Siloxanes in the Environment of the Inner Oslofjord

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Rapport 986/2007





Statlig program for forurensningsovervåking

Preface

The purpose of this study was to firstly to confirm the high concentrations of cyclic siloxanes measured in cod liver from Inner Oslofjord and secondly to gain a broader overview on the siloxane contamination of the Inner Oslofjord compared to other areas studied in the Nordic siloxane study published in 2005..

The study was led by the Norwegian Institute for Air Research (NILU), with the help of Norman Green and Merete Schøyen of the Norwegian Institute for Water Research (NIVA).

We would like to thank the Norwegian Pollution Control Authority (SFT) for funding this project.

We would like to thank Ola Glesne, who was responsible for this study at the Norwegian Pollution Control Authority.

Kjeller, June 2007.

Martin Schlabach
Project Manager, NILU

Table of Contents

1. Abstract 3

2. Sammendrag 4

3. Background 5

4. Methods 7
4.1 Sampling 7
4.2 Chemical Analysis 10
4.2.1 Analysis of sludge, sediment, water and soil samples 10
4.2.2 Analysis of biota samples 11

5. Results 13
5.1 Sewage water 13
5.2 Sewage sludge 14
5.3 Sea water 15
5.4 Sediment 15
5.5 Biota 16

6. Conclusions 22

7. References 23

1. Abstract

In order to confirm the high concentrations of cyclic siloxanes measured in cod liver from Inner Oslofjord and to gain a broader overview on the siloxane contamination of the Inner Oslofjord new samples of sewage water and sludge, sea water, sediments and biota were taken.

As in the Nordic screening project siloxanes were found in all kinad of samples analyzed with exception of sea water. The cyclic siloxanes are dominating in all sample types compared to the linear siloxanes. D5 is the most prominent of the cyclic siloxanes.

The concentration in both sewage water and sludge is in the same range as measured in the Nordic study at different STPs in Nordic countries.

The concentration in sediments from Inner Oslofjord are higher than for most of the urban area samples measured in the Nordic study. The highest sediment concentrations were measured close to the outlet of Bekkelaget STP, whereas the other samples taken further away from Bekkelaget STP are much lower but even higher than samples taken in Stockholm and Helsinki area (D5: 58 – 130 ng/g d.w.).

All marine biotas from the Inner Oslofjord shows measurable concentrations of D4, D5, and D6. In cod liver it was still possible to detect the linear siloxanes MDM, MD2M and MD3M.

In the Nordic screening study a pooled sample of cod liver from Inner Oslofjod showed elevated concentrations especially of D5. For that reason new samples of cod liver were taken showing the same level of contamination. The analysis of stomach content taken from the same cod samples showed slightly lower concentrations, in other organisms at a lower trophic level the concentrations were much lower. However, there are too many uncertainties to draw an unequivocal conclusion on biomagnification in the food chain in Inner Oslofjord.

2. Sammendrag

Tidligere ble det påvist høye konsentrasjoner av sykliske siloksaner i torskelver fra Indre Oslofjord. For å få en bedre oversikt over belastningen av miljøet med siloksaner ble det samlet inn nye prøver av avløpsvann og avløpsslam, sjøvann, sedimenter og biologisk materiale.

Som i den nordiske screeningundersøkelsen ble det påvist siloksaner i alle analyserte prøvetyper med unntak av sjøvann. Det er de sykliske siloksaner som dominerer i alle prøvetyper i forhold til de lineære. D5 er den mest framtredende av de sykliske siloksanene.

Konsentrasjonene målt i avløpsvann og –slam er på samme nivå som målt ved andre renseanlegg i de andre nordiske land.

Konsentrasjonene målt i sedimenter fra Indre Oslofjord er høyere enn for de fleste prøver fra urbane områder i den nordiske undersøkelsen. De høyeste sedimentkonsentrasjoner ble målt i nærheten av utløpet fra Bekkelaget renseanlegg, mens ander prøver tatt lengre vekk fra Bekkelaget viser mye lavere konsentrasjoner, men fortsatt høyere enn prøver fra Stockholm og Helsinki (D5: 58 – 130 ng/g t.v.).

Alle marine biologiske prøver fra Indre Oslofjord viser målbare konsentrasjoner av D4, D5 og D6. I torskelever var det til og med mulig å påvise lineære siloksaner MDM, MD2M og MD3M.

I den nordiske undersøkelsen viste en torskeleverprøve fra Indre Oslofjord forhøyete konsentrasjoner spesielt av D5. Av den grunnen ble det tatt nye prøver av torskelver som viste samme belastningsnivået. Analysen av mageinnhold av de samme torskeprøver viste et litt lavere konsentrasjonsnivå, mens i andre organismer på et lavere trofisk nivå fant man mye lavere siloksankonsentrasjoner. Det er imidlertid for mange usikkerhetsmomenter for å kunne dra en klar konklusjon om biomagnifisering av siloksaner i næringskjeden i Indre Oslofjord.

3. Background

This study presents additional measurements of the environmental occurrence and distribution of volatile methylated siloxanes in the environment of the Inner Oslofjord as a follow-up of an earlier Nordic screening (TemaNord 2005).

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 foamiers 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. Details on application and use, and on physical, chemical and toxicological properities are given in TemaNord 2005.

As a result of their wide use, siloxanes are 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.

This study include the following substances: the linear siloxanes hexamethyl-disiloxane (MM or HMDS), octamethyltrisolixane (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 biota, sediment, sludge, soil and water. Siloxanes were found in all the analysed samples types. 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. Table 1 below shows the observed concentration ranges in different matrices.

Substance	Air ($\mu g/m^3$)	Water (µg/L)		Sludge (ng/g dw)	Soil (ng/g dw)	Sediment (ng/g dw)	Biota (ng/g ww)
		Sewage/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

Table 1: Concentrations measured in the Nordic screening project in 2004/2005 (TemaNord 2005).

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.

In the Nordic screening study one pooled sample of cod liver from Inner Oslofjord showed highly elevated concentrations. To verify this finding the new study in the Inner Oslofjord was initiated by SFT in Norway.

4. Methods

4.1 Sampling

The following sample types were collected:

1. sewage water, sewage sludge from VEAS and Bekkelaget sewage treatment plant (STP),
2. seawater,
3. sediment, and
4. biota (blue mussels, flounder fillet, flounder liver, cod stomach content and cod liver)

The different sampling stations are shown and described in Figure 1, Figure 2, Figure 3, and Table 1.

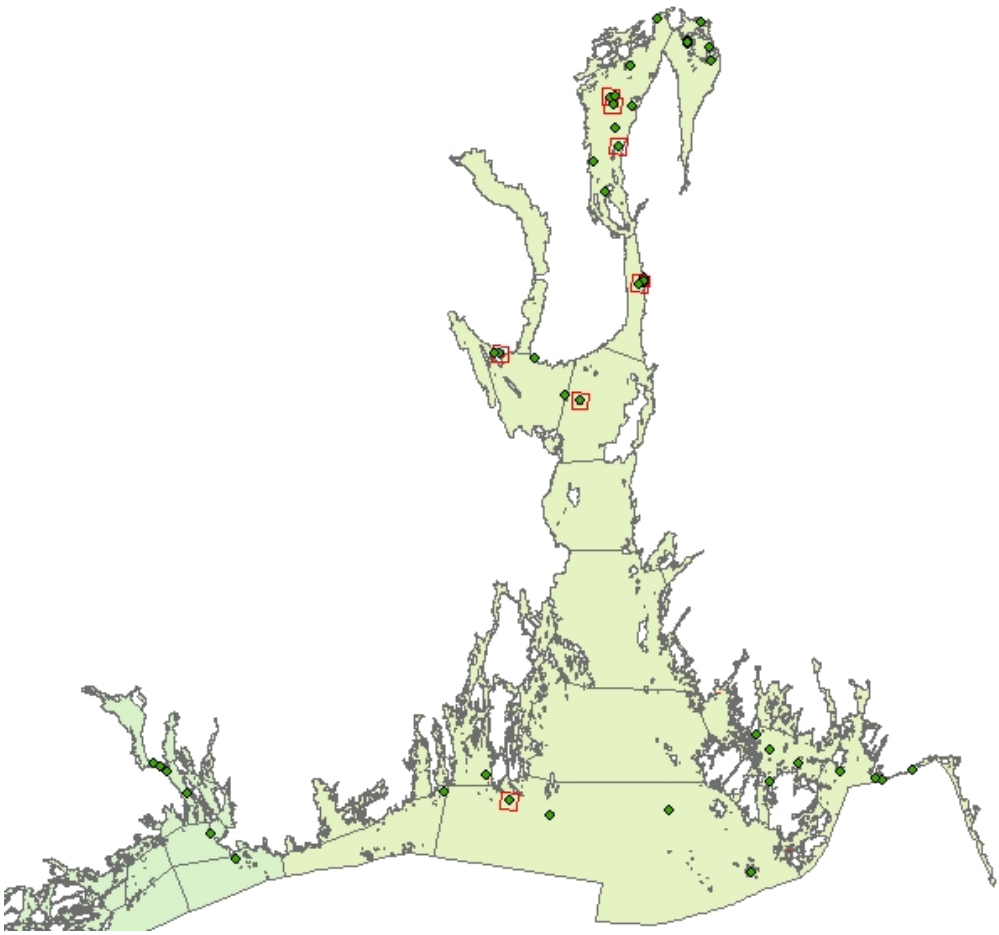


Figure 1: Sampling stations in the Oslofjord area

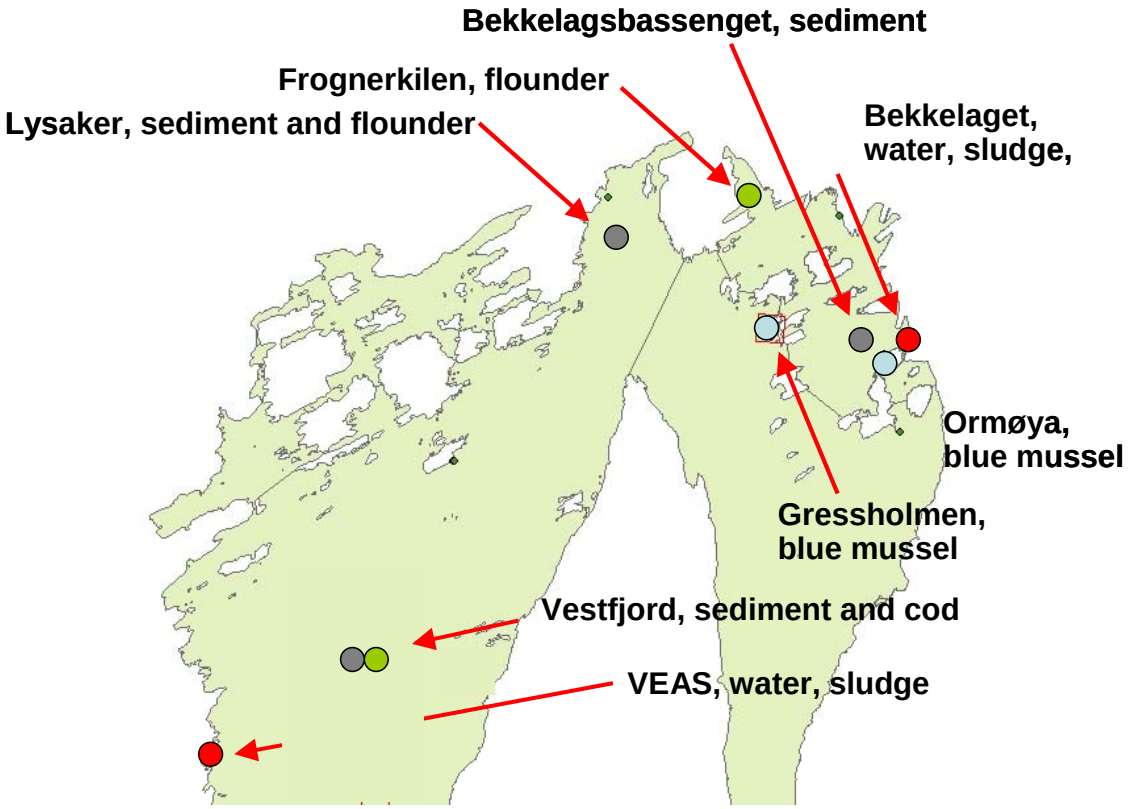


Figure 2: Sampling stations in the Inner Oslofjord

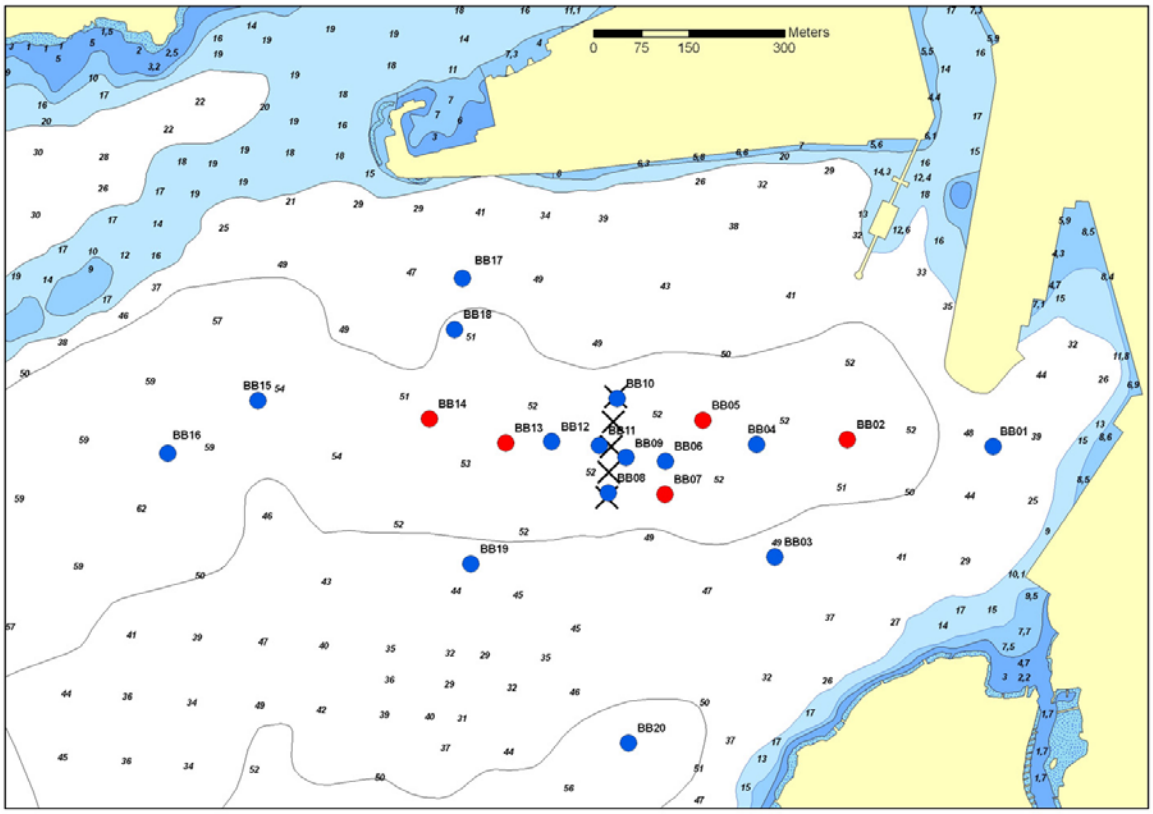


Figure 3: Sampling stations in the Bekkelaget basin

Table 2: Sample description

Sample ID	Location	Matrix	Position	Sampling date
MR 4999	Bekkelaget	Influent water	N59.882 E10.767E	6. September 2006
MR 5000	Bekkelaget	Effluent water	N59.882 E10.767E	6. September 2006
MR 4996	VEAS	Influent water	N59.789 E10.496	21-22.September 2006
MR 4997	VEAS	Effluent water	N59.789 E10.496	21-22.September 2006
MR 5001	Bekkelaget	Inlet sludge	N59.882 E10.767	6. September 2006
MR 5002	Bekkelaget	Outlet sludge	N59.882 E10.767	6. September 2006
MR 5267	VEAS	Inlet sludge	N59.789 E10.496	21-22.September 2006
MR 5268	VEAS	Outlet sludge	N59.789 E10.496	21-22.September 2006
MR 5003	Bekkelaget	Sea water	N59.8827 E10.7588	16. September 2006
MR 5007	Lysaker	Sea water	N59.8980 E10.6459	16. September 2006
MR 5269	30B Vestfjord (inner Oslofjord)	Sea water	N59.8183 E10.5633	25 October 2006
MR 5273	36A Færder	Sea water	N59.0272 E10.5255	8. November 2006
MR 5005	Bekkelagsbassenget, St BB5, 52m	Sediment	N59.8829 E10.7547	16. September 2006
MR 5006	Bekkelagsbassenget, St BB14, 53.5m	Sediment	N59.8826 E 10.7470	16. September 2006
MR 5008	Lysaker St.1, 60.4m	Sediment	N59.8980 E10.6459	16. September 2006
