent water
  - recipient water
  - surface runoff
- Sludge (from municipal sewage plants)
- Soil
- Sediment
- Biota
  - mussels (e.g. Mytilus edulis)

fish (liver)
seabird eggs
marine mammals (seal/pilot whale liver)

General sampling strategy

Sampling should be performed in accordance with general sampling strategies for organic trace analysis. In case of questions about the practicability of procedures or usability of special material and equipment NERI can be contacted for advice (Asger B. Hansen, phone: +45 46301243, e-mail: aha@dmu.dk; Pia Lassen, phone: +45 46301304, e-mail: pla@dmu.dk). The sampling strategy should take into account the specific objectives of the screening programme, including the representative and quantitative objectives. Natural variability within the samples, contamination/ cross-contamination should be reduced by applying the appropriate sampling strategy and technique. The sampling strategy is an intrinsic component of the data, and if not applied properly it may limit the use and interpretation of results.

Sampling site selection / representative sampling

The detailed sampling site selection lies within the responsibility of the sampling institutes and are based on previous experiences with some of the substances selected for this project and the objectives to study specific environmental conditions. The same institutions are also responsible for proper storage and transportation of the collected samples to the analytical laboratory (NERI, DK), that has been assigned to this screening study. Sampling sites must be indicated on the sampling protocols as accurate as possible (preferably with latitude/longitude data and a map).

Control samples/Quality assurance

Field blanks

Due to the constraints in the number of samples, field blanks are not included in this study.

Laboratory blanks

Laboratory equipment (glassware, filters etc.) and solvents will be controlled by analysing laboratory blanks together with each batch of samples.

Field replicates

Again, due to the constraints in the number of samples, field replicates are not included in this study.

Laboratory replicates

To assess the analytical repeatability, replicate samples for all matrices will be analysed (approximately 10% of all samples). These duplicate samples will be collected simultaneously from the primary sample homogenates.

Sampling equipment / risk of contamination

All utensils coming in contact with the samples should be solvent rinsed with 3 times acetone and 3 times dichloromethane (DCM) following the normal cleaning. Glass and metal utensils should eventually be heated for 2 hours at 450 °C; Teflon utensils should be heated for 12 hours at 200 °C.
Polymer materials based on phenolic resins pose a significant risk of contamination with phenols and equipment made of such material must be avoided when handling, storing or shipping samples. Generally, contact with polymer utensils should be kept at a minimum, and restricted to utensils made of Teflon and Nylon, the latter only in form of special sample bags as Rilsan® bags. Furthermore, detergents contain phenols and phenol ethoxylates and therefore all sampling equipment that has been washed should successively be carefully rinsed three times each with water, acetone and DCM. Samples should be collected in the same containers in which they are to be cooled/frozen, stored and shipped to the analysing laboratory to avoid losses due to adsorption and change of vessels.

Sample labelling

Immediate after sampling, all samples (i.e. sample containers) must be carefully labelled to uniquely identify each sample and to avoid sample mixing. For unique identification each sample must be labelled with the following information using waterproof labels and ink:

- sample type (according to the sample types above)
- species (for biota samples)
- date and time of sampling
- position of sampling (latitude and longitude)
- name and affiliation of sample collector

Together with each sample, an additional sampling protocol containing the same information together with a more detailed description of the sampling location and specific conditions regarding the sampling etc. must be provided.

Sample preservation/transportation

Generally, all collected samples are preserved by cooling to 0-5° C in dark immediately after sampling in the field; only water samples require additional preservation. After returning to the laboratory, all samples except water samples are additionally preserved by freezing down to -18° C in the dark. This preservation technique is fast, uncomplicated and effective for short-term storage. However, to prevent degradation or other changes of the analytes, all samples must be transported to the analysing laboratory (NERI, DK) as soon as possible after being collected. During transportation it is mandatory that all samples are kept frozen (water: cooled below 5° C) and in the dark.

Samples should be uniquely labelled and transported in special cooling boxes that are capable of maintaining the required low temperatures and furthermore secured sufficiently to avoid breakage (water samples, eggs). Copies of the sampling protocols should be send together with the samples; the original sampling protocols should be send to NERI by separate mail (or e-mailed as PDF files). Upon sending the sampling, NERI should advised on when they are to be expected and by whom the samples will delivered.

Samples should be sent to the following address:

National Environmental Research Institute (NERI)
Department of Environmental Chemistry & Microbiology
399 Frederiksbogvej
DK-4000 Roskilde
Att.: Asger B. Hansen

Contact persons:
Asger B. Hansen; telephone, +45 46301243; e-mail: aha@dmu.dk
Pia Lassen; telephone, +45 46301304; e-mail: pla@dmu.dk

Sampling descriptions

Water samples

Sample containers

Special cleaned and pre-treated sample containers (1 L Pyrex redcap bottles) will provided by NERI prior to the sampling.

