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# Siloxanes in the Nordic Environment

## **Siloxanes in the Nordic Environment**

TemaNord 2005:593

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Printed in Denmark

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## **Nordic Environmental Co-operation**

The Nordic Environmental Action Plan 2005-2008 forms the framework for the Nordic countries' environmental co-operation both within the Nordic region and in relation to the adjacent areas, the Arctic, the EU and other international forums. The programme aims for results that will consolidate the position of the Nordic region as the leader in the environmental field. One of the overall goals is to create a healthier living environment for the Nordic people.

### **Nordic co-operation**

Nordic co-operation, one of the oldest and most wide-ranging regional partnerships in the world, involves Denmark, Finland, Iceland, Norway, Sweden, the Faroe Islands, Greenland and Åland. Co-operation reinforces the sense of Nordic community while respecting national differences and similarities, makes it possible to uphold Nordic interests in the world at large and promotes positive relations between neighbouring peoples.

Co-operation was formalised in 1952 when *the Nordic Council* was set up as a forum for parliamentarians and governments. The Helsinki Treaty of 1962 has formed the framework for Nordic partnership ever since. The *Nordic Council of Ministers* was set up in 1971 as the formal forum for co-operation between the governments of the Nordic countries and the political leadership of the autonomous areas, i.e. the Faroe Islands, Greenland and Åland.

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# Preface

Since 2001 the Nordic countries have systematically been screening the environment for potentially hazardous substances.

The aim of the Nordic environmental screening of substances is to obtain a snapshot of the occurrence of potentially hazardous substances in the environment both in regions most likely to be polluted as well as in some very pristine environments. The focus is on little known, antropogenic substances and their derivatives, which are either used in high volumes or are likely to be persistent and hazardous to humans and other organisms. If substances being screened are found in significant amounts this may result in further investigations or monitoring on national level.

The Nordic screening project is run by a project group with representatives from the National Environmental Research Institute of Denmark, the Finnish Environment Institute, the Environment and Food Agency of Iceland, the Food-, Veterinary and Environmental Agency of the Faroe Islands, the Norwegian Pollution Control Authority and the Swedish Environmental Protection Agency.

The project is financed and supported by the Nordic Council of Ministers through the Nordic Chemicals Group and the Nordic Monitoring and Data Group as well as the participating institutions. The chemical analyses have been carried out jointly by the Norwegian Institute for Air Research (NILU) and the Swedish Environmental Research Institute (IVL).

The respective participating Nordic countries organised sample selection and collection and transport of samples based on a sample protocol and manuals provided by the analytical laboratories.





## Summary

The here presented screening study on environmental occurrence and distribution of volatile methylated siloxanes in the Nordic environment involved six countries: Denmark, Faroe Islands, Finland, Iceland, Norway and Sweden.

Siloxanes belong to a group of substances used in a number of industrial applications and in consumer products such as additives in fuel, car polish, cleaners, anti foamers and car waxes. Besides this, they are widely used in e.g. personal care and biomedical products. The widespread use of siloxanes, their broad application as well as their high volatility has raised the concern for these compounds within various disciplines of environmental science.

As a result of their wide use, siloxanes are presumably spread into the environment both via point sources and via diffuse sources and may be found everywhere in the environment. Recent studies have suggested that siloxanes may have direct or indirect toxic effects on various biological processes.

The screening included the following substances: the linear siloxanes hexamethyl-disiloxane (MM or HMDS), octamethyltrisiloxane (MDM), decamethyltetrasiloxane (MD2M), dodecamethylpentasiloxane (MD3M) and the cyclic siloxanes octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5) and dodeca-methylcyclohexasiloxane (D6). In addition, hexamethylcyclotrisiloxane (D3) was analysed in biota. This substance is very volatile and subject to analytical difficulties, which is why it was not analysed in any of the other matrices.

Sampled media types were air, biota, sediment, sludge, soil and water. Siloxanes were found in all the analysed samples types except soils. The results indicate that there is a general pollution of siloxanes in the Nordic environment. There was, however, a great variation in concentrations. The cyclic siloxanes occurred in all media in significantly higher concentrations than the linear siloxanes. The table below shows the observed concentration ranges in different matrices.

Sub- stance	Air ( $\mu\text{g}/\text{m}^3$ )	Water ( $\mu\text{g}/\text{L}$ )			Sludge (ng/g dw)	Soil (ng/g dw)	Sediment (ng/g dw)	Biota (ng/g ww)
		Sew- age/industrial*	Coastal/ Watercourse					
MM	<0.004	<0.0005-0.14	<0.0005-<0.0006	<0.5 - <3	<0.1	<0.02-<0.7	<0.4	
MDM	<0.008	<0.0005-0.014	<0.0005-<0.0006	<1-64	<0.1	<0.02-<0.7	<0.3	
MD2M	<0.006	<0.0005-0.078	<0.0005-<0.0006	1-450	<0.1	<0.02-29	<0.4 – 1.1	
MD3M	<0.02	<0.004-0.23	<0.002-<0.004	3-550	<0.1	<0.02-57	<0.5	
D3	n.a**	n.a	n.a	n.a	n.a	n.a	<50-90.4***	
D4	0.08-4.0	<0.06-3.7	<0.04-<0.09	96-960	<6-<10	<3-84	<5-70	
D5	0.05-19	<0.04-26	<0.02-<0.05	1100-89000	<3-<5	<2-2000	<5-2200	
D6	0.02-2.1	<0.04-3.8	<0.02-<0.05	220-11000	<2-<4	<1-170	<5-74	

\* Samples represent influent and effluents to and from sewage treatment plants, landfill leachate and industrial storm water

\*\* n.a = not analysed \*\*\* Detected levels were below limit of quantification

D5 was the dominating siloxane in all matrices but air, where D4 dominated. This is not in agreement with data on use in the Nordic countries, which indicates that the consumption of D5 and D4 is fairly equal. The results of air measurements indicate a regional variation, with highest concentrations in Norway and lowest in Sweden. Air concentrations of D5 detected inside sewage treatment plants were substantially elevated, and also D5 concentrations measured in other matrices surrounding such plants.

Diffuse sources seem to be most important for the observed concentrations of siloxanes. The concentrations were generally elevated in urban areas and in areas close to sewage treatment plants. The mean concentration of D5 in sludge is comparable to that of the widespread contaminant 4-nonylphenol, but this does not necessarily imply that the effects are the same.

The concentrations in fish liver were fairly variable. Siloxanes were mainly detected in fish samples from sites representing urban/diffuse sources and only a few background samples showed detectable levels. One pooled sample of cod liver from Inner Oslofjord showed highly elevated concentrations. On the whole, biota data indicate that siloxanes may bioaccumulate.

No Observed Effect Concentrations (NOECs) for D4 and estimated Chronic Values (ChV) for D5 were only exceeded in samples representing incoming sewage water to sewage treatment plants. These levels were, however, significantly reduced in the outgoing water from the same treatment plants. Since only little amounts of toxicity data are available for other siloxanes than D4 and No Observed Effect Levels and Chronic Values are estimated from a limited amount of data, the possibility of effects in the local environment close to emissions should not be excluded.

Conclusively, siloxanes are present as common pollutants in the Nordic environment and in many different matrices. They seem to be emitted through diffuse pathways and they enter the aquatic food chain. At present, the observed concentrations are not alarmingly high, and many

background sites seem to be non-contaminated. However, the use of siloxanes is extensive and it is possible that continued use will lead to increased environmental levels, eventually reaching effect concentrations.



# 1. Frame of the study

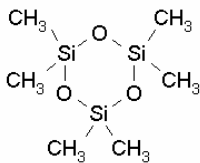
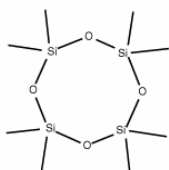
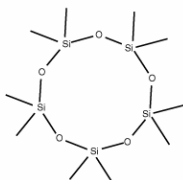
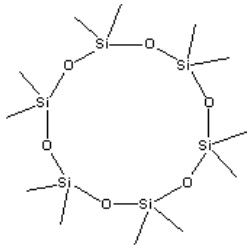
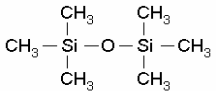
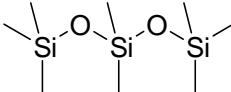
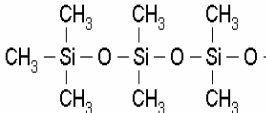
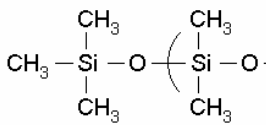
The aim of this screening programme was to investigate the occurrence and distribution of some siloxanes in environmental samples from the Nordic countries. The analytical results produced in this screening project will be a part of scientific measures to estimate the environmental risk posed by siloxanes in the vulnerable Nordic ecosystems.

Siloxanes are widely used chemicals and the selection of the substances to be included in the study was based on their use as well as on indications of their occurrence in the environment. The results from this study will indicate the level of contamination and give valuable information about the spatial distribution of siloxanes in the Nordic environment.

Initially, octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5) were selected for the Nordic screening study, due to their properties and widespread use in the Nordic countries. Additionally, dodecamethylcyclohexasiloxane (D6) and the non-cyclic analogues hexamethyldisiloxane (MM), octamethyltrisiloxane (MDM), decamethyltetrasiloxane (MD2M) and dodecamethylpentasiloxane (MD3M) have also been analysed. In addition, hexamethylcyclotrisiloxane (D3) was analysed in biota. This substance is very volatile and subject to analytical difficulties, which is why it was not analysed in any of the other matrices.

Siloxanes are referred to by their full names or abbreviations according to Table 1. The abbreviated names for siloxanes are taken from the General Electric's siloxane notation (Hurd, 1946).

**Table 1. Siloxane chemicals selected for the Nordic screening programme.**

Abbreviation	Name	CAS #	Structure
D3	Hexamethylcyclotrisiloxane	541-05-9	
D4	Octamethylcyclotetrasiloxane	556-67-2	
D5	Decamethylcyclopentasiloxane	541-02-6	
D6	Dodecamethylcyclohexasiloxane	540-97-6	
MM (or HMDS)	Hexamethyldisiloxane	107-46-0	
MDM	Octamethyltrisiloxane	107-51-7	
MD2M	Decamethyltetrasiloxane	141-62-8	
MD3M	Dodecamethylpentasiloxane	141-63-9	

## 2. Background

### 2.1 Chemical properties, fate and toxicity

Siloxanes form a large group of chemicals with molecular weights from a few hundreds to several hundred thousands. This study is limited to cyclic and linear polydimethylsiloxanes of low molecular weight. They occur as clear viscous liquids at room temperature and have varying physical-chemical properties according to Table 2.

**Table 2. Chemical and physical data for siloxanes**

Substance	MW (g/mol)	W <sub>sol</sub> (mg/l)	V <sub>p</sub> (mm Hg)	H (Atm m <sup>3</sup> /mol)	Log K <sub>ow</sub>	BCF (L/kg)	K <sub>oc</sub>
D3	222.5						
D4 <sup>a</sup>	296.6	0.9 (25°C)	1 (25°C)	0.42	-	12400	2.85×10 <sup>4</sup>
D5 <sup>b</sup>	370.8	0.24 <sup>b</sup> ; 0.017 <sup>c</sup> (25°C)	0.2 (25°C) <sup>b,c</sup>	0.4 <sup>b</sup> ; 0.3 <sup>c</sup>	5.7 <sup>b</sup> ; 5.2 <sup>c</sup>	5300 <sup>a</sup>	1.6×10 <sup>4b</sup>
D6 <sup>a</sup>	444.9						
MM <sup>a</sup>	162.4	2 (25°C)	42 (25°C)	4.5	4.2	900	4.6×10 <sup>3</sup>
MDM <sup>a</sup>	236.5						
MD2M <sup>a</sup>	310.7						
MD3M <sup>a</sup>	384.8	3.1×10 <sup>-4,c</sup>	0.102 <sup>c</sup>	0.79 <sup>c</sup>	6 <sup>c</sup>		

<sup>a</sup> HSDB, 2004; <sup>b</sup> ECB, 2005; <sup>c</sup> SRC, 2005

In the atmosphere, siloxanes may exist both in the vapour and particle phases, the most volatile mainly in the vapour phase. When in the particle phase, siloxanes are removed from the air mainly through wet and dry deposition whereas in the vapour phase they may also react with hydroxyl radicals (HSDB, 2004). Half-lives for reaction with hydroxyl radicals in air are given in Table 3.

**Table 3. Half-lives for reaction with hydroxyl radicals in air**

Substance	Half-life	References
MM	12 days	HSDB, 2004
D4	16 days	HSDB, 2004
D5	10 days	HSDB, 2004

MM, D4, and D5, have high vapour pressures and high Henry's law constants and presumably vaporise both from wet and dry soils as well as from water. Siloxanes have high K<sub>oc</sub> (Table 3) and are expected to be immobile in soil. They adsorb to particles in water and are likely to be enriched in sediments (HSDB, 2004).

Siloxanes are resistant to chemical reactions such as oxidation, reduction, and photodegradation (HSDB, 2004). Varying information exists on the possibility of siloxanes to undergo hydrolysis. While siloxanes in general are considered to be resistant to hydrolysis it was shown in a study of hydrolysis kinetics of D4 that in the pH range of 5-9 (25°C) D4 was degraded with a rate that was considered environmentally significant. Intermediate and final hydrolysis products were not established in the study (Durham et al., 2004).

A modelling exercise was performed using the Equilibrium Criterion (EQC) model (Mackay et al., 1996) in order to highlight the likely fate and partitioning behaviour of siloxanes. D5 and MD3M were selected as model substances for fate assessment. Physical-chemical properties were taken from Table 2. The degradation half-lives used were as follows; air: 170 h, water 550 h, soil 1700 h and sediment 5500 hours. The data was based on degradation data obtained from HSDB (2004), as well as estimated data using the EPIWIN software (Meylan, 1999) and classified according to Mackay (2001). Emission rates were set to 1000 kg/h, only for illustrative purposes. The outcome of the modelling exercise is shown in Table 4. The numbers given in the table should be regarded as indicative, as they are dependent on model structure as well as chemical property data.

**Table 4. Results from EQC modelling of D5 and MD3M, using emission rates of 1000 kg/h**

Emission medium	Percentage in air		Percentage in water		Percentage in soil		Percentage in sediment		Persistence (h)	
	D5	MD3M	D5	MD3M	D5	MD3M	D5	MD3M	D5	MD3M
Air	99.9	100	<0.001	<0.001	0.1	<0.1	<0.01	<0.001	71	71
Water	4	1	26	8	<0.01	<0.001	70	91	778	2271
Soil	50	81	<0.01	<0.001	50	19	<0.01	<0.01	138	87
All three	17	6.5	21	8	7	0.5	55	85	329	810

The overall residence time in the system of both substances is predicted to be fairly low, and generally lower for D5 (<14 days when emitted to all media) than for MD3M ( $\approx$ 30 days). It should be emphasised, however, that advective processes contribute significantly to this low residence time, and it does not necessarily imply that the chemical is ultimately removed from the environment. On the contrary, the atmospheric half-lives of 1-2 weeks (Table 3) and their general resistance to chemical reactions as mentioned above, imply that siloxanes are persistent enough to undergo long-range atmospheric transport.

The model results emphasise the high volatility of siloxanes, showing significant partitioning to air when emitted to air or soil. When emitted to water, however, a large amount is also expected to deposit to sediments, as a result of a relatively high LogK<sub>OW</sub>-value and a fair amount of D5 is predicted to remain in water. The primary receiving media are likely to be



air and water, based on the high volatility and the areas of use of siloxanes. Based on the model results, siloxanes are thus likely to be found in most environmental matrices.