MR 5009	Lysaker St.2, 60.4m	Sediment	N59.8980 E10.6459	16. September 2006
MR 5271	30S Vestfjord (inner Oslofjord)	Sediment	N59.8176 E10.5638	25. October 2006
MR 5272	30S Vestfjord (inner Oslofjord)	Sediment	N59.8176 E10.5638	25. October 2006
06/1576	36A Færder	Common mussel	N59.0272 E10.5255	8. November 2006
06/1575	30A Gressholmen	Common mussel	N59.8837 E10.7110	30 October 2006
06/4014	Ormøya	Common mussel	N59.8798 E10.7621	16. September 2006
07/327-1	Frognerkilen	Flounder liver	N59.9105 E10.6983	10. November 2006
07/327-2	Frognerkilen	Flounder fillet	N59.8798 E10.7621	10. November 2006
06/1527	30B Vestfjord (inner Oslofjord)	Cod stomach content	N59.8183 E10.5633	24. October 2006
06/1528	30B Vestfjord (inner Oslofjord)	Cod stomach content	N59.8183 E10.5633	24. October 2006
06/1529	30B Vestfjord (inner Oslofjord)	Cod stomach content	N59.8183 E10.5633	24. October 2006
06/1530	30B Vestfjord (inner Oslofjord)	Cod liver	N59.8183 E10.5633	24. October 2006
06/1531	30B Vestfjord (inner Oslofjord)	Cod liver	N59.8183 E10.5633	24. October 2006
06/1532	30B Vestfjord (inner Oslofjord)	Cod liver	N59.8183 E10.5633	24. October 2006
05/414	30B Vestfjord (inner Oslofjord) 2004	Cod liver 2004	N59.8183 E10.5633	15. October 2004

Detailed instructions for sampling, storing and transport were given in a sampling manual including protocols for all sample types (see TemaNord, 2005). 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.