Sampling technique

Generally for this screening project, water samples are collected as grab (or dip) samples. Samples should preferably be collected in the middle of the stream of flowing water at the sampling location. The closed sample bottle is held a few centimetres below the surface (to avoid collecting floating debris), with the opening facing upstream; the sample collector must always ensure that the hand that holds the bottle is downstream of the opening. The sample collector should move around carefully in the stream not to disturb the sampling site and avoid welling up material from the bottom. The sample collector then removes the lid and the let the bottle fill. The sampling bottle is rinsed three times with the sampled water before the final sample is collected. After the bottle eventually has been filled completely the lid is replaced and fastened securely.

Sample preservation

Preservation of water samples is of major concern as the alkyl phenol ethoxylate may be unstable in the water matrix. Two additives are generally used for conservation in relation to ethoxylates (e.g. Petrovic & Barcelo, Fres. J. Anal. Chem. 368: 676-683, 2000), acidification (pH < 3) or addition of formaldehyde (to a 3 % solution). None of these additives are 100 % effective with waste water samples, but as phenols may react with formaldehyde, acidification with H2SO4 (pH < 3) is recommended. Therefore, after sampling, a small amount of the water is removed and replaced with the acidifying agent (H2SO4) to lower pH < 3; after preservation, the water sample should be stored in a cooling box kept at 0° C (use ice). Despite preservation, water samples should be transported to NERI immediately after sampling. All time during storage and transportation it must assured that the water samples kept below 5°C and in the dark.

Sampling remarks

Fill out enclosed sampling protocol.

Sewage sludge samples

Sample containers

Sludge samples are collected either in Rilsan® (Nylon) or Teflon (Tedlar®) bags or cleaned and pre-treated glass jars, which will provided by NERI before the sampling period. After sampling the bags must closed by tying a tight knot at the upper part of the bag; please observe, that as much air as possible is squeezed out of the bag before tightening it. If a glass jar is used the lid should be tightly closed and secured by adhesive tape.

Sampling equipment

Sludge samples can be collected using a carefully cleaned stainless steel scoop or a trier. Cleaning can be performed by using a suitable detergent and successively applying the rinsing procedure described above. The equipment must also be carefully cleaned between each location for compo-site samples to avoid cross-contamination. Cleaning can be done by carefully rinsing with water.

Sampling technique

Municipal sewage sludge should be fresh from the sewage plant, collected within one hour from final dewatering/stabilization, following a period of normal weather conditions. A composite sample should consist of 3-5 sub-samples collected at random from the stabilized sludge heap. Each sub-sample should consist of 100-150 g to add up to a final amount of approximately 500 g for the composite sample.

Sample preservation

After sampling, the sample bag should be labelled as required and tightly closed as described above. The bag is the immediately placed in the dark in a cool box kept below 5° C. After returning from the field to the laboratory, the soil samples should be frozen down to and stored at -18°C. During transportation to NERI the sludge samples should be kept frozen all the time.

Sampling remarks

Fill out enclosed sampling protocol.

Soil samples

Sample containers

Soil samples are collected in Rilsan® (Nylon) or Teflon (Tedlar®) bags, which will provided by NERI before the sampling period. After sampling the bags must closed by tying a tight knot at the upper part of the bag;

please observe, that as much air as possible is squeezed out of the bag before tightening it.

Sampling equipment

Soil samples are collected using a carefully cleaned spade or scoop. Cleaning can be performed by using a suitable detergent and successively applying the rinsing procedure described previously. The spade can be used to remove and discard the upper surface layer, while the scoop may be more handy to collect the actual soil sample. After collecting a composite sample at one position, the equipment must be carefully cleaned to avoid cross-contamination before collecting a composite sample at a new position. In the field, this can be done by carefully rinsing with water, which is allowed to dry out before taking the new sample.

Sampling technique

At each sampling location a composite sample consisting of 3-5 sub-samples is collected at equidistant (1-2 m) positions from the centre. Before collecting the sample, the surface layer (upper 0,5-1 cm) is removed. The sub-sample is then collected a depth of down to 5 cm. Before adding the sub-sample to the sampling bag, non-soily material like stones, root and leaves should be removed. Each sub-sample must include 20-25 g depending on the number of sub-samples collected. In total, about 100 g must be collected. After pooling all sub-samples, the composite sample is mixed by carefully shaking the sample bag (be careful not to ruin the bag and as a precaution use double bags!).

Sample preservation

After sampling, the sample bag should be labelled as required and tightly closed as described above. The bag is the immediately placed in the dark in a cool box kept at 0° C (use ice). After returning from the field to the laboratory, the soil samples should be frozen down to and stored at -18°C. During transportation to NERI the soil samples should be kept frozen all the time.

Sampling remarks

Fill out enclosed sampling protocol.

Sediment samples

Sample containers

Sediment samples should be collected and stored in Rilsan® bags that are squeezed free of air and tightly closed by a knot after careful labelling.

Sampling equipment

Sediment samples should either be collected using a stainless steel "Haps" sampler or a stainless steel Kayak sampler. All equipment is carefully cleaned before use (using detergent and rinsing three times in water, acetone and DCM) as described previously.

Sampling technique

Sediments are collected as composite samples consisting of 3-5 sub-samples. It is important that the bottom is as undisturbed as possible before taking the samples. Sub-samples are collected at equidistant (1-2 m) positions from the centre of the sampling spot. Only the upper 2 cm of the core is used. Stones and organic material is removed before pooling the sub-samples. Each sub-sample should contain 20-25 g depending on the number of sub-samples to add up to a total of approximately 100 g of composite sample.