Bioconcentration factors calculated from the apparent octanol/water partition coefficients are generally low for siloxanes with low molecular weight and high for siloxanes with high molecular weight. Laboratory experiments have also shown high BCF for D4 (HSDB, 2004). In practice, the bioconcentration of heavier siloxanes can be restricted because of limited absorbance through cell membrane due to their large size. High vaporisation of siloxanes from water as a result of their high volatility, combined with high sedimentation rates further reduce the actual concentrations available for uptake in biota (HSDB, 2004).

MM is irritant to skin and D4 is classified as R62 “possible risk of impaired fertility” and as R53 “may cause long-term adverse effects in the aquatic environment” in the EU (KemI, 2004). Some evidence exists on the potential carcinogenicity of siloxane D5 (U.S. EPA, 2003).

**Table 5. Ecotox data for D4 (US EPA, 2005) IMBL: Immobilisation, GRO: growth, MOR: mortality, REP: Reproduction, ITX: intoxication, NOC, MULT: Multiple effects recorded as one result**

Common name,Scientific name	Endpoint	Effect	Duration	Conc (ug/L)
Opposum Shrimp ( <i>Americamysis bahia</i> )	NOEC	IMBL	14 d	9.1
Midge ( <i>Chironomus tentans</i> )	NOEC	GRO	14 d	>15
Midge ( <i>Chironomus tentans</i> )	NOEC	MOR	14 d	>15
Sheepshead minnow ( <i>Cyprinodon variegatus</i> )	NOEC	MOR	14 d	6.3
Water flea ( <i>Daphnia magna</i> )	NOEC	IMBL	48 h	>15
Water flea ( <i>Daphnia magna</i> )	NOEC	REP	21 d	1.7 - 15
Rainbow trout, donaldson trout ( <i>Oncorhynchus mykiss</i> )	LC50	MOR	14 d	10, 8.5 - 13
Rainbow trout, donaldson trout ( <i>Oncorhynchus mykiss</i> )	LOEC	MOR	14 d	6.9
Rainbow trout, donaldson trout ( <i>Oncorhynchus mykiss</i> )	NOEC	MOR	14 d	<=4.4
Rainbow trout, donaldson trout ( <i>Oncorhynchus mykiss</i> )	NOEC	NOC, MULT	93 d	4.4
Water flea ( <i>Daphnia magna</i> )		ITX, IMBL	21 d	1.7 – 15

The lowest value for No Observed Effect Concentrations (NOEC) was obtained for water fleas (*Daphnia magna*), a zooplankton that is an important grazer in many limnic ecosystems. In addition to the ecotoxicity data presented for D4 (Table 5), Lassen et al., (2005) have derived so-called Chronic Values (ChV) for fish for a number of siloxanes by using the U.S. EPA PBT Profiler software (U.S. EPA, 2005). ChV is the same as the chronic no effect concentration and shows at what concentration no long-term effects are expected. The results are listed in Table 6.

**Table 6. Chronic values for fish derived by Lassen et al., (2005)**

Chemical abbreviation	Fish ChV (mg/L)
D4	0.058
D5	0.021
MM	0.062
MDM	0.028



### 3.Applications and use of siloxanes

Siloxanes are widely used over the world. D4, D5, and MM are chemicals of high production volume within the European Union. In the Nordic countries there is a limited use of MD2M, MDM and MM, and more extensive use of D4 and D5 (Figure 1). The Norwegian and Finnish use of D6 is confidential, whereas Sweden reports 1 tonne in each of the years 2001 to 2003. Denmark reports occurrences of D6 in more than ten products, but no figures are given (SPIN, 2005). The consumption of MD3M is confidential (too few users) and restricted to Sweden. Only Denmark and Sweden have reported use of D3. Sweden and Denmark report occurrence in more than 15 products but no figures are given. In Norway the use of D3 is confidential (SPIN, 2005). Figure 2 shows a comparison of the D4 and D5 uses in the Nordic countries.

**Figure 1. Registered use of D4 (left) and D5 (right) in the Nordic countries (SPIN, 2005).**

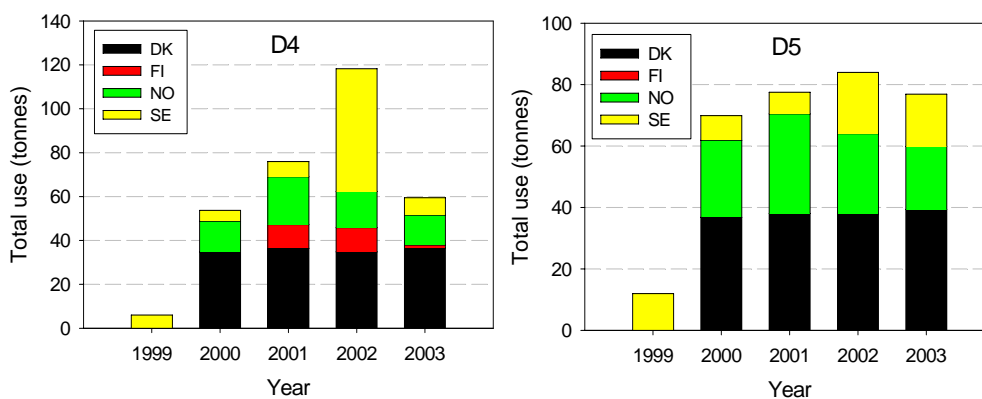
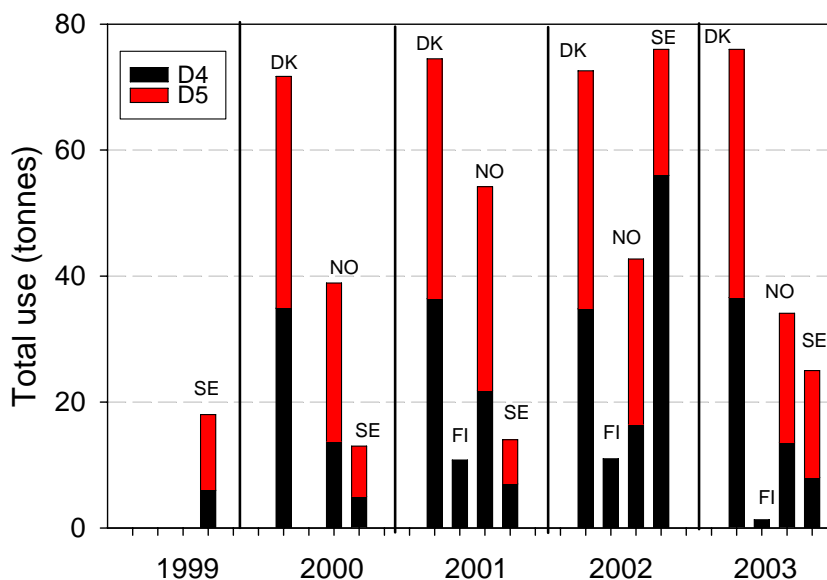


Figure 2. Comparison of use of D4 and D5 in the Nordic countries.



Hexamethyldisiloxane (MM) is included on the OSPAR candidate list for dangerous substances. D4 is classified as a PBT/vPvB chemical and hence as a phase-out substance in the priority database (PRIO) of the Swedish Chemicals Inspectorate. Thus, it is not supposed to be used in any new chemical applications within Sweden. In Denmark, the Association of Danish Cosmetics, Toiletries, Soap and Detergent Industries (SPT) is planning to introduce substitution of D4 (Danish EPA, 2004). Table 7 shows the fields of application of siloxanes in the Nordic countries.

Table 7. Areas of application of siloxanes in the Nordic countries (SPIN, 2005).

Substance	Area of application
D3	Industry for perfume, raw material and intermediaries for cosmetic production, manufacture of chemicals and chemical products. Sale, maintenance and repair of motor vehicles and motorcycles; retail sale of automotive fuel
D4	Fuel additives, Cleaning/washing agents, Impregnation materials, Adhesives, Binding agents, Surface treatment, Construction materials, Paints, laquers, varnishes, Fillers, Reprographic agents, Process regulators, Anti-set-off, Anti adhesive agents, Cosmetics
D5	Fuel additives, surface treatment, cleaning/washing agents, filler, impregnation material, adhesives, binding agents, paints, laquers, varnishes, reprographic agents, softeners, surface active agents, process regulators
D6	Surface treatment, paint, laquers, varnishes
MD, M, MD, 2M	Paint, laquers and varnishes

The figures from the SPIN database only represent the registered use in the Nordic countries. For most products, importers are not obliged to register the full content of chemicals. It is therefore difficult to estimate the true use of siloxanes in the Nordic countries. Judging from the many applications for siloxanes (Table 7) it can be assumed that the total use is larger than implied by the SPIN database.

In the cosmetics industry, the name cyclomethicone is used for the cyclic dimethylsiloxanes and blends thereof. In the cosmetic database of the Danish EPA cyclomethicone is found in 64 out of 766 products covered in the database. Product categories are body lotion, hair styling products, creams, lipstick, make-up for children and deodorants (Danish EPA, 2004).

### 3.1 Environmental levels and exposure

Data on the occurrence of siloxanes in the environment are scarce. In order to extend reference data, Table 8 shows results from previous measurements of polydimethylsiloxanes found in the literature, although the specific compounds were not specified in the study, and it is thus unclear whether the reported concentrations include chemicals investigated in the current study. Table 9 shows previously detected concentrations of MM and D4 in the environment.

**Table 8. Concentrations of polydimethylsiloxane in varying matrices (HSDB, 2004)**

Matrix	Concentration	Country	Year
Surface water near sewage treatment plant	0.8-5 µg/L	Australia, Japan and USA	1997
Surface water near industrial area	2.8 -54.2 µg/L	Japan	1997
Water from a sewage water treatment plant	Barely detected	USA and Japan	1997
Sludge	20-50100 mg/kg dw	Australia, Canada, Germany, Japan and USA	1997
Sediment	Nd - 314 mg/kg dw	Australia, Germany, Japan and USA	1997
Fish	0.6-0.7 mg/kg	HSDB	2004

**Table 9. Concentrations of siloxanes in various matrices.**

Country	Location	Matrix	MM	D4	Reference
Sweden	Landfill	Percolate water (µg/l)	2-106	1-2	Paxéus, 2000
Germany	Landfill 1	Biogas (mg/m <sup>3</sup> )	1.04-1.31	7.97-8.84	Schweigkopfler 1999
Germany	Landfill 2	Biogas (mg/m <sup>3</sup> )	0.38-0.77	4.24-5.03	Schweigkopfler 1999
Germany	STP 1	Biogas (mg/m <sup>3</sup> )	0.05	6.40-6.98	Schweigkopfler 1999
Germany	STP 2	Biogas (mg/m <sup>3</sup> )	0.01	2.87-3.02	Schweigkopfler 1999

As part of an interdisciplinary field study (DBH: Dampness in buildings and health) indoor air measurements in 400 Swedish homes has recently been carried out. NILU was responsible for the analysis of VOCs in children's bedrooms. The results from this study are summarised in Table 10.

**Table 10. Concentration of siloxanes in indoor air in Sweden.**

Siloxane	Number of homes with siloxane detected	Mean( $\mu\text{g}/\text{m}^3$ )	Min( $\mu\text{g}/\text{m}^3$ )	Max( $\mu\text{g}/\text{m}^3$ )
D5	250	9.7	0.5	79.4
D6	142	7.9	0.6	164
D4	73	9.0	0.6	51.2
D7	8	6.4	1.2	35.5
MD2M	5	20	5.3	73.2
MDM	2	7.4	2.5	12.3
MM	1	1.5	-	-
D3	1	7.3	-	-

## 4. Methodology

### 4.1 Sample selection: Criteria and priorities

All samples collected in this screening study are listed in Appendix 1, where also the sampling characteristics are given in detail. An overview of the sampling sites and their spatial distribution in the Nordic countries are shown for biota, sediment & soil, sludge, water and air in Figure 3 to Figure 7.

Each country made a selection of samples based on the knowledge of use and expected occurrence of siloxanes for that particular country. In all cases, samples were chosen to represent point sources as well as diffuse sources and in some cases also background areas. The goal was also to cover all the matrices air, water, sediment, sludge and biota. The strategies and samples selected for the different countries are outlined in the following sections.

#### 4.1.1 Denmark

##### Abiotic samples

Landfill leachate was collected from one old landfill at Uggeløse, which has received mixed waste including household waste in the past, and from one landfill at Avedøre, which is still in use. The latter does not receive household waste.

Sewage water and sewage sludge samples were collected from Lynetten (Copenhagen) as bulk samples. At Bjergmarken (Roskilde) one week integrated samples of sewage water were collected.

Air samples were taken in the background area of Sepstrup Sande, at street level in Copenhagen (Jagtvej), 22 m above the street level (HCØ, Copenhagen), and from Bjergmarken sewage treatment plant close to the aeration basins.

Surface water and sediment samples were collected at Roskilde inderfjord (near Roskilde), in Øresund near Lynetten sewage treatment plant (Copenhagen) and in Kattegat (no known point sources).

##### Biotic samples

Common seal, *Phoca vitulina* were found dead at the Danish shores after an epidemic in 2002. After dissection the samples have been kept frozen at  $-20^{\circ}\text{C}$ . Each sample consists of five subsamples of blubber from five individuals from each of four seal colonies. Marine fish were collected in the same area as water and sediment samples from Roskilde fjord, in



Øresund (Nivå bugt), which is influenced by cities along the coast of Denmark and Sweden and at two background areas at the Wadden Sea and the North Sea.

#### 4.1.2 Faroe Islands

##### Abiotic samples

Sludge and effluent water was collected at the Sersjantvíkin sewage treatment plant in Torshavn. Air samples were taken inside this same sewage treatment plant as well as in a downtown intersection during rush hours. Soil samples were taken from an abandoned landfill in Havnardalur and from Húsarhaga which is the operating landfill for the Torshavn area. From Húsarhaga also runoff water was sampled, with sampling in the well where water draining a larger part of the landfill is led.

Sediment samples were taken in the Kaldbaksfjord, at one of the stations that are used by the Fisheries Laboratory in their monitoring activities, at site KA05. The fjord is known to be influenced to some degree by pollution, but the sources have yet to be identified.

##### Biotic samples

Eggs from the seabird species fulmar (*Fulmarus glacialis*) and black guillemot (*Cepphus grylle*) were gathered in connection with environmental monitoring in various programs in the period 2000 to 2004, and stored at  $-20^{\circ}\text{C}$  in PC jars. Land-locked Arctic char and brown trout were taken in 2004 in the lake á Mýranar, a site used also for sampling to the Arctic Monitoring and Assessment Program, AMAP. Marine fish species sculpin (*Myoxocephalus scorpius*) and dab (*Limanda limanda*) were taken near the bottom of the Kaldbaksfjord in 2004. Cod (*Gadus morhua*) were taken north at the Faroe plateau at Mýlingsgrunnurin in october 2004, by the research vessel "Magnus Heinason". These fish samples are also part of other monitoring programs like OSPAR CEMP and AMAP.

Two species of toothed whales have been included in the sample set from the Faroe Islands, these are long-finned pilot whale (*Globicephala melas*) and whitesided dolphins (*Lagenorhynchus actutus*). Samples of blubber from both species were taken in 2004 in connection with the traditional drive hunt, the pilot whales in Torshavn (Sandagerði) and the dolphins in Gøtu (Syðrugøtu).

#### 4.1.3 Finland

##### Abiotic samples

Leachate water was collected from the solid waste treatment centre Ämmässuo in Espoo. The total amount of waste stored and dumped into the landfill was estimated to 8.5 millions  $\text{m}^3$  in 2004. Extensive water collec-

tion systems have been built to drain the waters from the landfill area to a municipal wastewater treatment plant in Espoo City. The landfill leachate water is led to a pool of the size 150 x 150 m and a depth of 5 m. Water samples from this pool were taken in August 2004 and in January 2005.

Wastewater and dehydrated sludge were collected from the main sewage treatment plants of Helsinki (population equivalent, pe 900 000), Espoo (pe 240 000), Porvoo (pe 30 000) and Nokia (pe 22 000). Samples of incoming wastewater from tyre and floor material industry in Nokia were included in the sampling programme. These are treated in the municipal treatment plant, but samples of incoming water were collected from a separate pipeline. As reference samples, sludge was collected from a small treatment plant of the Pornainen commune (pe <1000), where the main part of sewage originates from households.

One sediment sample (0-6 cm) was taken in the shallow bay near downtown Helsinki, which is also an outlet of the river Vantaanjoki. The bay has been target for pollution from several sources for decades. The other sediment sample is from area between Espoo and Kirkkonummi, about 10 – 15 km west of Helsinki City. This sea site is regarded as fairly polluted by strong yachting and shipping activities.

Air samples were collected at the sewage treatment plant in Nokia City and in the Ämmässuo waste treatment centre in Espoo. An air pump was placed near the exterior effluent pools in Nokia and near the large leachate water pool in the Ämmässuo landfill area. The sites were controlled so that the wind direction was adequate for operation and that the weather was good (no rain).

#### Biotic samples

Pikes (*Esox lucius*) from three separate sea bays of the Helsinki coast were caught. The study areas are shallow and eutrophic. The sea bay nearest downtown is the same where the sediment samples were taken (3 pooled liver samples). The other two inlet bays are slightly polluted by intensive boating and yachting (1 pooled liver sample per area).

#### 4.1.4 Iceland

##### Abiotic samples

All abiotic samples were collected in the vicinity of Reykjavik. Sewage sludge samples were collected on 13th of December 2004 from the two main sewage-pumping stations in Reykjavik, Ananaust and Klettagardar. Waste landfill water was collected the same day from the runoff of a nearby waste dump at Alfsnes. Sediment samples and sea water were collected on the 3rd of February 2005 from the sea just outside the Reykjavik municipal waste landfill at Gufunes. Air was collected in the park-

ing lot of Kringlan mall on 26th February 2005 and in the Grensas traffic junction 28th February 2005.

#### Biotic samples

Common porpoise samples are from the year 2000. The whales were caught accidentally in fishing nets Northwest of Iceland and subsequently brought to the Maritime Research Institute storage in specimen bank.

#### 4.1.5 Norway

##### Abiotic samples

In order to represent background areas (without known local input), sediment and water samples were collected from Lake Bergsjøen and Lake Røgden. A coastal background water sample, representing mainly long-range pollution, was collected at Færder in the Outer Oslofjord.

Representing possible point sources air samples from one sewage treatment plant plus runoff water from three waste deposits and one sewage treatment plant were taken.

As diffuse source samples, one sample was collected at NILUs air-pollution control site at Manglerud, a quite trafficked site in Oslo. Two of the air samples were taken at the Bekkelaget sewage treatment plant – about 2 m above incoming untreated water and mechanically treated water. The last sample was taken at the main hall of the Oslo Central station (railway station) on a Friday evening.

Sediment samples were collected from Leangbukta and Vrengensundet in Oslofjord and from the Ålesund harbour area on the West Coast. One water sample was taken at Steilene in the inner part of Oslofjord.

##### Biotic samples

Marine fish samples representing approximate background areas were collected in Farsund near Lista on the Norwegian South coast.

As diffuse source samples, marine and freshwater fish was collected from Lake Mjøsa, Inner Oslofjord (city), Inner Sørfjord and Ulsteinvik at the West Coast.

#### 4.1.6 Sweden

##### Abiotic samples

In order to represent background areas (without known local input) two sediment samples from the Baltic Sea (Ö Gotlandsdjupet, Ö Landsortsdjupet) were collected.

Representing possible point sources, air, water and sediment samples were collected in the proximity of a former rubber industry area (Gislaved) and from a municipal landfill (Högbytorp).

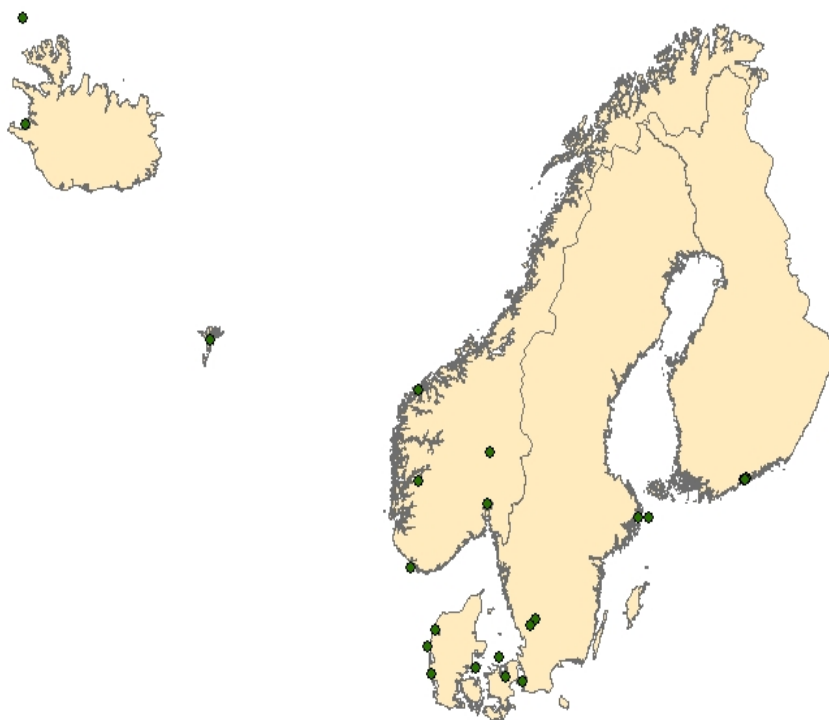
As diffuse source samples, air was collected in the centres of Stockholm and Gothenburg and sediment samples were collected from Essingen and Riddarfjärden in Stockholm. In addition sludge samples were collected from municipal wastewater treatment plants geographically distributed over Sweden (Skellefteå, Lerum, Eslöv and Kiruna).

#### Biotic samples

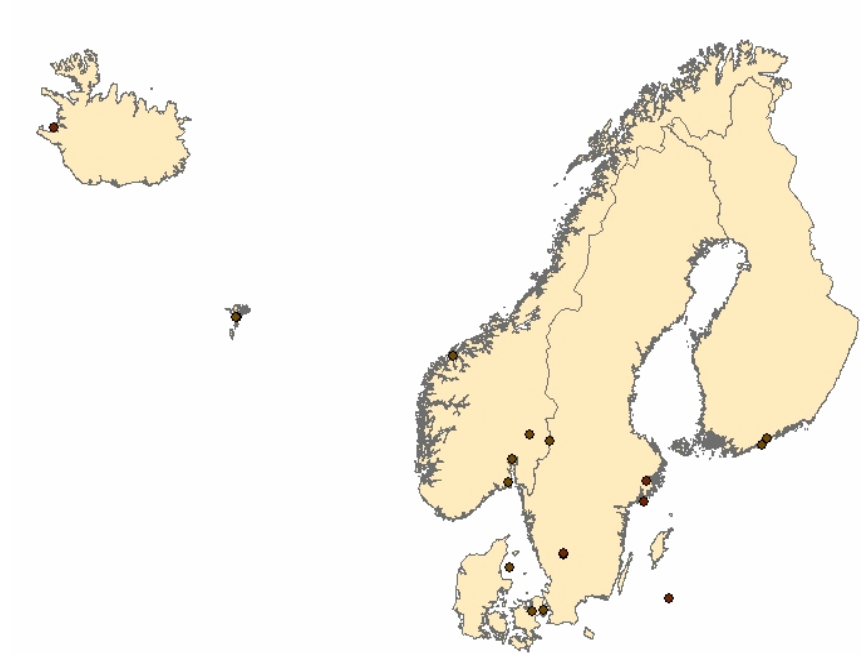
Eggs from herring gull (*Larus argentatus*) were collected and used as samples representing background conditions.

Freshwater fish (pike, *Esox lucius*) from the river Nissan (in the proximity of a rubber industry) were sampled to represent a point source area.

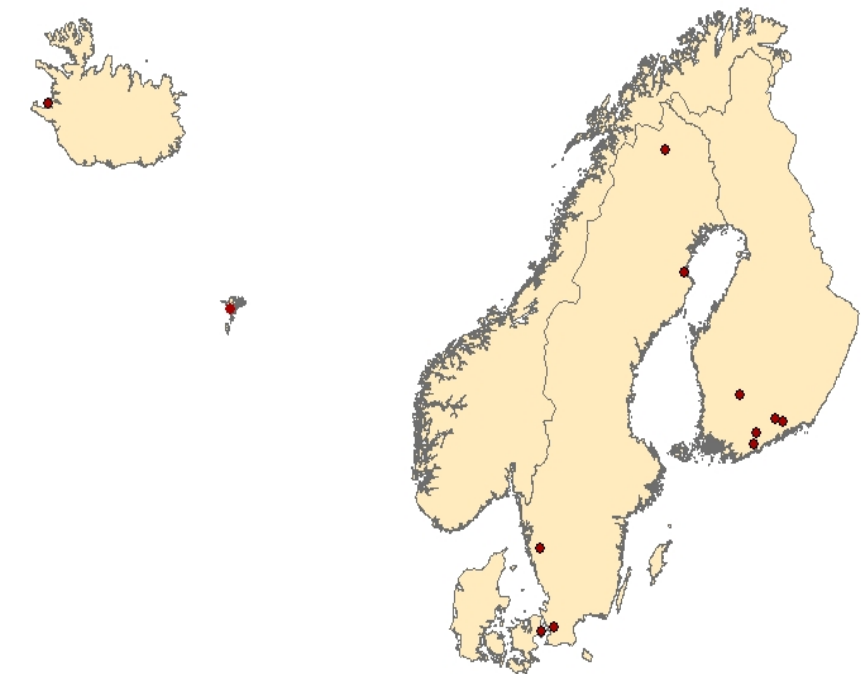
**Figure 3. Nordic sampling sites for biota.**



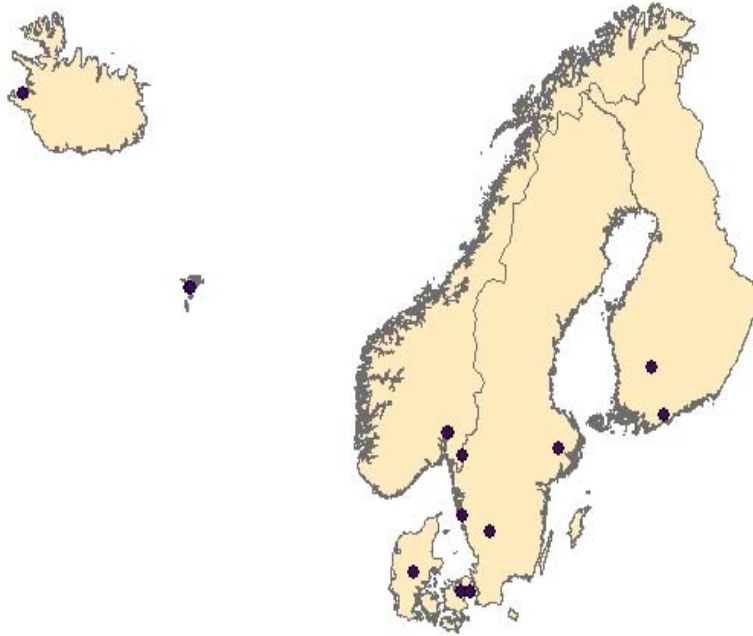
**Figure 4. Nordic sampling sites for sediment & soil.**



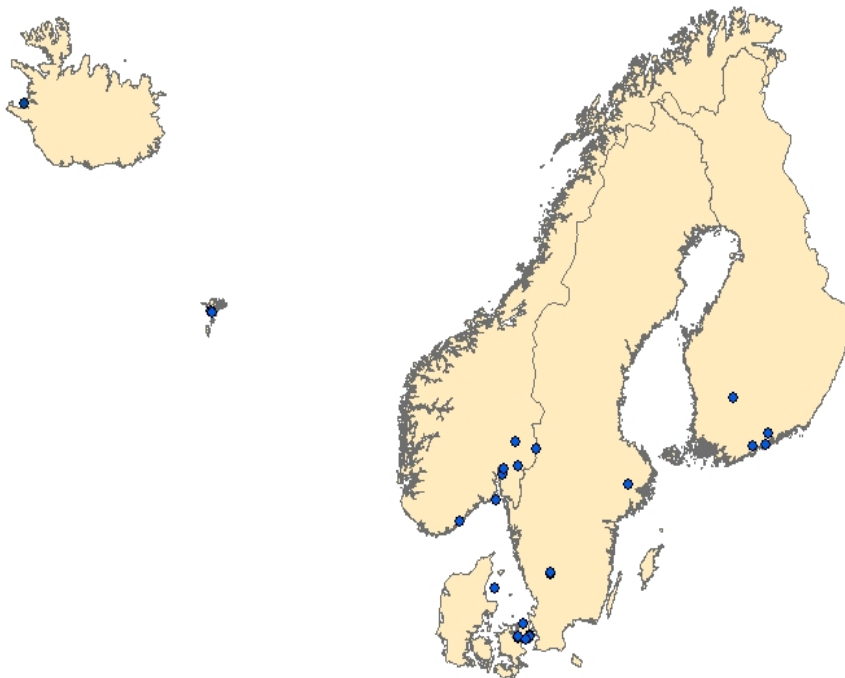
**Figure 5. Nordic sampling sites for sludge**



**Figure 6. Nordic sampling sites for water.**



**Figure 7. Nordic sampling sites for air.**



## 4.2 Sampling

As a guideline for adequate and consequent sampling, the laboratories in charge provided a manual (Appendix 3) for the sampling personnel in the Nordic countries participating in the screening. Detailed instructions for sampling, storing and transport were given. Sampling protocols for all sample types were included in the manual. The aim of the sampling protocol was to

1. Guide the personnel responsible for sampling on how to avoid contamination of the samples.
2. Ensure documentation of the sampling procedure, quality of the sample and environmental and physical circumstances during the sampling.

All samples were sent directly to the analytical laboratories by the national institutions responsible for sampling. Water, sludge and sediment/soil samples were sent to IVL in Sweden and the air and biota samples to NILU in Norway.

## 4.3 Method of analysis

### *4.3.1 Analysis of sludge, sediment, water and soil samples*

In short a sample was diluted with water and purged with a gas stream passing through an adsorbent trap from which the analytes were later thermally desorbed and analysed by GC-MS.

Approximately 2 g of wet sludge were diluted to 20 ml with MilliQ water and homogenised with a high frequency mixer (Polytron). Approximately 1 ml of the slurry was weighed in to the purge & trap vessel and diluted to 10 ml. Sediment was diluted in a similar way, but homogenised by shaking only. Water samples were homogenised by shaking. In all cases 0.5 ml buffer solution (2M  $K_2HPO_4$ , 0.4M HCl, 80g  $Na_2EDTA \cdot 2H_2O$  per litre) was added to the purge & trap vessel.

The purge & trap apparatus for sludge, sediment, and waste water samples consisted of a 25 ml graduated glass test tube with an adapter with one inlet for a Pasteur pipette extending to the bottom of the tube and one side arm to which an empty adsorbent tube was connected using flexible tubing (Viton). This tube acted as a short cooler and water trap. An adsorbent tube containing 0.25 g Tenax TA was connected to the empty tube, the Pasteur pipette was connected to the purge gas (nitrogen, 50 ml/min) and the tube was immersed in a thermostated water bath held

at 70°C. An electric fan facilitated air cooling of the upper part of the apparatus. Samples were purged for 20 min (analysis of MM) and for 2h (all other siloxanes). For low contaminated water samples gas washing bottles with glas frit gas inlet was used as purge vessels. Water volume was 60 - 150 ml, the other conditions were the same as above.

The adsorbent tube was transferred to a thermal desorber (Unity, Mar-kes) connected to a GC-MS instrument (6890N, 5973N, Agilent). Pre-purge time was 2 min, tube desorption time 5 min at 225°C, the trap was held at 3°C and heated at 32°C/s to 250°C. The desorbing flow was 30 ml/min and the split flow 10 ml/min. The flow path temperature was 150 °C and it connected directly to the GC-column, which was a CP-Sil 8CB 30 m × 0.25 mm id, film thickness 0.5µm (Varian). The column temperature was 40°C for 3 min, programmed to 200°C at 12°C/min and to 260°C at 30°C/min. The carrier gas was helium held at constant pressure 10 psi measured at 40°C. The massspectrometric detector was used in electron impact single ion recording mode.

500 mg each of D3, D4, D5, MM, MDM, MD2M, MD3M (Aldrich) and D6 (Gelest) were mixed in a test tube. The chemicals were of 97% declared purity or better. 200 mg of the mixture was dissolved in methanol and diluted to 25 ml. This made a stock solution of 1 mg/ml for each component. This solution was further diluted with methanol. Different amounts of this solution were added to 10 ml MilliQ water and 0.5 ml buffer solution in the purge & trap apparatus and analysed as samples. In this way a seven-point linear calibration curve was constructed and used for quantification of the samples. The blank level and calibration was regularly checked by running water blanks and one or more of the calibration points together with the samples.

The two soil samples from Faroe Islands were analysed according to the procedure described for sediments.

#### *4.3.2 Analysis of biota samples*

Different methods for determination of D4 and D5 have been described in literature (Flassbeck et al., 2001; Flassbeck et al., 2003; Kala et al., 1997; and Varaprath et al., 2000). However, none of the described methods were using high resolution mass spectrometry for quantification.

Due to the ubiquitous nature of the cyclic siloxanes great care was given to reduce the risk for contamination of the samples with siloxanes through direct contact with the lab staff, the equipment used for sample storage, preparation, and extraction. To avoid evaporation loss of the volatile siloxanes and to reduce the contamination risk a very short and comprehensive sample preparation and quantification method was developed and validated.



#### Sample preparation

Typically, the sample material was thawed and homogenised with a household mixer. A 0.30 g aliquot of the sample was mixed thoroughly with 1 mL n-hexane on a whirl mixer for 5 min. The mixture was separated by centrifugation at 10000 rpm and the clear solution was carefully removed with a Pasteur pipette and transferred without any further treatment into a GC/MS vial. There was no significant difference in the results from sample extracts which were dried with sodium sulfate according to the procedure published by Dow Corning (Varaprath et al., 2000) and the results from undried extracts.

#### GC/MS quantification

For method testing and calibration a solution was prepared containing D3, D4, D5, D6, MM, MDM, MD2M, and MD3M at concentrations of about 3 ng/μL and about 30 ng/μL in n-hexane.

The sample extracts were analysed on a GC/HRMS system (GC: 6890 Agilent, MS: Micromass Ultra Autospec) using the following parameters:

- Gas chromatograph:  
Splitless injection (injector temp: 200°C), Helium as carrier gas (1 mL/min; constant flow), 25m×0.2mm×0.11 μm Agilent Ultra2 capillary; Temperature program: 35°C, 3min, 7°/min, 130°C, 0 min, 30°/min, 325° C, 5 min. Interface temperature: 250 ° C.
- Mass spectrometer:  
Ion source temperature: 200° C; Electron impact mode with accelerating voltage 8000 V, Resolution: 10000 at 5 %; Single ion monitoring mode acquiring the following masses (m/z): 147.0661 (MM), 207.0329 (D3), 221.0849 (MDM), 281.0517 (D4), 295.1037 (MD2M), 355.0705 (D5), 369.1225

Before and after a series of 10 samples including a complete method blank the calibration solution was injected in 2 parallels. Quantification was performed as external standard quantification.

#### 4.3.3 Analysis of air samples

Perkin Elmer adsorption tubes filled with 200 mg Tenax TA were used for sampling. The tubes were plugged on both ends with brass swagelock caps with PTFE ferrules. The sampling pumps were adjusted to slightly below 100 mL/min. Air samples were sucked through the tubes with the pumps at the back end. Metal Bellow Ultra Clean air-pumps were used for all sampling except the samples taken in Sweden (SKC Pocket Pump 210-1002). Field blank tubes were in each shipment of samples to the different sampling sites.

The samples were analysed on an Automatic Thermo Desorption Unit ATD 400 (Perkin Elmer) coupled to a Hewlett Packard 1800 A GCD GC/MS-system. Tubes were desorbed at 275°C for 20 min, preconcentrated at -30°C and separated on J&W DB1701 capillary column (30 m×0.22 mm×1.0 µm). The mass spectrometer was used in single ion monitoring mode (SIM) acquiring the following masses (m/z): 207.208 (D3); 281.282 (D4); 267.355 (D5); 341.147 (D6); 147.148 (MM); 221.222 (MDM); 207.295 (M2DM); 281.369 (MD3M); 355.221 (MD4M); 355.295 (MD5M). The quantification was performed with external standards on pre-cleaned tubes.

#### 4.4 Quality control and method comparison

Adequate quality control measures and documentation were introduced covering the entire analytical procedure: sampling, storage, transport, sample preparation, analysis and quantification. To assure a correct sampling procedure and reduce the risk of contamination as well as to assure documentation of possible deviations during sampling and transport, sampling protocol was developed in close co-operation between the different analytical laboratories and the screening group's steering committee (see section 4.2).

##### 4.4.1 Limit of detection/limit of quantification

Limit of detection (LoD) and limit of quantification (LoQ) are considered as two priority parameters, describing the quality of a quantitative analytical method. According to IUPAC (McNaught and Wilkinson 1997, Thomsen et al. 2003), the LoD, expressed as the concentration, cL, or the quantity, qL, is derived from the smallest measure, xL, that can be detected with reasonable certainty for a given analytical procedure. The value of xL is given by the equation:  $xL = \bar{x}_{bi} + k s_{bi}$  where  $\bar{x}_{bi}$  is the mean of the blank measures,  $s_{bi}$  is the standard deviation of the blank measures, and k is a numerical factor chosen according to the confidence level desired. For abiotic and biotic samples  $k = 3$  (3 x signal/noise) was chosen for the present screening study. In the last Nordic screening report (Kallenborn et al., 2004) the following definition of the limit of quantification was used: the lowest concentration of an analyte that produces a signal/response that is sufficiently greater than the signal/response of lab reagent blanks to enable reliable detection (and thus quantification) during routine laboratory operating conditions. The analyte response at the limit of quantification (LoQ) should be at least 5 times the response compared to the blank response. LoD and LoQ determination was performed in accordance to the guidelines given in the above described documents.

For air samples there are only reported concentrations of D4, D5, and D6. Due to a very high background level, D3 results were omitted from

the report (see also 4.4.3). The lowest concentration reported for air samples is 0.02 ng/L of D4 in one of the Swedish samples. Concentrations below that do not give good enough signal-to-noise on the equipment used. None of the air samples had significant peaks in order to quantify linear siloxanes.

#### 4.4.2 Laboratory and field blanks

Based on measurements of water blanks, LoD expressed in ng for sludge, sediment, and water samples were calculated (Table 11). As different sample amounts were analysed, individual samples will have varying LoDs in units related to sample mass. Individual LoDs are given in Appendix 2.

**Table 11. Limit of detection, LoD, ng/sample (see above).**

	D4	D5	D6	MM	MDM	MD2M	MD3M
Sludge, sediment	3.9	1.9	1.5	0.04	0.04	0.04	0.04
Water	4.7	2.5	2.6	0.03	0.04	0.03	0.25

Twelve water field blanks were analysed. All results were below LoD except in one case where MM was 17% of the measured concentration in the corresponding run off water sample.

For the biological samples no relevant surrogate for field blanks could be found and therefore only laboratory blanks are performed as given in Table 12. In addition, the LoD and LoQ calculated according to the formula given in 4.4.1 and the LoD which is used in the results table in Appendix 2 is listed.

**Table 12. Laboratory blanks (complete method blanks) for the analysis of biological material (ng/g).**

Chemical	1	2	3	4	5	6	7	8	9	10	Average	Stddev	LoD calc	LoQ calc	LoD used	LoQ used
D3	34.9	15.2	22.5	26.2	18.1	18.0	17.4	15.9	16.7	18.1	20.3	6.1	38.6	102	50	150
D4	1.4	1.6	3.8	4.7	1.7	1.5	1.5	1.4	1.4	1.3	2.0	1.2	5.6	10.2	5	15
D5	1.3	1.1	1.9	3.5	1.9	ND	1.4	1.8	0.5	ND	1.7	0.9	4.3	8.4	5	15
D6	1.5	0.6	ND	ND	3.0	ND	ND	1.8	ND	ND	1.7	1.0	4.7	8.6	5	15

For air samples, all blank values were below 5% of the actually measured compounds in the air samples. An exception was D3, where blank samples compared to real air samples showed much higher values – in some

cases values as high or even higher than those actually measured at the sampling sites. It was therefore decided not to report D3-values from air samples – due to these contamination problems.

#### 4.4.3 Performance tests

To give an estimate of the coefficient of variation, a sludge sample were analysed in triplicate and one wastewater sample four times. The sludge subsamples were taken from the same homogenised predilution (see 4.3.1). Comparison of different homogenates would give higher CV reflecting sample inhomogenities. The results are given in Table 13.

**Table 13. Coefficient of variation (CV%) for repeated analysis of the same sample.**

	D4	D5	D6	MM	MDM	MD2M	MD3M
Sludge n=3	14	12	14		12	8.8	
Waste water n=4	16	10	13	4.6	17	13	14

The sampling method for air has been tested. Tubes coupled in series were used in order to control the sampling efficiency of the adsorbents. For this test the normally used flow rate of 100 mL/min was applied. For air samples with a sample volume of more than 20 L there was a break trough of compounds in the order of 10%. Therefore it was decided to keep the actual sampling time to less than 3 hours.

#### 4.4.4 Laboratory intercomparison

IVL prepared two sets of adsorption tubes using their own standard solution containing 25 ng of each compound. The sample tubes were shipped to NILU and analysed at NILU using their own standard solutions.

**Table 14. Results of a laboratory intercomparison. Samples spiked at IVL and quantified at NILU.**

Compound	Spiking level (IVL) in ng	GC/MS results (NILU) in ng
D4	25	25.33
D5	25	25.83
D6	25	31.50



## 5. Results and discussion

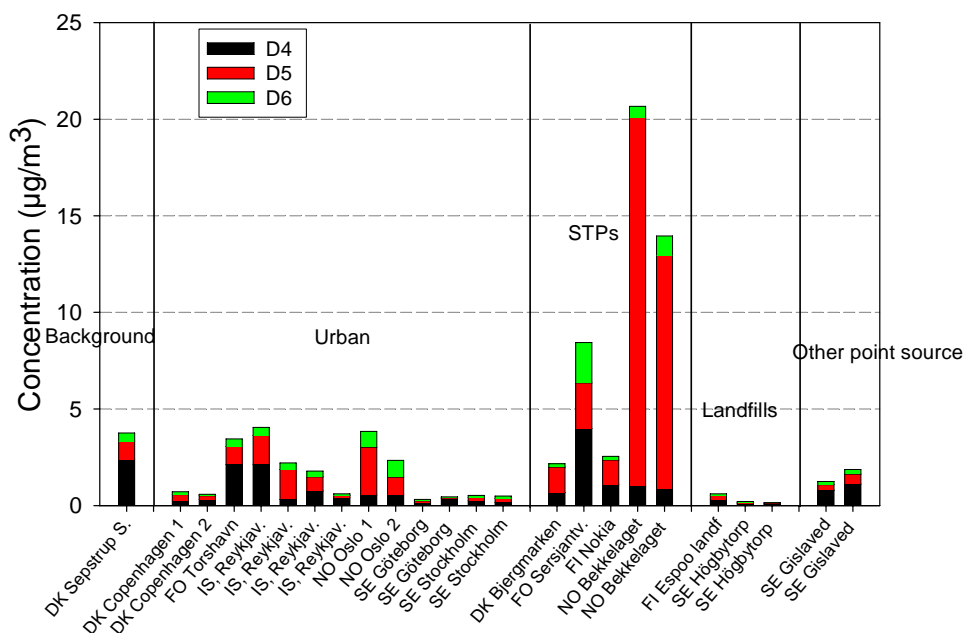
### 5.1 Environmental concentrations

The concentrations of siloxanes found in sediment, soil, sludge, water, biota, and air are given in Appendix 2.

#### 5.1.1 Air

Concentrations of cyclic siloxanes found in air are shown in Figure 8 where the total (sum of D4, D5 and D6) concentrations as well as the relative distribution between D4, D5 and D6 are illustrated.

**Figure 8. Concentration of siloxanes in air, divided by source types**



The measured concentrations of the sum D4, D5 and D6 in air were generally within the range 0.1-5  $\mu\text{g}/\text{m}^3$ , with the exception of samples taken inside sewage treatment plants (STPs), which were higher. The samples from Bekkelaget STP in Norway were taken indoors, about 2 m above incoming, untreated water and mechanically treated water and show concentrations as high as 14 and 21  $\mu\text{g}/\text{m}^3$  respectively. This is comparable to measured concentrations of D5 in children's bedrooms in Sweden (mean: 9  $\mu\text{g}/\text{m}^3$ , n=250; Table 10). The sample from Sersjantviken STP,

showing the third highest concentration, was also taken inside the plant. The outdoor samples from Bjergholmen STP and Nokia STP did not show elevated concentrations in comparison to other sites.

No increased concentrations of siloxanes in air were found close to the other point sources. The concentration of individual siloxanes in urban air was between 0.1 and 2  $\mu\text{g}/\text{m}^3$  with the highest concentrations in urban areas towards the northwest (Norway, Faroe Islands and Iceland) and the lowest in the south (Sweden and Denmark). No urban air samples were collected in Finland. As only one background air sample was taken (Sepstrup Sande), it is difficult to speculate whether the geographical variations are due to differences in local releases or whether there might be an influence of long-range atmospheric transport.

A difference in relative proportions of individual siloxanes was found. The Norwegian samples contained higher concentration of D5 relative to the other siloxanes, whereas D4 dominated in most of the samples from the other countries. This is not in agreement with data on use, where the relative consumption of D4, D5 and D6 is fairly similar in the different Nordic countries (see Figure 2).

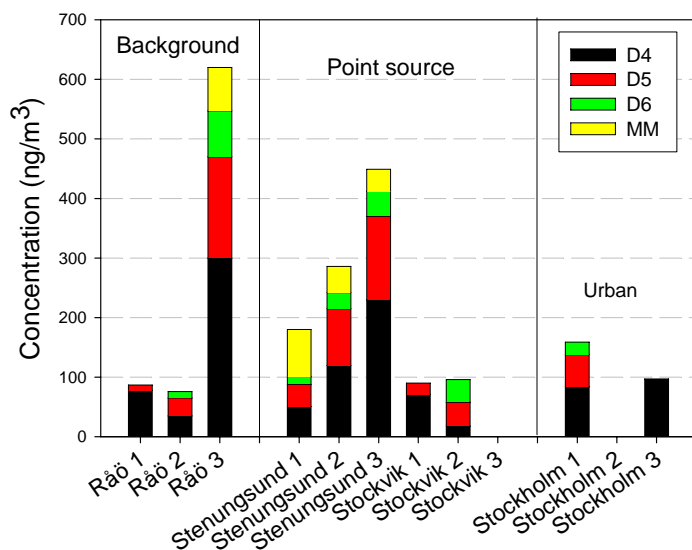
The concentrations of linear siloxanes were below the detection limits in all samples analysed, these being shown in Table 15.

**Table 15. Detection limits of siloxanes in air.**

Siloxane	D3	D4	D5	D6	MM	MDM	MD2M	MD3M
LoD ( $\mu\text{g}/\text{m}^3$ )	0.01	0.006	0.02	0.03	0.004	0.008	0.006	0.02

As an assignment from the Swedish Environmental Protection Agency, IVL has performed a National Screening Study of siloxanes during 2004-2005 (Kaj et al 2005). This screening was carried out in parallel to this Nordic Screening. The results of the air measurements from the Swedish screening are shown in Figure 9.

**Figure 9. Results from measurements of siloxanes in air in the Swedish screening study (Kaj et al., 2005). Note that the concentration is expressed in ng/m<sup>3</sup>.**



The concentrations in the air samples collected within the Nordic screening were generally higher than concentrations of siloxanes in Swedish air, where levels varied between 0.1 and 0.7  $\mu\text{g}/\text{m}^3$  (100 – 700  $\text{ng}/\text{m}^3$ ). D4 dominated in most of the Swedish samples. In contrast to the Nordic study, the linear MM was found in some of the Swedish air samples, in concentrations similar to D6 (see Figure 9). The background samples from Råö show largely varying concentrations, with 6 times higher concentrations at the last occasion. This higher concentration is still as low as the lowest concentrations observed in the Nordic study. All Swedish background samples were taken in November 2004, thus the observed difference cannot be a result of seasonal variations. Back trajectories using the HYSPLIT model (NOAA, 2005) does not indicate any clear correlation between wind direction and observed concentration. In all three cases, the predominant wind direction was from the west and on occasion 1 and 3 the wind package originated from the Atlantic, passing over Norway (case 1) or Denmark (case 3). On occasion 2 the wind package originated from the Norway area but passed over the inner parts of Sweden before reaching the sampling station. It is therefore difficult to state the reason for the elevated siloxane concentrations observed at Råö on sampling occasion 3. Contamination of the sample cannot be ruled out.

The results from the siloxane measurements in air do not give any clear clues about the atmospheric dispersion pattern in air of these compounds. It seems that sewage treatment plants and certain other diffuse/urban sources may generate slightly elevated concentrations of si-



loxanes in air. However, the air outside sewage treatment plants did not contain elevated levels, and about 50 % of the urban samples showed concentrations lower than background concentrations. Conclusively, more extensive air monitoring, e.g. along urban-rural transects or with increasing distance from sewage treatment plants would be needed to fully answer these questions.

### 5.1.2 Sludge

The cyclic siloxanes D4, D5, and D6 were found in all the sludge samples analysed (see Appendix 2). D5 was the dominant species in all cases, making up 78 - 94 % of the total amount. The range of concentrations found is illustrated in the "box plots" in Figure 10. Results for individual samples including relative distribution between different siloxanes are illustrated in Figure 11.

**Figure 10.. Measured concentrations of cyclic siloxanes in sludge in the Nordic screening programme. The lower and upper boundaries of the box represent the 25- and 75-percentiles, and the line within the box is the median concentration. The whiskers represent the 10- and 90-percentiles, and the dots are outliers.**

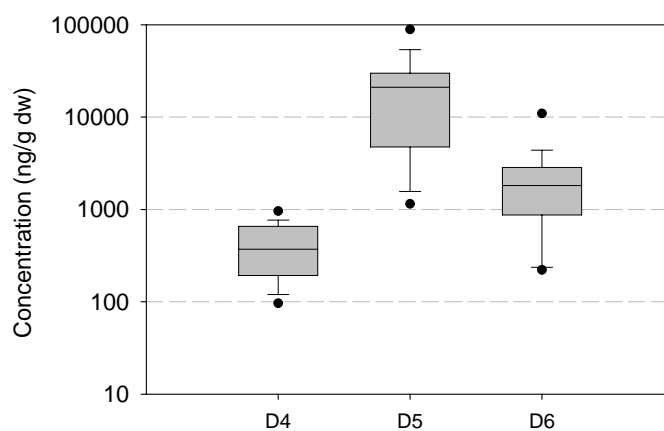
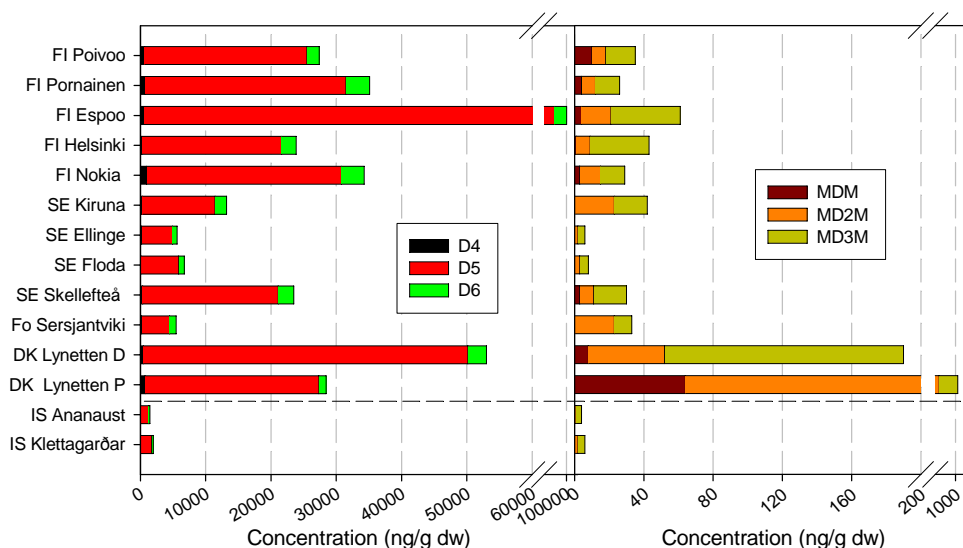


Figure 11.. Concentration of cyclic (left) and linear (right) siloxanes in sludge. The samples from Iceland (IS Ananaust and Klettagarðar) are separated because they represent a different type of sludge.



The two samples from Iceland (Ananaust and Klettagarðar) represent material from mechanical treatment only, while the other samples represent biologically digested sewage sludge. Thus, the Icelandic samples are likely to be less concentrated than the others and concentrations are therefore not directly comparable. The difference in concentration between the two samples from Lynetten, Denmark may be related to the fact that one represents primary and the other represents digested sludge.

Excluding the Icelandic samples yields an average concentration of the sum of D4, D5, and D6 (D456) of 30 000 ng/g dw. Including them gives an average D456 concentration of 26 000 ng/g dw. The sample from Espoo sewage treatment plant in Finland showed the highest concentration of D456, 100 000 ng/g dw. Apart from the Icelandic samples, the lowest concentrations were found in sludge from two small Swedish sewage treatment plants, Ellinge and Floda, and in the sample from Sersjantvíkin in Faroe Islands, with concentrations of 5 600, 6 700 and 5 500 ng/g dw. No Norwegian sludge samples were included in the study.

D5 and D4 are chemicals of high production volume in Europe. D5 was the dominating siloxane in all sludge samples. This is not explained by data on use in the Nordic countries, where the consumption of D5 and D4 is fairly equal (Figure 1, Figure 2).

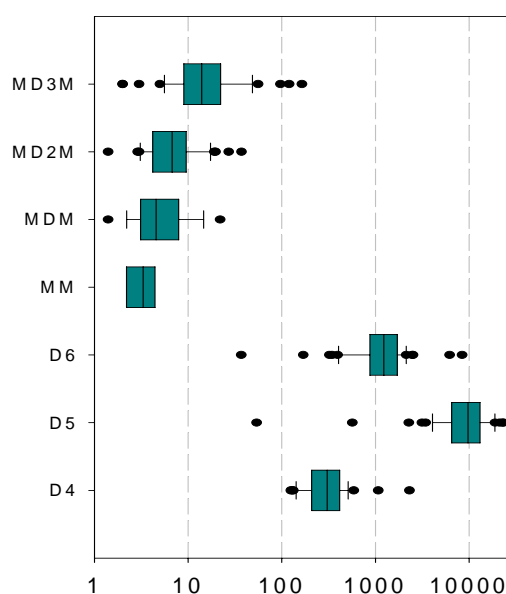
The linear dimethylsiloxanes measured here (MM, MDM, MD2M and MD3M) occurred in significantly lower concentrations than the cyclic analogues, with an average concentration of 110 ng/g dw (sum of 4). The concentrations are illustrated in Figure 9. (Please note the different scales

on the concentration axes in the left and right part of the figure). The highest concentrations were observed in two Danish samples, primary and digested sludge from Lynetten sewage treatment plant, Copenhagen, 1 060 and 190 ng/g dw respectively. Apart from the Icelandic samples, the lowest concentrations were found in Ellinge and Floda sewage treatment plants, Sweden with 6 and 8 ng/g dw respectively.

In all samples the relative concentration increased in the order MM, MDM, MD2M, MD3M. MM, which is a high production volume (HPV) chemical, was not detected in any of the sludge samples. MM may be too volatile to be able to accumulate in sludge.

The concentration of D5 observed in the current study are comparable to those found in the national sampling programme within the recent Swedish screening study of siloxanes (Kaj et al., 2005), where an average concentration of 11 000 ng/g dw (D5) was obtained. D6 and D4 followed with concentrations close to 3000 and 300 ng/g dw respectively. The concentrations of the linear analogues were substantially lower: MM and MDM <2, MD2M 8-16 and MD3M 24-46 ng/g dw. In addition to the national sampling programme, regional samples were also collected by different county administrations adding up to a total sum of 51 sludge samples collected at municipal sewage treatment plants with regional distribution and varying size. As a comparison to results in this study, the Swedish data are summarised as box plots in Figure 12. D5 and D6 were detected in all samples and the linear siloxanes were detected in 47 of the samples.

**Figure 12.. Concentration of siloxanes (ng/g dw, logarithmic scale) in sludge from Swedish municipal sewage treatment plants. The lower and upper boundaries of the box represent the 25- and 75-percentiles, and the line within the box is the median concentration. The whiskers represent the 10- and 90-percentiles, and the dots are outliers.**

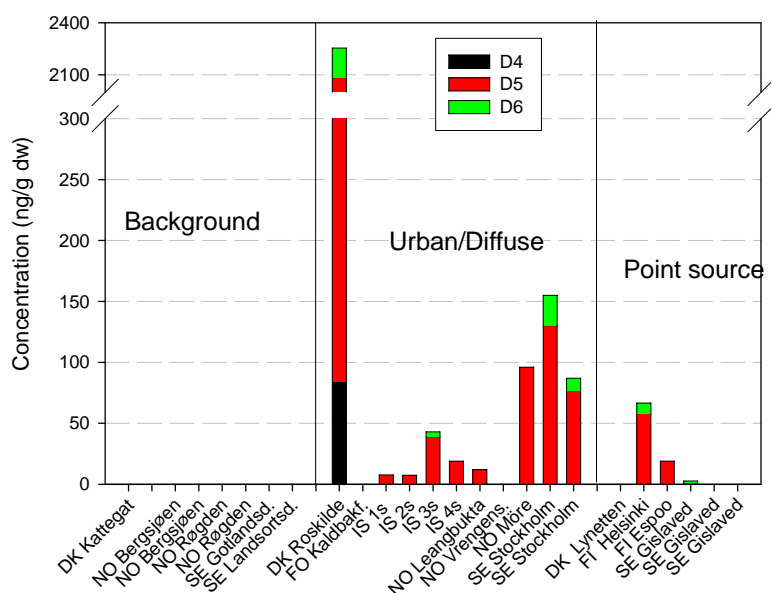


### 5.1.3 Soil and sediment

Two soil samples from Faroese landfills were analysed for siloxanes. The concentrations of all siloxanes were below the detection limits, which varied from 0.1 to 10 ng/g dw for different siloxanes.

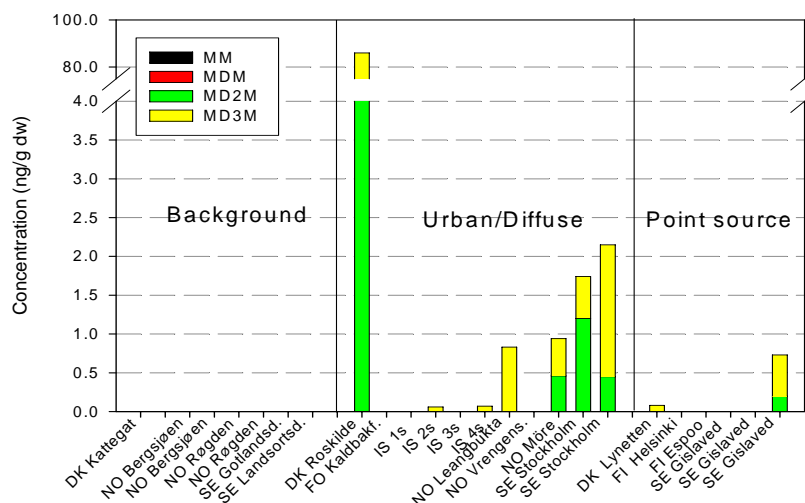
The results of the siloxane measurements in sediment are shown in Figure 13 (cyclic siloxanes) and in Figure 14 (linear siloxanes), where the total concentrations as well as the relative distribution between the different siloxanes are illustrated. As for the sludge samples, there was a great variation in sediment concentrations. The highest concentrations occurred in sediments collected close to urban areas.

**Figure 13. Concentrations of cyclic siloxanes in sediment.**



The cyclic siloxanes were not detected in any of the samples collected at the background sites, but in all but one sample from urban areas. The sample collected near Roskilde in Denmark contained the highest concentrations (2 300 ng/g dw), which was almost 15 times higher than the second highest concentration from Essingen in Stockholm, Sweden (160 ng/g dw). D5, which dominated in all sludge samples, was the dominating siloxane also in the sediments.