Immediately after collection the samples of common mussels were immersed for 1 hour in clean water to allow for depuration of detrital material.

4.2 Chemical Analysis

4.2.1 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 $Na_2EDTA\ 2H_2O$ 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, Markes) connected to a GC-MS instrument (6890N, 5973N, Agilent). Prepurge 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 masspectrometric 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.

4.2.2 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 ubiquitary 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.

4.2.2.1 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.

4.2.2.2 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×0.11µm 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.

5. Results

5.1 Sewage water

Four samples of sewage water from Bekkelaget STP and VEAS STP (influent and effluent) were analyzed in this study. The results are shown in Table 3 and Figure 4.

Sample ID	Location	Matrix	µg/L						
			D4	D5	D6	MM	MDM	MD2M	MD3M
MR 4999	Bekkelaget	Influent water	0,1	9,8	0,5	<0.0003	0,001	0,009	0,017
MR 5000	Bekkelaget	Effluent water	<0.03	0,2	<0.02	<0.0003	<0.0003	<0.0003	<0.002
MR 4996	VEAS	Influent water	0,2	12,0	1,0	<0.0003	0,032	0,015	0,035
MR 4997	VEAS	Effluent water	0,1	1,0	0,1	<0.0003	<0.0003	<0.0003	<0.002

Table 3: Concentrations of siloxanes in influent and effluent water from Bekkelaget and VEAS STP.

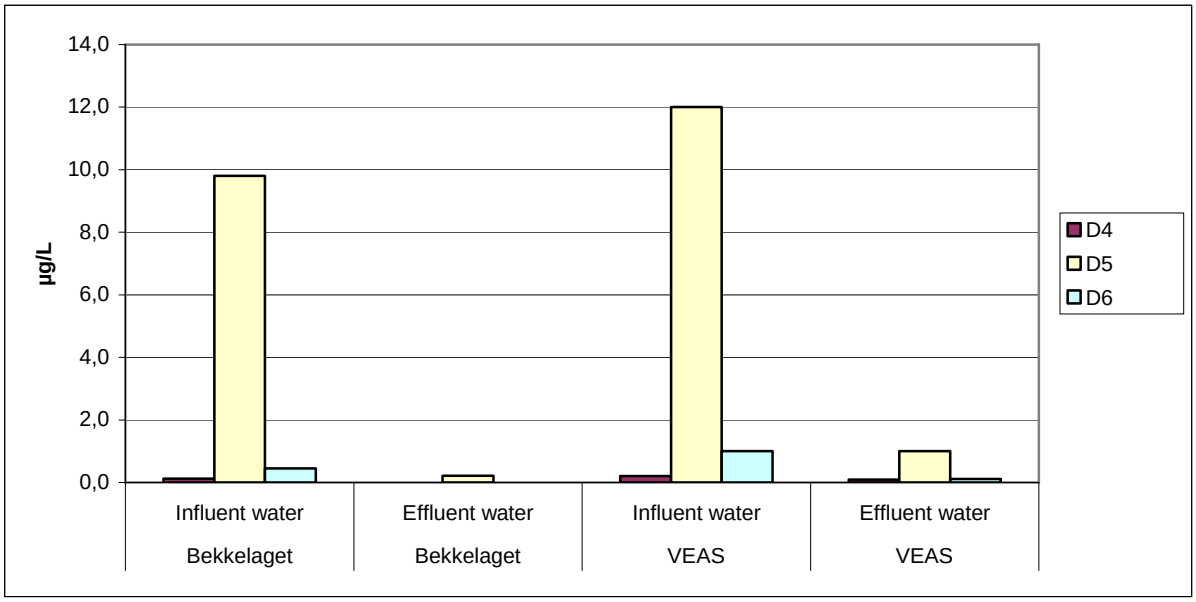


Figure 4: Concentrations of siloxanes in influent and effluent water from Bekkelaget and VEAS STP.

The cyclic siloxanes were found in much higher concentrations than the linear analogues. In all samples D5 was dominating. The concentration measured at Bekkelaget and VEAS were in the same concentration range as the samples from the Arendal STP measured in the Nordic screening study (TemaNord 2005). However, the Danish samples of the prior study showed a factor 2 higher concentration in the influent water.

5.2 Sewage sludge

Four samples of sewage sludge from Bekkelaget STP and VEAS STP (influent and effluent) were analyzed in this study. The results are shown in Table 4 and Figure 5.

Sample ID	Location	ng/g dw							
		D4	D5	D6	MM	MDM	MD2M	MD3M	dw %
MR 5001	Bekkelaget inlet	1100	130000	14000	<7	11,0	95,0	400	4,5
MR 5002	Bekkelaget outlet	2700	1900	960	29,0	12,0	66,4	<33	95,6
MR 5267	VEAS inlet	<180	25000	3400	<0.7	<2	21,0	120	56,2
MR 5268	VEAS outlet	1000	62000	4700	<2	31,0	75,0	170	6,8

d.w.: dry weight

Table 4: Concentrations of siloxanes in sewage sludge from Bekkelaget and VEAS STP.

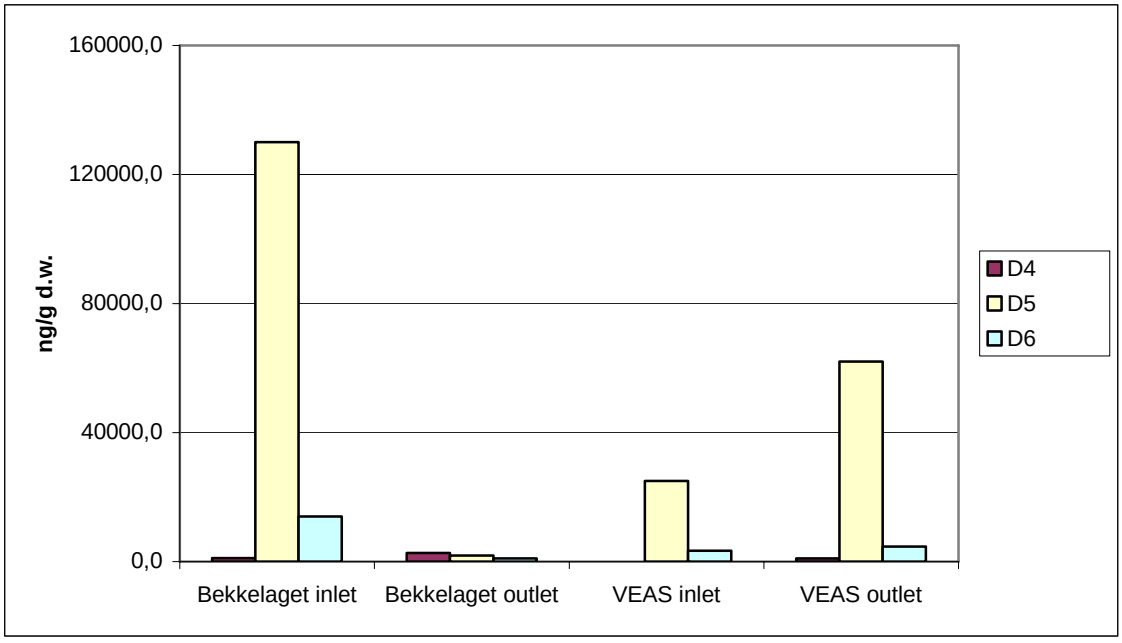


Figure 5: Concentrations of siloxanes in sewage sludge from Bekkelaget and VEAS STP.

The cyclic siloxanes were found in much higher concentrations than the linear analogues. In all samples D5 was dominating. The concentration measured at Bekkelaget and VEAS were in the same concentration range as the sludge samples measured in the Nordic screening study (TemNord 2005).

5.3 Sea water

Four samples of sea water from the Inner and Outer Oslofjord were analyzed. As in the Nordic study (TemaNord 2005) all samples were below the limit of detection as shown in Table 5.

Table 5: Concentrations of siloxanes in sea water from the Oslofjord area.

Sample ID	Location	µg/L						
		D4	D5	D6	MM	MDM	MD2M	MD3M
MR 5003	Bekkelaget	<0.03	<0.02	<0.02	<0.0003	<0.0003	<0.0003	<0.002
MR 5007	Lysaker	<0.03	<0.02	<0.02	<0.0003	<0.0003	<0.0003	<0.002
MR 5269	30B Nesodden	<0.03	<0.02	<0.02	<0.0003	<0.0003	<0.0003	<0.002
MR 5273	36A Færder	<0.03	<0.02	<0.02	<0.0003	<0.0003	<0.0003	<0.002

5.4 Sediment

Six samples of sediments from the Inner Oslofjord were analyzed in this study. The results are shown in Table 6 and Figure 6.

Table 6: Concentrations of siloxanes in sediment from the Oslofjord area.

Sample ID	Location	ng/g dw							
		D4	D5	D6	MM	MDM	MD2M	MD3M	dw %
MR 5005	Bekkelagsbassenget, St BB5	<4	920,0	100,0	<0.2	<0.4	29	54,7	22,7
MR 5006	Bekkelagsbassenget, St BB14	<38	690,0	72,0	<0.2	<0.3	13	21,5	23,6
MR 5008	Lysaker 1	<33	200,0	27,0	<0.2	<0.3	1,8	3,4	32
MR 5009	Lysaker 2	<31	93,0	<17	<0.2	<0.3	0,81	<1.7	41,8
MR 5271	Oslofj A1	<24	250,0	24,0	<0.2	<0.2	<0.2	<1.3	39,8
MR 5272	Oslofj A2	<23	280,0	22,0	<0.2	<0.2	<0.3	<1.3	28,7

d.w.: dry weight

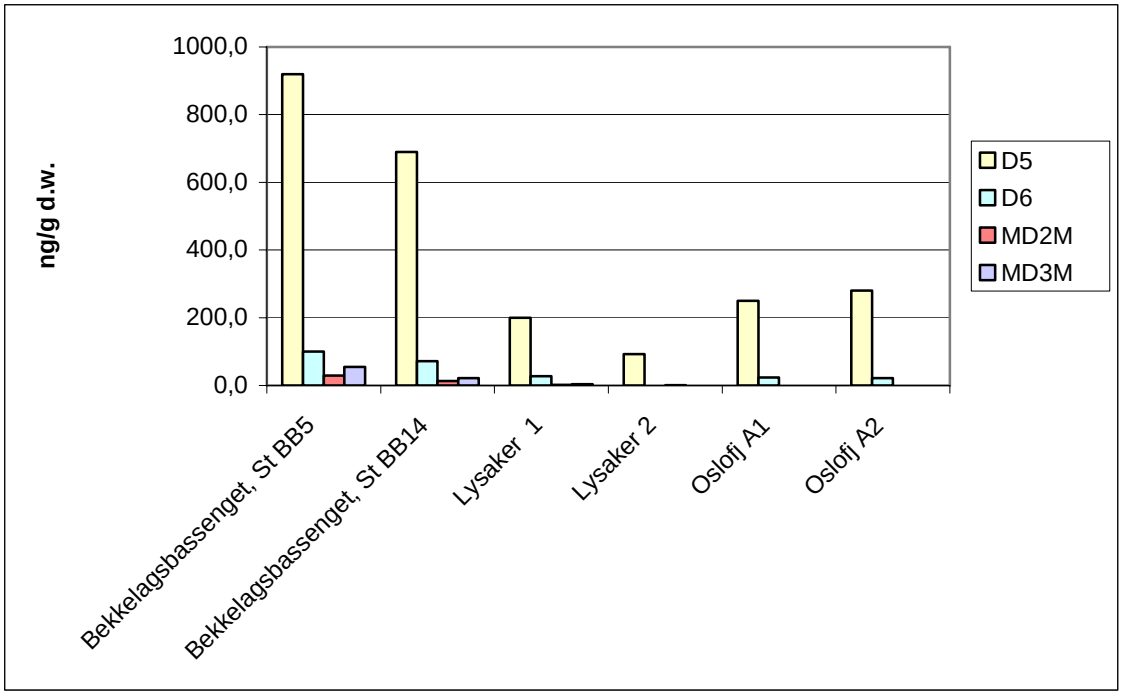


Figure 6: Concentrations of siloxanes in sediment from the Oslofjord area.

The cyclic siloxanes were found in much higher concentrations than the linear analogues. In all samples D5 was dominating. The samples taken close to the Bekkelaget STP showed a considerably higher concentration (D5 690 – 920 ng/g d.w.) than sediment samples from the Stockholm and Helsinki harbour area (D5 77 – 130 ng/g d.w.) measured in the Nordic screening study (TemaNord 2005).

5.5 Biota

In total 11 samples biological samples from Inner and Outer Oslofjord were analyzed. The results are shown in and Figure 8.

Table 7: Concentrations of siloxanes in biological samples from the Oslofjord area in ng/g wet weight.

Sample ID	Location	Matrix	ng/g w.w.						
			D3	D4	D5	D6	MDM	MD2M	MD3M
06/1576	36A Færder	Common mussel	<50	1,9	5,6	1,7	< 0,04	< 0,2	< 0,2
06/1575	30A Gressholmen	Common mussel	<50	2,3	8,7	1,8	< 0,04	< 0,2	< 0,2
06/4014	Ormøya	Common mussel	<50	1,3	3,3	1,3	< 0,04	< 0,2	< 0,2
07/327-1	Frognerkilen	Flounder liver	<50	2,6	27,1	1,4	< 0,04	< 0,2	< 0,2
07/327-2	Frognerkilen	Flounder fillet	<50	1,9	3,4	0,9	< 0,04	< 0,2	< 0,2
06/1527	30B Nesodden	Cod stomach content	53,3	5,0	22,9	1,8	< 0,04	< 0,2	< 0,2
06/1528	30B Nesodden	Cod stomach content	66,6	7,4	85,3	3,3	< 0,04	< 0,2	< 0,2
06/1529	30B Nesodden	Cod stomach content	58,5	9,3	149,3	3,3	< 0,04	< 0,2	< 0,2
06/1530	30B Nesodden	Cod liver	321,3	134,4	1502,5	129,6	< 0,04	1,5	0,8
06/1531	30B Nesodden	Cod liver	152,1	121,4	1490,8	151,5	0,1	2,9	1,0
06/1532	30B Nesodden	Cod liver	58,0	81,2	1978,5	109,1	0,1	2,4	1,5
05/414	30B Nesodden 2004	Cod liver 2004	<50	70,0	2200,0	74,0	<0.3	1,1	<0.5

Table 8: Concentrations of siloxanes in biological samples from the Oslofjord area in ng/g lipid weight.

Sample ID	Location	Matrix	ng/g l.w.							Lipid content
			D3	D4	D5	D6	MDM	MD2M	MD3M	%
06/1576	36A Færder	Common mussel	< 2 200	84,2	244	73,6	< 2	< 9	< 9	2,3
06/1575	30A Gressholmen	Common mussel	< 9 500	439	1 624	339	< 8	< 40	< 40	0,5
06/4014	Ormøya	Common mussel	< 5 100	130	337	132	< 4	< 20	< 20	1,0
07/327-1	Frognerkilen	Flounder liver	< 300	16,2	172	8,84	< 0,3	< 1	< 1	15,8
07/327-2	Frognerkilen	Flounder fillet	< 3 600	139	248	67,3	< 3	< 15	< 15	1,4
06/1527	30B Nesodden	Cod stomach content	2 996	283	1 289	103	< 2	< 12	< 12	1,8
06/1528	30B Nesodden	Cod stomach content	3 331	372	4 269	165	< 2	< 10	< 10	2,0
06/1529	30B Nesodden	Cod stomach content	2 993	474	7 637	167	< 2	< 10	< 10	2,0
06/1530	30B Nesodden	Cod liver	2 054	860	9 607	829	< 0,3	9,68	5,01	15,6
06/1531	30B Nesodden	Cod liver	613	490	6 011	611	0,26	11,5	3,99	24,8
06/1532	30B Nesodden	Cod liver	174	244	5 943	328	0,20	7,11	4,40	33,3

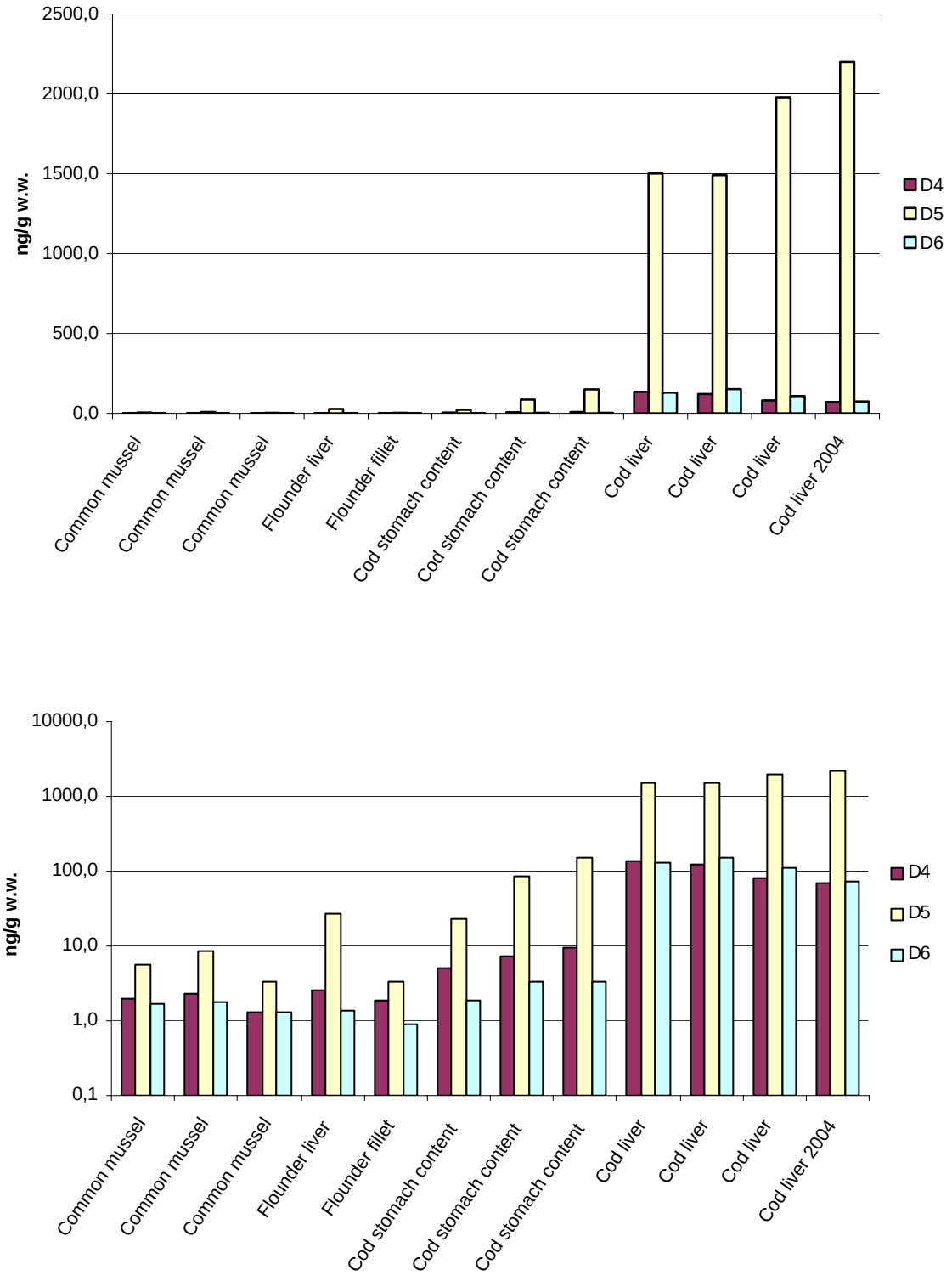


Figure 7: Concentrations of siloxanes in biological samples from the Oslofjord area given in ng/g wet weight shown with linear and logarithmic scale.

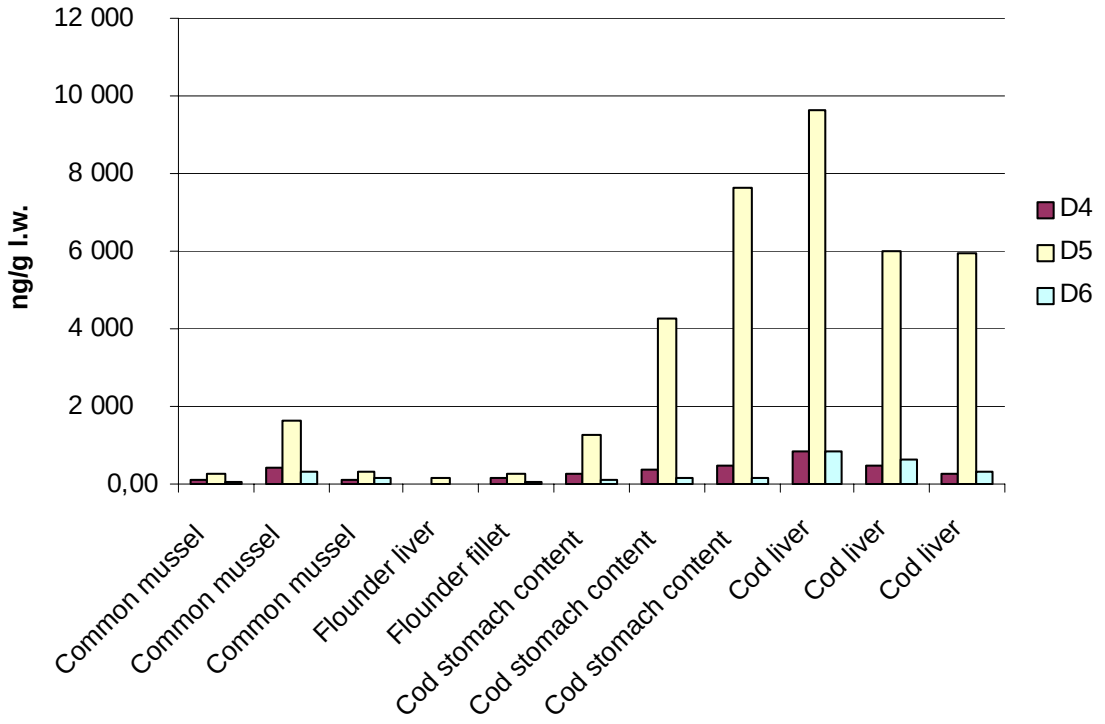


Figure 8: Concentrations of siloxanes in biological samples from the Oslofjord area given in ng/g lipid weight with a linear scale.

In all biological samples the cyclic siloxanes D4, D5, and D6 were detected with D5 as the dominating compound. In cod liver it was also possible to measure the linear siloxanes MDM, MD2M, and MD3M, however, the concentration level was a factor of 1000 lower than for the cyclic analogues (D5 1490 – 2200 ng/g w.w.).

The samples of common mussels together with the sample of flounder fillet showed the lowest concentrations in biota in this study. The concentrations of D4 and D5 in common mussel is very uniform and it is not possible to see any local trend. Common mussels seem to be less contaminated than sediment samples from the same area. Siloxanes are volatile and will vaporise from water. In addition, they have high K_{oc} and are expected to adsorb to particles in water and are likely to be enriched in sediments (HSDB, 2004). Common mussels which are filtering surface water, are therefore likely lesser exposed to siloxanes than sediments and organisms living in deeper water or sediment.

The three different samples of cod liver (pooled samples from 5 fishes each) showed only small variations and were in the same range as the sample from 2004 (TemaNord 2005).

To study biomagnification there were also sampled and analyzed species which were ranked at lower trophic levels: common mussel (D5 3,3 – 5,6 ng/g w.w. or 244 – 1600 ng/ l.w.), flounder (D5 3,4 ng/g w.w. or 250 ng/g l.w. fillet; 27,1 ng/g w.w. or 170 ng/g l.w. liver), and the pooled stomach content of the same cod individuals which were used for pooled liver samples (krill, shrimps, and small crabs) (D5 23 – 150 ng/g w.w. or 1300 – 7600 ng/g l.w.).

Even compared on a lipid weight base cod liver samples are much higher contaminated than species which are on a lower trophic level as common mussel or flounder. To proove that this

contamination is due to biomagnification, that means the increase in concentration of a compound that occurs in the food chain, we also measured the siloxane concentration in the stomach of the same pooled fish samples as the cod liver. However, a comparison based on a lipid weight there is only a slight increase in siloxane concentration from the partially digested food (Average of 3 samples: 4400 ng/g l.w.) to the cod liver (Average of 3 samples: 7200 ng/g l.w.). The great variation in the concentration of the stomach content where one stomach sample has an even higher D5 concentration than the corresponding cod liver sample, do not allow to draw an unequivocal conclusion if there is biomagnification step from the cod feed to the cod liver. However, it is important to recognize that biomagnification cannot be excluded either.