Sampling remarks

Fill out enclosed sampling protocol.

Biological samples

Sample containers

Generally, biota samples are collected in Rilsan® bags (for precaution use double bags) that will be provided by NERI before the sampling period. After sampling, the bags must be labelled and closed by tying a tight knot at the upper part of the bag and securing that with either a string or a plastic strip; please observe, that as much air as possible is squeezed out of the bag before tightening it.

Sampling equipment

Fish are sampled by using either fishing net, hoop net or fishing rod. Mussels are collected by hand or trawl. Details on how marine mammals are collected should be provided by the institute.

Sampling technique

Mussel samples are collected as 30 – 40 preferably bottom-dwelling individuals at 40 – 60 mm length (and pooled in two size fractions: 40-50 and 50-60 cm) after the spawning season (in October). Only living mussels are collected, and the shells are rinsed for sand etc. with water from the sampling place. Eventually, the mussels are depurated in a carefully cleaned glass tank for 24 hours in fresh water from the sampling station.

Fish caught during the non-breeding season is preferred over fish from the breeding period.

Bird eggs are collected from nesting colonies early in the breeding season (and should preferably not contain embryos). At least five eggs from individual nests of the same species should be collected from each colony.

Sample preservation

Fish samples: Immediately after being caught the fish are killed. Before being stored, the weight, length and sex of the fish should be recorded. Then they are stored in Rilsan® bags (one fish in each bag), which are squeezed free of air and tightly closed by a knot. After carefully labelling, the sample bags are stored in a cooling box kept at 0° C (use ice). At the arrival at the laboratory, the fish are frozen and stored below -18° C. During transportation to NERI, the samples must also be kept below -18° C.

Mussel samples: After opening and passive dewatering for 10 seconds, all the soft tissue (incl. the adductor muscle) is removed and the length of the shell measured. The soft tissue (incl. the adductor muscle) from all the mussels are pooled in a Rilsan® bag, and frozen at - 20 °C. During transportation to NERI, the samples must also be kept below -18° C.

Marine mammals: The liver samples from seals and pilot whales are transferred to a Rilsan® bag (one sample in each bag) that is carefully labelled, squeezed free of air and tightly closed by a knot. The Rilsan® bag is stored in a cooling box kept at 0° C (use ice). As soon as possible, the samples are transported to the laboratory, where they are frozen below -18° C. During transportation to NERI, the samples must also be kept below -18° C.

Bird eggs: Collected eggs are stored homogenized and frozen to -18°C in Rilsan® bags. They should remain frozen while being to NERI for analysis.

Sampling remarks

Fill out enclosed sampling protocol.

Annex 1: Sampling protocol for water samples

Sample name:	**Sample material:**
Sampling	**Comments**
Date and time:	
Site (description, preferably with latitude/longitude data):	
Total sample amount:	
Water temperature:	
Sample preservation:	
Storage temperature after sampling:	
Origin of water (industry, households, hospital etc.):	
Effluent treatment prior to sampling (biological, filtration etc.):	
Storage	**Comments**
Storage time:	
Storage temperature:	
Special observations:	
Transportation to NERI	**Comments**
Date of shipping:	
Shipping temperature:	
Date of arrival at NERI*:	
Temperature at arrival*:	
General condition at arrival*:	

*To be filled in by NERI upon arrival of samples.

Name/signature:
Institute/affiliation:

Annex 2: Sampling protocol for sludge samples

Sample name:	**Sample material:**

Sampling	**Comments**
Date and time:	
Site (description, preferably with latitude/longitude data):	
Special observations regarding sampling site/sludge treatment:	
Special observations regarding sludge condition:	
Total sample amount:	
Sample preservation:	
Storage temperature after sampling:	
Special observations/deviations from sampling guideline:	

Storage	**Comments**
Storage time:	
Storage temperature:	
Special observations:	

Transportation to NERI	**Comments**
Date of shipping:	
Shipping temperature:	
Date of arrival at NERI*:	
Temperature at arrival*:	
General condition at arrival*:	

*To be filled in by NERI upon arrival of samples.

Name/signature:
Institute/affiliation:

Annex 3: Sampling protocol for biological samples

Sample name:	**Sample material:**
Sampling	**Comments**
Date and time:	
Site (description, preferably with latitude/longitude data):	
Observations regarding sampling site (current, depth, hotspots etc.):	
Number/size fraction of individuals for pooled samples:	
Storage temperature after sampling:	
Conditions for depuration (date, duration, temperature of water etc.):	
Date and conditions for dissection:	
Total sample amount:	
Special observations/deviations from sampling guideline:	
Storage	**Comments**
Storage time:	
Storage temperature:	
Special observations:	
Transportation to NERI	**Comments**
Date of shipping:	
Shipping temperature:	
Date of arrival at NERI*:	
Temperature at arrival*:	
General condition at arrival*:	

*To be filled in by NERI upon arrival of samples.

Name/signature:
Institute/affiliation: