



## Oslo fjord

Investigation of chemicals released from the Malmøkalven dumping area.

Polychlorinated naphthalenes

ExposMeter AB
Tavelsjö
2007 08 28
Project report 2006N-002

## Investigation of chemicals released from Malmøkalven dumping area. Polychlorinated naphthalenes

#### Investigation of chemicals released from Malmøkalven dumping area.

#### **Polychlorinated naphthalenes**

Project report 2006N-002

ExposMeter AB Tavelsjö 2007 08 28

Per-Anders Bergqvist, PhD, and Audrone Zaliauskiene, TechD, ExposMeter AB.

GIS-preparation: Ecovision Nord, **Ola Löfgren PhD**.

Copyright © ExposMeter AB, Tavelsjö, Sweden.

Without limiting the rights under copyright reserved above, no part of this publication may be reproduced, stored in or introduced into a retrieval system, or transmitted, in any form, or by any means (electronic, mechanical, photocopying, recording or otherwise), without the prior written permission of the copyright owner.



#### **Definitions**

The following terms and definitions are used in this report:

- Hydrophobic organic compounds compounds that are only slightly soluble in water and soluble in lipids. Hydrophobic molecules have no charge and repel water.
- ExposMeter Hydrophobic Device (EHD) –Standard Semipermeable Membrane

  Device (Standard SPMD) supplied by ExposMeter AB'
- ExposMeter Metal Device Standard Diffusive Gradient in Thin film Device (DGT) supplied by ExposMeter AB
- Standard SPMD 2.5 cm wide (layflat) by 92 cm long LDPE tube, with a 70-95 μm thick wall and ca. 450 cm² or 100 cm² surface area per g SPMD, containing 1 mL (0.915 g) of triolein as a thin film.
- *LDPE* specially prepared low density polyethylene, produced as layflat tubes with no additive, used for EHDs.
- Field control EHD quality control EHD to record any chemicals accumulated in sampling devices during their production, transportation, deployment, retrieval and analysis.

## Investigation of chemicals released from Malmøkalven dumping area. Polychlorinated naphthalenes

Performance reference compounds (PRCs) - compounds added ('spiked') to the triolein in the laboratory when EHDs are assembled that have low to moderate fugacity from them, and do not interfere with the sampling and analytical processes.

*Target Compound(s)* - compounds specifically sampled and analyzed in the study.



### **Contents**

DEFINITIONS	
CONTENTS	5
LEGENDS	
LIST OF TABLES	
SUMMARY	9
INTRODUCTION	11
METHOD DESCRIPTION	
SAMPLING METHODOLOGY	
RESULTS	
PCNS AMOUNTS AT DIFFERENT SITES	
REFERENCES	54