An other, or additional process, explaining the much higher concentration of D5 in cod liver and in the feed of the cod compared to common mussels could be as following: Siloxanes are lipophilic (D5: log K_{ow} = 5,7 (HSDB, 2005)) and volatile compounds. Therefore siloxanes which are emitted to the Oslofjord via sewage water will either already be bound to particles or very soon become bound to particles. In addition the potentially major emission sources (Bekkelaget and VEAS STP) are emitting to the deeper water layers. Furthermore the volatility of siloxanes will cause the siloxanes in surface water to evaporate to the air. Taken together this means that at the bottom of the nearly locked Inner Oslofjord the bioavailable amount of siloxanes should be higher than in surface water. In consequence common mussel, living in surface water, are much less exposed to siloxanes than typical cod feed as crabs, shrimps, and polychaetes.

6. Conclusions

As in the Nordic screening project siloxanes were found in all analyzed matrix with the exception of sea water. The cyclic siloxanes are prevailing in all sample types compared to the linear siloxanes. D5 is the most prominent of the cyclic siloxanes.

The concentration in both sewage water and sludge are in the same range as measured in the Nordic study at different STPs in Nordic countries.

The concentration in sediments from Inner Oslofjord are higher than for most of the urban samples measured in the Nordic study. The highest sediment concentrations were measured close to the outlet of Bekkelaget STP, whereas the other samples taken further away from Bekkelaget STP are much lower but even higher than samples taken in Stockholm and Helsinki area (D5: 58 – 130 ng/g d.w.).

All marine biota from the Inner Oslofjord show measurable concentrations of D4, D5, and D6. In cod liver it was even possible to detect the linear siloxanes MDM, MD2M and MD3M.

In the Nordic screening study a pooled sample of cod liver from Inner Oslofjod showed highly elevated concentrations especially of D5. For that reason new samples of cod liver were taken showing the same level of contamination. The analysis of stomach content taken from the same cod samples showed slightly lower concentrations. In other organisms at a lower trophic level the concentrations were much lower. However, there are too many uncertainties to draw an unequivocal conclusion on biomagnification in the food chain in Inner Oslofjord.

7. References

Flassbeck, D., Pfleiderer, B., Grumping, R. and Hirner, A.V. (2001) Determination of low molecular weight silicones in plasma and blood of women after exposure to silicone breast implants by GC/MS. *Anal. Chem., 73*, 606-611.

Flassbeck, D., Pfleiderer, B., Klemens, P., Heumann, K.G., Eltze, E. and Hirner, A.V. (2003) Determination of siloxanes, silicon, and platinum in tissues of women with silicone gel-filled implants. *Anal. Bioanal. Chem., 375*, 356-362.

Kala, S.V., Lykissa, E.D.and Lebovitz, R.M. (1997) Detection and characterization of poly(dimethylsiloxane)s in biological tissues by GC/AED and GC/MS. *Anal. Chem., 69*, 1267-1272.

Kala, S.V., Lykissa, E.D., Neely M.W. and Lieberman, M.W. (1998) Low molecular weight silicones are widely distributed after a single subcutaneous injection in mice. *Am. J. Pathol., 152*, 645-649.

Nordic Council of Ministers (2005) Siloxanes in the Nordic environment. Copenhagen (TemaNord 2005:593).
URL: http://www.norden.org/pub/miljo/miljo/uk/TN2005593.pdf [22.06.2007]

Varaprath, S., Seaton, M., McNett, D., Cao, L. and Plotzke, K.P. (2000) Quantitative determination of octamethylcyclotetrasiloxane (D-4) in extracts of biological matrices by gas chromatography-mass spectrometry. *Internat. J. Environ. Anal. Chem., 77*, 203-219.

Appendix

The stomach volume content of pooled samples, of five atlantic cod stomachs in each, were analysed. The stomach volume content was described on a subjective scale from 0 to 5:

0: empty
1: trace
2: small amount
3: moderate
4: full, but not packed
5: packed

The cod stomachs contained digested remains, shrimps, krill, crabs claws, fish larvae, brittle star remains, pearls and otoliths. One cod stomach was empty. The results are shown in Table 9.

Table 9: Results from cod stomach dissection.

Bulked sample no.	Fish no.	Average fish length (cm)	Average fish weight (g)	Average stomach content (g)	Average stomach volume content (0-5)	Total stomach content
1	1,2,3,4,5	38,36	509,4	43,4	1,8	60 % digested remains 25% shrimps 15 % krill
2	6,7,8,9, 10	44,46	832,6	163,9	3,6	60 % shrimps 22 % digested remains 14 % krill 4 % crabs claw
3	11,12,13, 14,15	41,84	732,6	63,0	2,4	30 % digested remains 30 % krill 20 % empty 17 % shrimps 2 % brittle star remains 1 % fish larvae 2 small pearls 2 otoliths

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TITLE

Siloxanes in the Environment of the Inner Oslofjord

ABSTRACT

In order to confirm the high concentrations of cyclic siloxanes measured in cod liver from Inner Oslofjord and to gain a broader overview on the siloxane contamination of the Inner Oslofjord new samples of sewage water and sludge, sea water, sediments and biota were taken. As in the Nordic screening project siloxanes were found in all analyzed matrix with the exception of sea water. The concentration in sediments from Inner Oslofjord are higher than for most of the urban samples measured in the Nordic study. All marine biota from the Inner Oslofjord show measurable concentrations of cyclic siloxanes. In the Nordic screening study a pooled sample of cod liver from Inner Oslofjod showed highly elevated concentrations especially of D5. New samples of cod liver were taken showing the same level of contamination. The analysis of stomach content taken from the same cod samples showed slightly lower concentrations, in other organisms at a lower trophic level the concentrations were much lower.

** Kategorier:*
- *A Åpen - kan bestilles fra NILU*
- *B Begrenset distribusjon*
- *C Kan ikke utleveres*

Statlig program for forurensningsovervåking omfatter overvåking av forurensningsforholdene i luft og nedbør, skog, grunnvann, vassdrag, fjorder og havområder.

Overvåkingsprogrammet dekker langsiktige undersøkelser av:

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Overvåkingsprogrammet skal gi informasjon om tilstanden og utviklingen av forurensningssituasjonen, og påvise eventuell uheldig utvikling på et tidlig tidspunkt. Programmet skal dekke myndighetenes informasjonsbehov om forurensningsforholdene, registrere virkningen av iverksatte tiltak for å redusere forurensningen, og danne grunnlag for vurdering av nye tiltak. SFT er ansvarlig for gjennomføringen av overvåkingsprogrammet.

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