**Figure 14. Concentrations of linear siloxanes in sediment samples. MD3M dominates all samples but one from Stockholm. The inserted break hides the MD3M contribution to the sample from Roskilde.**

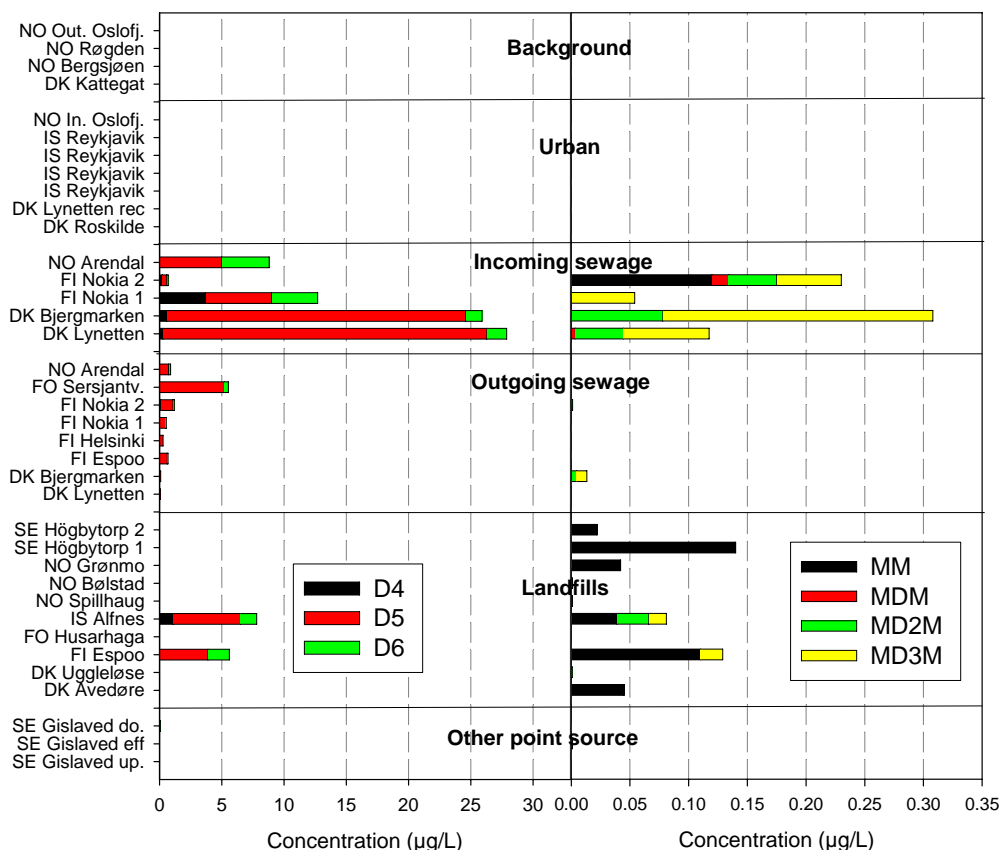


Similar to the cyclic siloxanes, the linear siloxanes were only detected in urban/diffuse samples and in samples close to potential point sources, and generally in those samples that showed the highest concentration of cyclic siloxanes. Like the cyclic siloxanes, the sediment sample from Roskilde contained the highest concentrations, 87 ng/g dw, which was about 40 times higher than the second highest concentration (2.2 ng/g dw) in sediments from Stockholm (Figure 14). MD3M was the dominating linear siloxane in all sediment samples except for one sample from Stockholm, Sweden.

#### 5.1.4 Water

The concentrations of siloxanes in water are given in Appendix 2 and shown in Figure 15, where the total concentrations as well as the relative distribution between the different siloxanes are illustrated.

**Figure 15. Concentrations of cyclic (left) and linear (right) siloxanes in water. Note the different scales on the x-axes.**



There were no detectable amounts of siloxanes in the water samples collected at the background or urban sites. Neither were they found in the three water samples from Swedish point sources. The detection limit was below 0.1 µg /l for the individual cyclic siloxanes and below 0.006 µg/L for the linear siloxanes.

Substantial amounts of both cyclic and linear siloxanes occurred in samples from incoming water to sewage treatment plants. There was, however, a great variation in concentrations among the different samples. The concentrations of the cyclic siloxanes were about 100 times higher than the concentrations of the linear analogues.

In most of the samples of incoming water the relative distribution of D4, D5 and D6 was similar to that in sludge with D5 as the dominating siloxane. A different distribution was found in one of the samples from Nokia, Finland, representing wastewater from a tyre manufactory, where D4 and D6 occurred in substantial amounts. The distribution of the linear siloxanes varied for the different samples, MD3M was highest in the samples from Denmark and one of the Finnish samples (tyre wastewater),

while MM was present in highest concentration Finnish sample from Nokia, representing wastewater from the floor manufactory. Significantly lower concentrations were detected in outgoing water from sewage treatment plants. Linear siloxanes were only detected in one of these samples.

Cyclic siloxanes were only detected in two of the samples from landfills, while the linear siloxanes were found in 6 of the samples. Alfnes landfill in Iceland, which contained relatively high concentrations of cyclic siloxanes, receives all the waste from the Reykjavik area, as well as dry material from the two plants Ananaust and Klettagarðar. In contrast to water samples from sewage treatment plants, MM dominated in the landfill samples, although the absolute concentrations were lower than concentrations of cyclic compounds in the samples where both were detected.

The shift from cyclic to linear (especially MM) dominance in the water samples from landfills relative to sewage treatment plant samples is noteworthy. The physical-chemical properties of MM indicates that it is more water soluble than other siloxanes, but also more volatile, thus the properties cannot explain the observed pattern. Further measurements in leachate and exploration of the degradation route of other siloxanes under landfill-like conditions could help addressing this issue.

#### 5.1.5 Biota

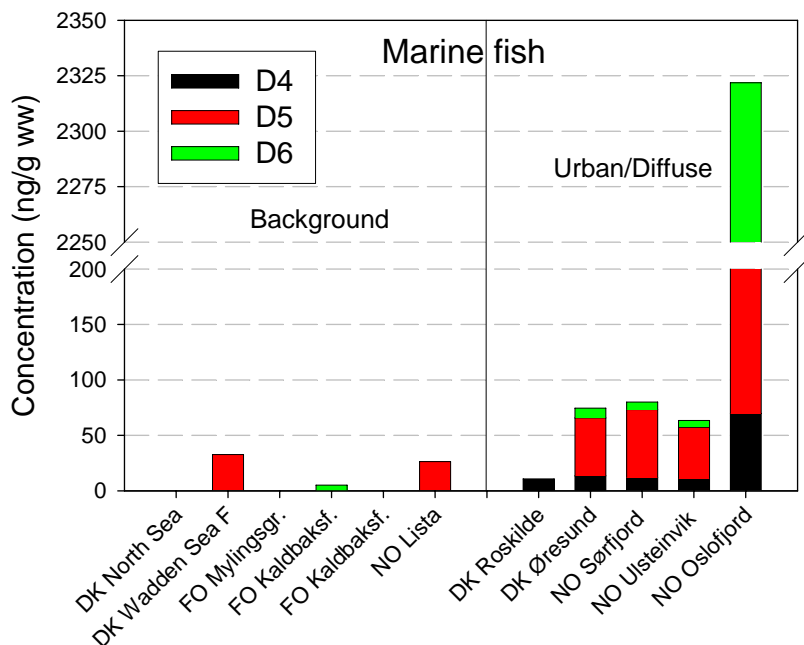
The results from the measurements in biota are presented below. The results have been divided into the subgroups marine and freshwater fish, seabird eggs and marine mammals, and results are illustrated by source type in the respective group. All results and detection limits are also presented in Appendix 2.

The cyclic siloxanes D4, D5 and D6 were detected in fish samples and marine mammals. D3 was detected in a few samples, but as the concentrations were below the limit of quantification in all cases they are not included in the figures. The concentrations of other siloxanes were between the limit of detection and the limit of quantification in a number of samples. For details on the individual samples, see Appendix 2.

##### Marine fish

Figure 16 shows the measured concentrations of cyclic siloxanes in liver from marine fish species. The species are not specified in the figure, but include eelpout, flounder, cod, sculpin and dab (Appendix 2). Results are presented based on type of sampling site. With one exception (see below) no linear siloxanes were detected in marine fish samples, LoD varying between 0.3 and 0.5 ng/g ww.

**Figure 16. Concentrations and distribution of cyclic siloxanes in marine fish liver.** Some of the reported concentrations were between the limits of detection and quantification and thus have a larger uncertainty. See Appendix 2 for details.



The concentrations in marine fish liver were fairly variable, typically in the range of <5 - 100 ng/g ww. Only one sample of cod liver (9 livers pooled) from Inner Oslofjord, close to the city center, exceeded this range with a concentration of 2200 ng/g ww (Figure 16). This is in the same order of magnitude as the concentration in human fatty tissue of a woman with a leaking silicone gel-filled breast implant (Flassbeck et al., 2003). This result is extraordinary compared to the other fish samples from urban or polluted areas. The cod liver sample from Oslofjord was the only biological sample where a linear siloxane was detected (MD2M: 1.1 ng/g ww.). D5 was generally the dominating siloxane in the marine fish liver samples.

Siloxanes were mainly detected in marine fish liver samples from sites representing urban/diffuse sources and only a few background samples showed detectable levels. The concentrations are not directly comparable as they represent different species of varying age and gender. However, diffuse sources may contribute to the observed concentrations in marine fish.

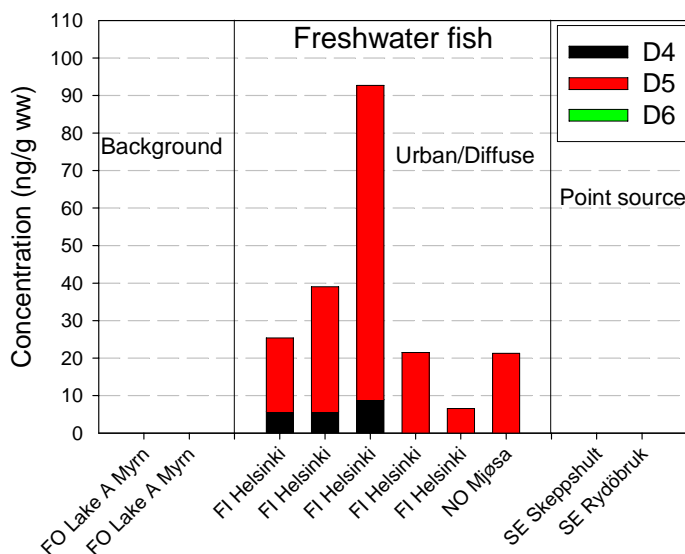
#### Freshwater fish

Figure 17 shows the measured concentrations of cyclic siloxanes in liver from freshwater fish species. The species are not specified in the figure, but include arctic char, brown trout, pike and vendace (Appendix 2). Results are presented based on type of sampling site. No linear siloxanes



were detected in freshwater fish samples, LoD varying between 0.3 and 0.5 ng/g ww.

**Figure 17. Concentrations and distribution of cyclic siloxanes in freshwater fish liver. Some of the reported concentrations were between the limits of detection and quantification and thus have a larger uncertainty. See Appendix 2 for details.**



Just like the marine fish liver samples, the concentrations in freshwater fish varied in the range <5-100 ng/g ww. D5 was the dominating siloxane in all freshwater fish liver samples and D6 was not at all detected. Siloxanes were only detected in freshwater fish liver samples from sites representing urban/diffuse sources and not at all in the background samples from Faroe Islands or in samples representing point sources in Sweden. The detected concentrations are comparable, as all the Finnish samples are pikes, however the Norwegian sample is vendace. Urban and diffuse sources appear to contribute significantly to the observed concentrations in freshwater fish.

#### Seabird eggs

No siloxanes were detected in samples of seabird eggs (Fulmar, black guillemot and herring gull) from Sweden and Faroe Islands. The detection limits for the seabird eggs are given in Table 16 and in Appendix 2.

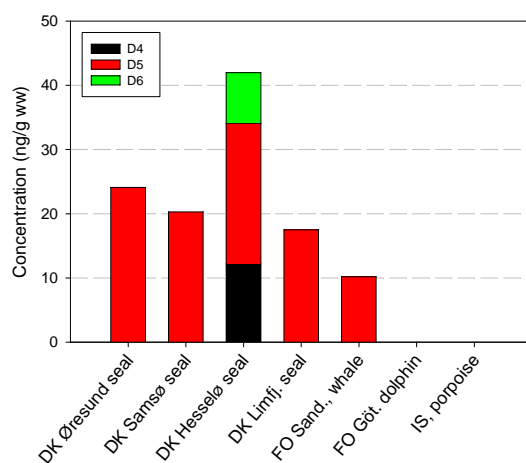
**Table 16. Limit of detection for seabird eggs (ng/g wet weight)**

D3	D4	D5	D6	MM	MDM	MD2M	MD3M
50	5	5	5	0.4	0.3	0.4	0.5

### Marine mammals

Figure 18 shows the measured concentrations of cyclic siloxanes in marine mammals. No linear siloxanes were detected in mammals, LoD varying between 0.3 and 0.5 ng/g ww.

**Figure 18. Concentrations of siloxanes in marine mammals. Some of the reported concentrations were between the limits of detection and quantification and thus have a larger uncertainty. See Appendix 2 for details**



Among the mammal samples, seal and pilot whale showed detectable concentrations of siloxanes, and D5 was the dominating compound. In fact, other cyclic siloxanes were only detected in one seal sample from Hesselø in Denmark. All the Danish seal samples were taken away from cities. Some of the reported concentrations were between the limit of detection and the limit of quantification, see Appendix 2 for details. D3 was detected in one sample, but it has not been included in the figure as it was below the limit of quantification (see Appendix 2).

## 5.2 Comparison of biota and water concentrations

A comparison of observed concentrations in water and biota can give useful information on the potential for biotic uptake of siloxanes. The results in the current study show water concentrations of D5 that vary between limit of detection ( $<0.02 \mu\text{g/L}$ ) and  $26 \mu\text{g/L}$ . Excluding incoming sewage water (to which aquatic organisms are not likely to be exposed) and non-detected concentrations gives a range of  $0.06\text{--}5.4 \mu\text{g/L}$ . Using a BCF of 5300 (Table 2), this would represent an expected range of  $300\text{--}28000 \text{ ng/g ww}$  in fish. The observed range for detected concentrations in biota is  $6\text{--}2200 \text{ ng/g ww}$ , including values below the limit of

quantification. Consequently, the observed concentrations in biota are 10 to 100 times lower than would be expected from the observed concentrations in water (neglecting the influence of uptake via the food chain). This can not be regarded as a high discrepancy considering that most of the detected water concentrations were related to effluent water. Water samples from seawater and freshwater were generally below detection limits. Biota and water was in most cases not sampled in the same region, but also at those locations (Lynetten, Bjergmarken) where fish and recipient water was sampled in the same area, the water concentrations were generally below the detection limit. Regarding this, the levels we find in biota may be a confirmation of the expected bioconcentration.

On the whole, data show that siloxanes have the potential to bioaccumulate. It is, however, not possible to state whether the observed occurrence in aquatic organisms is due to uptake via water, via the food chain or a combination of these processes. In order to draw such conclusions, it would be necessary to analyse surface water and organisms belonging to different trophic levels at the same sampling location.

### 5.3 Concentration patterns at geographically related sites

In some Nordic countries several samples, representing different matrices, were collected in the same area. Examples of sites following this sampling strategy are given below.

#### 5.3.1 Copenhagen, Lynetten area

In the area surrounding Lynetten sewage treatment plant (STP) in Denmark, samples of water, sludge, sediment and fish were collected and included in the study. Elevated concentrations of all siloxanes except MM were found in incoming water and sludge in the STP. In effluent water, only D5 was detected and in significantly lower concentrations, 0.2 % of that in the influent. The cyclic siloxanes were below the detection limits in the recipient water and sediment samples from this area but they were detected in fish collected in the recipient area (Table 17).