## Legends

FIGURE 1 MAP OF INNER OSLO FJORD. (FROM "KONSEKVENSUTREDNING" 2001, OSLO COMMUNE)	
FIGURE 2. SAMPLING PLACES IN OSLO FJORD DURING THE PERIOD 30.10 – 12.12 2006.	
FIGURE 3. STANDARD SPMD CONFIGURATION BEFORE DEPLOYMENT. A 92 CM MEMBRANE IS APPI	LIED TO
THE STAINLESS STEEL SPIDER BEFORE PLACEMENT IN THE PROTECTIVE STAINLESS STEEL DE	<b>VICE.</b> 17
FIGURE 4. COMMERCIALLY AVAILABLE STAINLESS STEEL SPMD DEPLOYMENT APPARATUS: ON T	HE
PICTURE IS A PROTECTIVE STAINLESS STEEL CAGE FOR FIVE SPMD SPIDERS ATTACHED TO R	OPES
FOR BEING SUBMERGED INTO THE OSLO FJORD.	
FIGURE 5. DEPLOYMENT IN WATER OF PROTECTIVE CAGE WITH SPMDs INSIDE. HEAVY ANCHOR	
BOTTOM AND FLOATING DEVICES LIFTING THE ROPE TO THE SURFACE. **	
FIGURE 6. EXAMPLE ON EHD MEMBRANE RETRIEVED FROM THE OSLO FJORD AFTER 21 DAYS OF	
EXPOSURE.	20
FIGURE 7. SCHEMATIC REPRESENTATION OF SPMD TREATMENT.	
FIGURE 8. SUM OF ALL PCNs SAMPLED IN PERIOD 1 AT THE DIFFERENT SITES, PG/L	
FIGURE 9. SUM OF ALL PCNs SAMPLED IN PERIOD 2 AT THE DIFFERENT SITES, PG/L	
FIGURE 10. SUM OF PCN FOR EACH CONGENER GROUP SAMPLED IN PERIOD 1 AT THE DIFFERENT S	
PG/L	
FIGURE 11. SUM OF PCN FOR EACH CONGENER GROUP SAMPLED IN PERIOD 2 AT THE DIFFERENT S	
PG/L	
FIGURE 12. DI-, TRI-PCN IN PERIOD 1 FROM DIFFERENT SITES IN THE OSLO FJORD STUDY, PG/L	
FIGURE 13. DI-, TRI- PCN IN PERIOD 2 FROM DIFFERENT SITES IN THE OSLO FJORD STUDY, PG/L	
FIGURE 14. TETRA-, PENTA-, HEXA- PCN IN PERIOD 1 FROM DIFFERENT SITES IN THE OSLO FJORD	
PG/L.	
FIGURE 15. TETRA-, PENTA-, HEXA- PCN IN PERIOD 2 FROM DIFFERENT SITES IN THE OSLO FJORD	
PG/L	
FIGURE 16 VARIATION OF SALINITY AT 25 METER FROM SEA BOTTOM.	
FIGURE 17 VARIATION OF SALINITY AT DIFFERENT DEPTHS DURING THE STUDY	
FIGURE 18 SALINITY PROFILE AT SITE 05, FROM SURFACE TO BOTTOM AT FOUR DIFFERENT DATES DURI	
TWO SAMPLING PERIODS.	
FIGURE 19 SALINITY PROFILE AT SITE 07, FROM SURFACE TO BOTTOM AT FOUR DIFFERENT DATES DURI	
TWO SAMPLING PERIODS.	
FIGURE 20. SALINITY PROFILE AT SITE 12, FROM SURFACE TO BOTTOM AT FOUR DIFFERENT DATES DURI	ING THE
TWO SAMPLING PERIODS.	
FIGURE 21. TEMPERATURE PROFILE AT SITE 05, FROM SURFACE TO BOTTOM AT FOUR DIFFERENT DATES	
DURING THE TWO SAMPLING PERIODS.	
FIGURE 22. TEMPERATURE PROFILE AT SITE 12, FROM SURFACE TO BOTTOM AT FOUR DIFFERENT I	DATES
DURING THE TWO SAMPLING PERIODS.	
FIGURE 23 TEMPERATURE PROFILE AT SITE 07, FROM SURFACE TO BOTTOM AT FOUR DIFFERENT D	DATES
DURING THE TWO SAMPLING PERIODS.	
FIGURE 24. MAP SHOWING SUM OF PCN WATER CONCENTRATIONS AT 3 METER FROM THE BOTTO	
THE INNER OSLO FJORD AND ESPECIALLY AROUND THE MALMØKALVEN DUMPING AREA FRO	M THE
FIRST SAMPLING PERIOD.	
FIGURE 25. MAP SHOWING SUM OF PCN WATER CONCENTRATIONS AT 10 METER FROM THE BOTTO	
THE INNER OSLO FJORD AND ESPECIALLY AROUND THE MALMØKALVEN DUMPING AREA FRO	
FIRST SAMPLING PERIOD.	
FIGURE 26. MAP SHOWING SUM OF PCN WATER CONCENTRATIONS AT 25 METER FROM THE BOTT	
THE INNER OSLO FJORD AND ESPECIALLY AROUND THE MALMØKALVEN DUMPING AREA FRO	
FIRST SAMPLING PERIOD	43



## Investigation of chemicals released from Malmøkalven dumping area. Polychlorinated naphthalenes

FIGURE 27. MAP SHOWING SUM OF PCN WATER CONCENTRATIONS AT 40 METER FROM THE BOTTOM IN
THE INNER OSLO FJORD AND ESPECIALLY AROUND THE MALMØKALVEN DUMPING AREA FROM THE
FIRST SAMPLING PERIOD. 44
FIGURE 28. MAP SHOWING SUM OF PCN WATER CONCENTRATION AT 3 METER FROM THE BOTTOM IN THE
INNER OSLO FJORD AND ESPECIALLY AROUND THE MALMØKALVEN DUMPING AREA FROM THE
SECOND SAMPLING PERIOD. 45
FIGURE 29. MAP SHOWING SUM OF PCN WATER CONCENTRATIONS AT 10 METER FROM THE BOTTOM IN
THE INNER OSLO FJORD AND ESPECIALLY AROUND THE MALMØKALVEN DUMPING AREA FROM THE
SECOND SAMPLING PERIOD. 46
FIGURE 30. MAP SHOWING SUM OF PCN WATER CONCENTRATIONS AT 25 METER FROM THE BOTTOM IN
THE INNER OSLO FJORD AND ESPECIALLY AROUND THE MALMØKALVEN DUMPING AREA FROM THE
SECOND SAMPLING PERIOD. 47
FIGURE 31. MAP SHOWING SUM OF PCN WATER CONCENTRATIONS AT 40 METER FROM THE BOTTOM IN
THE INNER OSLO FJORD AND ESPECIALLY AROUND THE MALMØKALVEN DUMPING AREA FROM THE
SECOND SAMPLING PERIOD. IT IS WRONG TEXT INSIDE FIGURE 24, SINCE THE DISTANCE FROM
BOTTOM IS 40M. 48
FIGURE 32. T1/T2 SCATTER PLOT OF ALL PCN DATA FROM THE FIRST SAMPLING PERIOD
FIGURE 33, P1/P2 SCATTER PLOT OF ALL PCN DATA FROM THE FIRST SAMPLING PERIOD.
FIGURE 34. T1/T2 SCATTER PLOT OF ALL PCN DATA FROM THE SECOND SAMPLING PERIOD
FIGURE 35, P1/P2 SCATTER PLOT OF ALL PCN DATA FROM THE SECOND SAMPLING PERIOD,

## Investigation of chemicals released from Malmøkalven dumping area. Polychlorinated naphthalenes

### **List of Tables**

TABLE 1. PCNS ANALYZED IN THE EHD EXTRACTS.	. 23
TADI E 2. SAMDI INC CITEC AND CAMDI INC TIMEC DIDING THE TWO CAMDI INC DEDICDS ADE DESCRIPED	2/



### Summary

During autumn 2006 ExposMeter AB was asked by the Neptun foundation in Norway to investigate pollutants in the vicinity of a deep-water dumping ground near Malmøkalven in Oslo fjord, where excavated sediments are being pumped to the bottom. The task assigned was to:

- 1. investigate whether chemicals are migrating from dumping of sediment material, to the surrounding environment outside the (of SFT) marked dumping area.
- 2. The investigation was to start as soon as possible.

The conclusions would be solely ExposMeter AB's opinions. However, Neptun encouraged the publication of any results obtained in open scientific literature and gave ExposMeter AB full rights to do so.

The ExposMeter Hydrophobic passive samplers used in the study "only" sample truly dissolved compounds in the investigated water. Thus, all of the measured concentrations of the analyzed compounds are readily available for bioaccumulation in biota and might been released from the sediment particles during the remediation process and thus increased their toxic potency.

## Investigation of chemicals released from Malmøkalven dumping area. Polychlorinated naphthalenes

#### The investigation has shown that:

- 1. Elevated levels of PCNs are found outside the (of SFT marked) dumping area.
- 2. The levels decrease with the distance from the dumping area.
- 3. Elevated levels of PCN are found at one sampling period from bottom up to 40 meters above sea bottom close to the dumping area. This is based on one sample and one analysis, since it is outside the scope of this investigation to study this question
- 4. The PCN "fingerprint" close to dumping area resembles the pattern that was identified in Oslo harbor close to the excavating activities. Samples taken close to dumping area showed the closest agreement.
- 5. The PCN concentration were approximately 3 times lower than the PCB concentration

This report is the second in a series describing different compounds spreading around the Malmøkalven dumping area.



#### Introduction

Two kinds of passive monitors – ExposMeter Hydrophobic Devices (EHDs, based on SPMD technology) and ExposMeter Metal Devices (EMDs, based on DGT technology), were used to detect chemicals in and transported from the dumping area. The devices are easy to install, they require no battery or other electricity supply, and they can provide both 21-day time-weighted average values of the concentrations of individual dissolved chemical compounds and indications of the integrated toxicity of pollutants in the sampled water. Since they monitor dissolved concentrations, EHDs have advantages over devices that measure particles in the water (turbidity) as indicators of spreading pollution, since they can detect specific compounds and provide information on mixtures/fingerprints of pollutants. During the sampling no metabolism or other sort of transformation of the chemicals occurs of the sampled compounds and the sampling is not generally affected by pollution levels or water conditions. Provided appropriate sampling locations are selected and the subsequent chemical analysis is reliable, EHDs can also indicate likely pollution sources and serve as efficient tools for risk assessment.