**Table 17. Detected concentrations in geographically related samples from the Lynetten area, Denmark. Biota values written in italic letters represent concentrations below the limit of quantification.**

Sample ID	Sample type	Unit	D3	D4	D5	D6	MM	MDM	MD2M	MD3M
MR-3915	Waste water influent	µg/L		<b>0.28</b>	<b>26</b>	<b>1.6</b>	<0.01	<b>0.0034</b>	<b>0.041</b>	<b>0.073</b>
MR-3917	Primary sludge	ng/g DW		<b>740</b>	<b>27000</b>	<b>1100</b>	<3	<b>64</b>	<b>450</b>	<b>550</b>
MR-3918	Digested sludge	ng/g DW		<b>470</b>	<b>50000</b>	<b>2800</b>	<1	<b>8</b>	<b>44</b>	<b>140</b>
MR-3916	Waste water, effluent	µg/L			<b>0.063</b>			<0.001	<0.02	
MR-3717	Water, recipient	µg/L				<0.0005	<0.04			
MR-3718	Sediment, recipient	ng/g DW				<0.05	<5			<b>0.08</b>
MR-3714	Sediment, distant	ng/g DW				<0.03	<3			
05/400	Fish, recipient area	ng/g ww	<b>90.4</b>	<b>13.5</b>	<b>52.3</b>	<b>8.73</b>			<0.3	<0.5

### 5.3.2 Roskilde, Bjergmarken sewage treatment plant

At the Bjergmarken STP in Roskilde, samples of wastewater, recipient water, sediment and fish as well as air were collected. D4, D6, D5, MD2M, and MD3M were detected in influent water and the latter three also in the effluent. The concentration of D5 in the effluent was 0.4 % of that in the influent while the concentrations of MD2M and MD3M were 6 and 4 % of that in the influent, respectively. Siloxanes were not found in recipient water, but the sediment was polluted. The relative concentrations of D4, D5, and D6 in the sediment were similar to the pattern in the influent water. D4 was also found in the fish sample. The air samples contained elevated concentrations compared to background areas (Table 18).

**Table 18. Detected concentrations in geographically related samples from the Bjergmarken area, Denmark.**

Sample ID	Sample type	Unit	D3	D4	D5	D6	MM	MDM	MD2M	MD3M
MR-3920	Waste water influent	µg/L		<b>0.60</b>	<b>24</b>	<b>1.3</b>	<0.01	<0.01	<b>0.078</b>	<b>0.23</b>
MR-3921	Waste water, effluent	µg/L		<0.06	<b>0.092</b>		<0.04	<0.0005	<b>0.0045</b>	<b>0.0087</b>
458-nilu238	Air at STP	µg/m <sup>3</sup>		<b>0.66</b>	<b>1.33</b>	<b>0.17</b>	<	<	<	<
MR-3716	Water, recipient	µg/L					<0.0005	<0.04		
MR-3723	Sediment, recipient	ng/g DW		<b>84</b>	<b>2000</b>	<b>170</b>	<0.3	<0.71	<b>29</b>	<b>57</b>
05/399	Fish, recipient	ng/g ww	<50	<b>10.7</b>			<0.3	<5		
MR-3713	Water, distant	µg/L					<0.0005	<0.04		

### 5.3.3 Finland Nokia

At Nokia in Finland, wastewater and sludge samples from the industry as well as from STPs were included. One air sample was also collected. The sample from the floor industry contained all the siloxanes analysed. The concentration in water after treatment was 16% of that in untreated water and concentrations of cyclic siloxanes in STP sludge were the third highest in among all of the Nordic samples. The air concentration at the STP

was in the same order of magnitude as the Danish background sample but about ten times higher than background levels found in the Swedish screening study (Kaj et al., 2005) (Table 19).

**Table 19. Detected concentrations in geographically related samples from the Nokia area, Finland.**

Sample ID	Location	Matrix	Unit	D4	D5	D6	MM	MDM	MD2M	MD3M
MR-3940	Tyre industry waste water pipeline	Water	µg/L	3.7	5.3	3.7		<0.007		0.054
MR-3941	Floor industry 1B	Water	µg/L	0.25	0.33	0.12	0.12	0.014	0.041	0.055
MR-3942	Kulloonvuori STP effluent 1	Water	µg/L	<0.06	0.48	0.03		<0.001 - <0.004		
MR-3943	Kulloonvuori STP Effluent 2	Water	µg/L	0.11	0.98	0.045	<0.001	<0.001	0.0012	<0.005
MR3932	Nokia Kulloonvuori	Sludge	ng/g DW	960	30000	3500	<2	3	12	14
344-nilu106	Nokia City ww-treatment	Air	µg/m <sup>3</sup>	1.08	1.27	0.2	<	<	<	<

Conclusively, it seems that STPs and some industrial sources (floor, tyre industry) are important sources for the occurrence of siloxanes in the environment. Possibly, sewage treatment plants located near certain industry types receive a larger amount of siloxanes than others.

#### 5.4 Concentrations of D5 in sludge compared to other contaminants

Sludge is a common matrix for analysis of organic pollutants as it receives a fair amount of chemicals used in households and consumer products, as well as in industrial processes. Numerous substances have been detected in sludge in concentrations high enough to raise concern, as sludge has been proposed to be used as a source of nutrients within agriculture. The average concentration of D5 in biological sludge from STPs in the current study (12 samples) was 27 000 ng/g dw and in the similar study covering 54 STPs in Sweden (Kaj et al., 2005), the average concentration of D5 was 11 000 ng/g dw. These rather high concentration levels can be compared to those for other widespread organic contaminants found in sludge. Due to physico-chemical properties this does not necessarily imply that the effects are the same. In a recent study concerning sludge from 20 Swedish STPs di-(ethylhexyl)-phthalate (DEHP) averaged to 49 000 and 4-nonylphenol to 9 000 ng/g dw (Bignert and Remberger, 2005). In another study including 23 Swedish STPs the average concentration of 4-nonylphenol was 15 000 ng/g dw (Remberger et al., 2004). Thus the concentration level of D5 found in the present study is similar to that for 4-nonylphenol and somewhat lower than that for DEHP. Siloxanes therefore add to the list of organic pollutants that may make it problematic to use municipal sewage sludge in a sustainable way, i.e. as a source of nutrients in agriculture.

## 5.5 Toxicity and ecotoxicity

No Observed Effect Concentrations (NOECs) for D4 (Table 5) were only exceeded in samples representing incoming sewage water to sewage treatment plants (STPs). These levels were, however, significantly reduced in the outgoing water from the same STPs. In the latter, D4 levels were about one order of magnitude lower than any NOECs found in literature. In landfill leachate from Iceland, the concentration of D4 (1.1 µg/L) was in the lower end of the NOEC range for *Daphnia Magna* (1.7 – 15 µg/L). The estimated chronic value (ChV, see Table 6) for D5 was exceeded in two samples of incoming sewage water, but in no other water samples. The ChV was not exceeded for any other siloxanes.

Detailed ecotoxicity data was only obtained for D4. D5 is, however, a suspected carcinogen and may also have other toxic effects in ecosystems. Toxic effects of D6 are less known but its similarity to the other cyclic siloxanes still makes it interesting. Uptake in biota is known to decrease with increasing molecular size due to difficulties when passing through the cell membrane, which may reduce the toxic effects of D5 and D6 relative to D4. The concentrations of D5 and D6 were highest in incoming water to sewage treatment plants and, as in the case of D4, substantially reduced in outgoing water. The concentrations of D5 and D6 in leachate water as well as in sewage water were higher than the concentrations of D4. In two leachate water samples (Alfnes and Ämmässuo) D5 and D6 reached levels that were in the same range as several NOECs for D4. In some effluent samples D5 and D6 were detected in concentrations slightly lower than NOECs for D4. Since only limited amounts of toxicity data are available for other siloxanes than D4 and No Observed Effect Levels and Chronic Values are estimated based on a limited amount of data (and as such objects of some uncertainty) the possibility of effects in the local environment close to emissions should not be excluded. No detailed toxicity data could be found for linear siloxanes and measured concentrations were also lower than for cyclic siloxanes.

Siloxanes were not detected in any background samples or in the recipient water outside Lynetten sewage treatment plant. Siloxanes reaching the aquatic environment are probably quickly diluted in the receiving water. Acute and possibly also chronic toxic effects are hence probably limited to locations in very close proximity of outlets from STPs, landfills or other point sources. Observed levels in fish and sediment still show that siloxanes are present in several aquatic systems, and are likely to occur also in the water phase, even though in concentrations lower than the limit of detection.



## 6. Conclusions

Siloxanes were found in all the analysed media but soil: air, water, sediment, sludge and biota. The results indicate that there is a general pollution of siloxanes in the Nordic countries. There was, however, a great variation in concentrations. The cyclic siloxanes occurred in all media in significantly higher concentrations than the linear siloxanes.

D5 was the dominating siloxane in most samples, which is not in agreement with data on use in the Nordic countries, where the consumption of D5 and D4 is fairly equal. D4 occurred in the highest concentration in the air samples with the exception of all Norwegian samples (4), one Icelandic sample, one Finnish sample, two Danish samples and one Swedish sample.

The results of air measurements in urban areas indicate a regional variation, with the highest concentration in Norway and the lowest in Sweden. The air concentrations were highest inside sewage treatment plants, and elevated levels were commonly observed in other matrices surrounding STPs. No other obvious point sources were found.

Diffuse sources seem to be most important for the observed concentrations of siloxanes in the Nordic environment. The concentrations were generally elevated in urban areas and in areas close to sewage treatment plants. The mean concentration of D5 in biological sludge from STPs (27 000 ng/g dw) is in the lower range of what has been found elsewhere (see Table 8) and comparable to that of the widespread contaminant 4-nonylphenol.

The concentrations in fish liver were fairly variable. Siloxanes were mainly detected in fish liver samples from sites representing urban/diffuse sources and only a few background samples showed detectable levels. One pooled sample of cod liver from Inner Oslofjord showed highly elevated concentrations. On the whole, biota data indicate that siloxanes may bioaccumulate.

No Observed Effect Concentrations for D4 and estimated Chronic Values for D5 were only exceeded in samples representing incoming sewage water to sewage treatment plants. These levels were, however, significantly reduced in the outgoing water from the same treatment plants. Since only limited amounts of toxicity data are available for other siloxanes than D4 and No Observed Effect Levels and Chronic Values are estimated, the possibility of effects in the local environment close to emissions should therefore not be excluded.

Conclusively, siloxanes are present as a common pollutant in the Nordic environment and in many different matrices. They seem to be emitted through diffuse pathways and they enter the aquatic food chain. At pre-



sent, the observed concentrations are not alarmingly high, and many background sites seem to be non-contaminated. However, the use of siloxanes is extensive and it is possible that continued use will lead to increased environmental levels, eventually reaching effect concentrations.

## 7. Acknowledgements

*Norway:* Thanks to Norman Green, Sigurd Rognerud, Helge Liltved and Eirik Fjeld at NIVA for providing samples of marine and limnic water, runoff from municipal sewage treatment, sediment and fish, to Trine Eggen at JORDFORSK for providing samples of runoff from waste deposits and to Norbert Schmidbauer at NILU for providing air samples.

*Denmark:* Thank you for kindly providing assistance with collection of samples to AV-miljø deponeringsanlæg (Jonas Nederskov), Bjergholm rensningsanlæg (Ove Petersen), Lynettefællesskabet A/S laboratoriet (Lene Vig), Roskilde Amt (Bruno Hansen, Ribe Amt (Kaisa Toudal) Jonas Theilman at DMU for providing seal samples and to (Martin Larsen (DMU) for assisting with the logistics.

*Finland:* SYKE's Contaminants Research Unit and Laboratory Unit (1) performed the sample collection, preparation and storing in collaboration with several municipal institutions and their staff. Great thanks belong to (2) the Regional Environment Centre of Uusimaa (Nyland) for assisting in seawater and sediment sampling; (3) Helsinki City for providing sludge and effluent samples and performing pike fish collection in the coastal sea area; (4) the Nokia City, (5) Espoo City, (6) Porvoo City and (7) Pornainen commune for providing sludge and effluent samples; (4) Nokia City and (8) the Council of Helsinki Metropolitan Area for contributing to collection of air samples and landfill leachate water.

*Iceland:* Thanks to Guðjón Atli Auðunsson at the Maritime Research Institute for supplying common porcupine samples from specimen bank, Kristján Tómasson at the Technical division of the City of Reykjavik for assisting in sampling of sewage sludge, Guðmar Finnur Guðmundsson at Sorpa for assistance in sampling waste water runoff from municipal landfill at Álfsnes. Jörundur Svavarsson at the Biological Institute of the University of Iceland supplied the sediment and sea samples and Sigurdur G. Finnson at the Environment and Food Agency, who assisted in air sampling.

*Faroe Islands:* The sampling of seabirds eggs were done by Poul Johannes Simonsen, Bjørn Patursson, Jóannes Mikkelsen for the purpose of environmental monitoring, and by locals in Skúvoy coordinated by Bergur Olsen, in connection with the egg sampling for food. The samples of whitesided dolphins were made available by Bjarni Mikkelsen at the Mu-

seum of Natural History. The sampling of fish was done by the Faroese Anglers Association, and by Lise Ofstad, Høgni Arnbjarnason and Katrin Hoydal. Thanks are due to staff in Tórshavn Kommune for assisting in landfill sampling and to Katrin Hoydal for sampling of pilot whales and sample preparation. Hjalmar Jacobsens Bókhandil assisted in the downtown air sampling.

*Sweden:* Thanks to Anders Bignert, NRM, Ingemar Cato, SGU, Carl Dahlberg at Gislaved Municipality and staff at concerned municipal STPs for assistance with sampling.

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## Sammanfattning

Den här presenterade "screeningstudien" avseende spridning och förekomst av flyktiga metylerade siloxaner i den nordiska miljön involverar sex länder: Danmark, Färöarna, Finland, Island, Norge och Sverige.

Siloxaner hör till en grupp ämnen som används i ett stort antal olika industriella applikationer samt i konsumtionsprodukter såsom additiv i bränsle, bilvaxer, rengöringsmedel samt antiskummedel. Dessutom förekommer de i olika hygien- och kosmetikaprodukter. Den omfattande användningen, de många applikationsområdena samt den höga flyktigheten har orsakat intresse för siloxaner inom flera olika miljövetenskapliga discipliner.

Till följd av deras omfattande användning sprids siloxaner sannolikt både via punktkällor samt via diffusa källor, och förväntas kunna återfinnas överallt i miljön. Nyligen utförda studier har pekat på att siloxaner kan ha direkta eller indirekta toxiska effekter på olika biologiska processer.

Screeningstudien inkluderade följande ämnen: de linjära siloxanerna hexametyl-disiloxan (MM eller HMDS), oktametyltrisiloxan (MDM), dekametyltetrasiloxan (MD2M), dodekametylpentasiloxan (MD3M) och de cykliska siloxanerna oktametylcyclotetrasiloxan (D4), dekametylcyklopentasiloxan (D5) och dodekametyl-cyklohexasiloxan (D6). Dessutom analyserades hexametylcyclotrisiloxan (D3) i biota. Detta ämne är starkt flyktigt och förorsakar analytiska svårigheter, varför den ej analyserades i övriga matriser.

Siloxaner hittades i alla matriser som studerats förutom jord: luft, vatten, sediment, slam och biota. Resultaten tyder på att siloxaner är allmänt förekommande föroreningar i den nordiska miljön. Det fanns dock en stor variation i observerade koncentrationer. De cykliska siloxanerna förekom i avsevärt högre koncentrationer än de linjära i alla matriser som analyserats. Tabellen nedan visar de uppmätta intervallen av olika siloxaner i olika matriser.

Ämne	Luft ( $\mu\text{g}/\text{m}^3$ )	Vatten ( $\mu\text{g}/\text{L}$ )		Slam ( $\text{ng}/\text{g dw}$ )	Jord ( $\text{ng}/\text{g dw}$ )	Sediment ( $\text{ng}/\text{g dw}$ )	Biota ( $\text{ng}/\text{g ww}$ )
		Av- lopp/industriellt*	Kust/ vattendrag				
MM	<0.004	<0.0005-0.14	<0.0005-<0.0006	<0.5 - <3	<0.1	<0.02-<0.7	<0.4
MDM	<0.008	<0.0005-0.014	<0.0005-<0.0006	<1-64	<0.1	<0.02-<0.7	<0.3
MD2M	<0.006	<0.0005-0.078	<0.0005-<0.0006	1-450	<0.1	<0.02-29	<0.4 – 1.1
MD3M	<0.02	<0.004-0.23	<0.002-<0.004	3-550	<0.1	<0.02-57	<0.5
D3	n.a**	n.a	n.a	n.a	n.a	n.a	<50-90.4***
D4	0.08-4.0	<0.06-3.7	<0.04-<0.09	96-960	<6-<10	<3-84	<5-70
D5	0.05-19	<0.04-26	<0.02-<0.05	1100-89000	<3-<5	<2-2000	<5-2200
D6	0.02-2.1	<0.04-3.8	<0.02-<0.05	220-11000	<2-<4	<1-170	<5-74

\*Proverna representerar in- och utgående avloppsvatten till och från reningsverk, lakvatten från deponier samt industriellt dagvatten \*\*n.a = ej analyserad \*\*\*Detekterade halter låg under kvantifieringsgränsen

D5 var den dominerande siloxanen i samtliga matriser utom luft, där D4 generellt förekom i högre halter. Detta överensstämmer inte med konsumtionsdata för Norden, där användningen av D5 och D4 uppges vara ganska lika. Resultaten från luftmätningarna indikerar en regional variation, med högst koncentrationer i Norge och lägst i Sverige. Uppmätta koncentrationer av D5 i luft inne i reningsverk var markant förhöjda i jämförelse med andra luftprover, likaså var koncentrationer av D5 i andra matriser i anslutning till reningsverk förhöjda.

Diffusa källor tycks vara av störst betydelse för de observerade siloxan-koncentrationerna. Halterna var allmänt sett förhöjda i urbana områden samt i områden nära reningsverk. Medelhalten av D5 i slam är jämförbar med vad som observerats för 4-nonylfenol, men detta innebär inte nödvändigtvis att det er likedana effekter som kan observeras.

Halterna i fisklever var varierande. Siloxaner hittades främst i fiskprover från lokaler som representerar urbana/diffusa källor och endast ett fåtal bakgrundsprover uppvisade detekterbara halter. Ett poolat prov av torsklever från inre Oslofjorden hade starkt förhöjda halter. Totalt sett indikerar biota data att siloxaner kan bioackumuleras.

No Observed Effect Concentrations (NOECs) för D4 samt uppskattade sk ”Chronic Values” (ChV) för D5 överskreds endast i prover av inkommande avloppsvatten till reningsverk. Dessa koncentrationer reducerades avsevärt i utgående vatten från samma reningsverk. Då tillgången på toxicitetsdata är ytterst begränsad för andra siloxaner än D4 och NOECs samt ChV är uppskattade värden, kan det inte helt uteslutas att effekter kan uppkomma lokalt i direkt anslutning till emissionspunkter.

Sammanfattningsvis kan konstateras att siloxaner är allmänt förekommande miljöföroreningar i den nordiska miljön och hittas i många olika matriser. De verkar släppas ut framför allt genom diffusa spridningsvägar och de tas upp i den akvatiska näringskedjan. I dagsläget är halterna inte alarmerande höga, och många bakkgrundsstationer verkar vara fria från föroreningar. Användningen av siloxaner är dock omfattan-

de och det går inte att utesluta att fortsatt användning skulle kunna leda till ökande halter som på lång sikt kan nå effektnivåer.





## Appendix 1: Sample characteristics















## Appendix 2: Results tables

















# Appendix 3: Sampling manual

Analysis of siloxanes in a Nordic cooperation on screening  
Sampling and sample handling manual

IVL/NILU

1. Air samples
2. Sediment, sludge, soil, and water samples
3. Biological samples
4. Sampling forms

## Air sampling

### *General remarks*

Sampling of Siloxanes in air is a challenging task since Siloxanes are widely used within personal care products like deodorants, skin lotions and perfumes and other household products. A lot of flexible tubing, often used together with air sampling equipment are also source of siloxanes.

It is therefore necessary to avoid contact between the sampling tube and bare skin. Together with the sampling equipment we will provide you with disposable gloves. In order to avoid contamination of the sampling tubes by the persons taking the samples – there should be as little as possible contact time. While sampling in closed indoor environment the sampling personnel should not stay close to the pump and adsorption tube. Sampling outdoors the personnel should stay down wind the sampling equipment.

- Please don't use any kind of water-resistant permanent markers to write information onto the tube or the pen-clip.
- Each tube has its own id-number which should be used together with the sampling-form for adsorption tubes.
- Please do not use any type of glue or tape in connection with the sampling.

## Sampling procedure

### *Use disposable gloves.*

The adsorption-tubes are sealed with a unit of a brass nut and brass cap at both ends with a teflon –sealing inside. On each tube is a pen-clip with an ID-number and arrows showing the correct direction of the air-flow.

You need two spanners or a set of 1/2 inch and 9/16 inch tools to loosen the unit with about half a turn and then remove the brass unit as one piece from the adsorption tube. At first remove the brass unit from the tube at the side to where the arrows on the ID-clip is pointing. This is the side, which is connected to the Inlet Port of the pump. This port is equipped with a Swagelock-type brass unit with teflon sealing inside. Push the end of the tube into it – tighten the nut with your fingers and use a 9/16 inch tool to tighten (maximum 1/4 of a full turn). Right before starting sampling the other brass unit has to be removed.

Fill inn the sampling form.

The sampling time will be 1 hour for indoor, industrial or urban sites and 2 hours for rural or background sites.

After sampling the adsorption tube has to be reassembled with the brass caps. Please start to tighten the unit with your fingers and use the 9/16 inch tool to tighten (maximum ¼ of a full turn).

Both empty and exposed adsorption tubes can be stored at normal indoor or outdoor temperature conditions.

## Address

NILU v/Schmidbauer eller Lunder  
P.b. 100  
2027 Kjeller Tf 63898000

## Sampling of sediment, sludge, soil, and water

### *General remarks*

Siloxanes are frequently used in cosmetic formulations. Do not use products such as antiperspirant, eye shadow, hair spray, or skin lotions on the day of sampling. Only specially cleaned sampling containers provided by the laboratory should be used.

To check for contamination sampling blanks are used. The sampling blank to be used for sediment, sludge, and soil sampling contains silica particles, the one to be used for water contains MilliQ-water. The sampling blanks should not be emptied or filled. They shall only be opened and closed at the time of sampling.

The number of sampling blanks is limited. If the number of samples per sample type (water, sediment, sludge, soil) and country is one to four the number of sampling blanks is one. If the number of samples per sample type and country is five or more the number of sampling blanks is two. The sites used for blank sampling should be selected at random before the start of sampling.

### *Sampling*

Arrange the sampling bottle to be used (and, if the site is selected for blank sampling, one sampling blank) on a clean spot on the sampling site. Put on the supplied gloves.

Immediately before sampling open the lid of the sampling container (and the sampling blank).

Fill the sample container, if required using the enclosed spoon. If the Al-foil protecting the lids is ruptured replace it with new Al-foil and close the lid on the sample bottles (and sample blank). Label the sample containers. Put each container in a plastic bag.

Fill in the sample protocol.

### *Storage and transport*

Store the samples refrigerated (or in a freezer - be aware of the risk for damage to glass containers!) and send to the laboratory as soon as possible in such a way that the samples will reach the laboratory within one day. When sending the samples please send an e-mail including a list specifying the samples to Lennart Kaj ([lennart.kaj@ivl.se](mailto:lennart.kaj@ivl.se)).

## Address

IVL Swedish Environmental Research Institute  
Lennart Kaj  
Hälsingegatan 43  
SE-113 31 Stockholm.  
Sweden.

## Biological samples

### *General remarks*

Sampling should be performed in accordance with general sampling strategies for chemical trace analysis. In case of questions about the practicability of procedures or usability of special material and equipment NILU must be contacted (Biological samples: Martin Schlabach, Tel: +47 6389 8213, Fax: +47 6389 8050, [msc@nilu.no](mailto:msc@nilu.no)). The sampling strategy should take into account the specific objectives of the monitoring programme, including the quantitative objectives. Natural variability within the samples should be reduced by an appropriate sampling design. The sampling strategy is an intrinsic component of the data, and may limit their use and interpretation.

Nothing is known about the homogeneity of the distribution of siloxanes in the Nordic environment, since no comprehensive screening has been performed in these countries yet. Therefore, it is difficult to give recommendations about the choice of representative sampling sites. Only a relatively high number of samples taken from as many different places as possible can overcome this challenge and will add to our knowledge about distribution patterns of PFAS in the environment. The detailed sampling site selection lies within the responsibility of the sampling institutes. Sampling sites must be indicated on the sampling protocols as accurate as possible (preferably with latitude/longitude data).

### *Risk of contamination / Risk of evaporation loss*

Siloxanes are widely used in cosmetics (especially deodorants and creams) and a row of technical products (paints and plastics), so great care has to be taken to avoid contamination of the samples. When handling the samples gloves are mandatory, and measures should be taken to exclude that the personnel involved are using cosmetics containing siloxanes during the sample-handling period. Even cleaned laboratory air can contain vapors of siloxanes; so prolonged direct contact with the laboratory air should be avoided. Furthermore all utensils coming in contact with the samples should be solvent rinsed with 3 times acetone and 3 times n-pentane following the normal cleaning. Glass and metal utensils should finally be heated for 2 hours at 450 °C. Direct contact with polymer utensils should be kept at a minimum.

In contrast to the compounds of the two preceding NMR-screening studies siloxanes can be characterized as typical volatile organic compounds (VOC) and thus evaporation loss during sample handling is a risk which we must try to hold at a minimum. We propose therefore to keep

the biological samples as intact as possible. This means that whole fishes, complete livers, whole eggs, or pieces of seal/whale meat/blubber are preferred instead of homogenized small samples.

All samples of one kind from each country should be sent together to NILU as soon as possible after the sampling. NILU should be notified about the arrival of samples in order to ensure that the samples are received and handled properly.

*NILU must be contacted in case of questions about the usability of certain materials in contact with samples.*

#### *Field sampling and required sample size*

All biological samples must be frozen immediately after catch and preparation.

#### *Fish and fish liver*

Fish should be dissected immediately after collection. Small fishes shall be packed and sent as whole fish. From bigger fishes at least a 10 cm chop from the middle part of each fish shall be sent. Liver samples shall be packed and sent as whole pieces.

#### *Bird eggs*

Only newly laid eggs are usable for this study, since the siloxanes will truly be volatilized and lost during breeding several weeks at 37 °C. Fresh eggs shall be packed separately, frozen and sent.

#### *Seal and whale*

The seal or whale should be dissected immediately after collection. From each individual a 5 \* 5 cm slice of meat or blubber shall be taken, packed and sent.

## Storage and shipping of samples

All samples must be collected, stored and shipped in clean, siloxane-free packaging. We suggest to wrap the samples tightly with aluminium foil, and pack these packages in a polyethylene zip-bag

Biological samples must be kept frozen during storage (< -18 °C). During transportation, an insulated box should be used to ensure that the temperature does not exceed thawing temperature (< 0 °C). All samples must be clearly and unmistakably marked with a sample name and sent

together with their sampling protocols by an express delivery service (TNT, DHL, EMS or similar) to the following address:

Norwegian Institute for Air Research (NILU)  
Att Martin Schlabach  
Instituttveien 18  
NO-2027 Kjeller  
Norway

To assure that samples reach the destination within short time (usually within the same day), they should be sent early in the morning and not on a Friday (preferably Monday to Wednesday). When sending the samples a notice including the airway bill number (AWB) of the package must be sent to NILU to the following fax number: ++47 6389 8050 addressed to Martin Schlabach or e-mail to [msc@nilu.no](mailto:msc@nilu.no). The delivery should be marked with “samples NMR-siloxane study” to avoid unnecessary delays during the registration procedure at the analysing institute.



## Sampling forms

### *Sampling form – adsorption tubes*

#### **Sampling with pump**

Country			
Sampling site			
Coordinates			
Sample taken by : (name)			
Pump ID			

Tube ID	Start/Stop Date, time (precise)	Place (e.g on a table or at the floor – approximately height above ground)	Remarks

*Questions about sampling, call NILU at + 47 63 89 82 15*

Sent to NILU:	
Received at NILU:	

Address:  
 NILU Attn: Schmidbauer / Lunder  
 P.b 100  
 2027 Kjeller

When sending the samples a list of the samples together with the airway bill number (AWB) of the package must be sent to NILU to the following fax number: ++47 6389 8050 or e-mail to [ns@nilu.no](mailto:ns@nilu.no).

## Sampling form – Sediment, sludge, soil and water samples

Sample type:

- |  |  |
|--|--|
| <input type="checkbox"/> Sewage water            | <input type="checkbox"/> Digested sludge |
| <input type="checkbox"/> Surface water           | <input type="checkbox"/> Sediment        |
| <input type="checkbox"/> Soil                    |  |
| <input type="checkbox"/> Sampling blank included |  |

Sample name / identity:

Coordinates for the sample site:

Sampling day:

Shipped to IVL:

Received at IVL:

Used sampling equipment:

Responsible person:

Sample storage:

- Freezer     Fridge     Other

Sample preservation:

- NaN<sub>3</sub>     phosphoric acid     Other

Address:

IVL Swedish Environmental Research Institute  
Lennart Kaj  
Hälsingegatan 43  
SE-113 31 Stockholm

When sending the samples please send an e-mail including a list specifying the samples to Lennart Kaj ([lennart.kaj@ivl.se](mailto:lennart.kaj@ivl.se)).

## Sampling form -Biological samples

<b>Sample name:</b>	<b>Sample material:</b>
---------------------	-------------------------

Sampling		Comments
Date:		
Site (description, preferably with latitude/longitude data):		
Number and size of individuals used for the pooled sample:		
Age and sex of the individuals		
Storage temp. after sampling:		
Date and site of dissection:		
Total sample amount:		
Special observations:		
Storage		Comments
Storage time:		
Storage temperature:		
Special observations:		
Shipping		Comments
Date sample sent:		
Shipping temperature:		
Date sample received*:		
Condition upon receipt*:		
Special observations*:		

\* To be filled in by NILU

Send to:

Norwegian Institute for Air Research (NILU)  
 Att Martin Schlabach  
 Instituttveien 18  
 NO-2027 Kjeller  
 Norway

When sending the samples a list of the samples together with the airway bill number (AWB) of the package must be sent to NILU to the following fax number: ++47 6389 8050 or e-mail to [msc@nilu.no](mailto:msc@nilu.no).