Results from the analysis of EHD extracts with performance reference compounds allow time-weighted average concentrations (TWAs) of pollutants in the sampled water throughout the deployment time to be calculated. EHDs are usually deployed for 3-4 weeks. Longer deployment times lead to the equilibrium sampling of more and more compounds by the samplers, and hence should be avoided since, according to theory regarding the uptake of pollutants by EHDs described by Huckins et al. (2002) integrated



water concentrations can only be calculated for compounds for which uptake is still in the kinetic phase at the end of the sampling period. We have combined two deployments following one after each other which gave us the knowledge about TWA concentrations of the investigated compounds in the sampled waters spanning the period from October 30 until December 12 2006.

In addition to sampling in the vicinity of the dumping area (near Malmøkalven), we also sampled water close to the area (Bjørvika) in which the excavated sediment is being extracted, to obtain "fingerprints" of the pollutants to facilitate tracing of the origin of the water pollution (see figure 1). Since public concern has been expressed about the possible effects of the dumping in the vicinities of Hovedøya and Akers brugge, samples were collected at these sites during the sampling campaign to assess whether or not there was valid cause for alarm. The data from these two sites is not directly involved in this investigation and thus scarcely mentioned below.

The following considerations were applied in the design of the sampling program:

- sampling points were chosen at various depths, the lowest 3 m from the bottom of the fjord;
- monitors were deployed at sites with bottom water flows;
- sampling points were selected that would provide information on possible gradients of pollutants spreading from the dumping area;



- monitors were placed near the sediment excavation area to obtain a pollution fingerprint
- the scope for obtaining information on the influence of other possible sources of pollution were also considered when deployment locations were selected

The map describing the bottom situation in the area is presented in figure 1.



FIGURE 1 MAP OF INNER OSLO FJORD. (FROM "KONSEKVENSUTREDNING" 2001, OSLO COMMUNE)



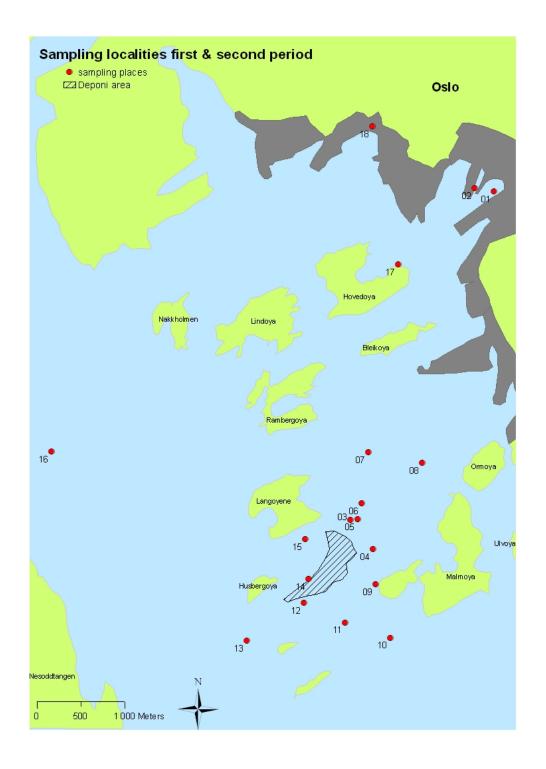


Figure 2. Sampling places in Oslo Fjord during the period  $30.10-12.12\,2006$ .



### **Method description**

Since they were first described in the scientific literature two decades ago, passive monitors have become globally accepted, standardized devices for:

- screening for the presence of pollutants
- monitoring temporal and spatial pollution trends
- toxicity assessments
- investigative monitoring

SPMDs (also known as EHDs) are the most comprehensively established types of passive monitor for hydrophobic organic compounds ( $\lg K_{ow} > 3$ ). Theoretical and empirical aspects of their use have been discussed in over 200 scientific publications, and they have been deployed in hundreds of field applications.

Standard SPMDs are designed to sequester and concentrate bioavailable dissolved aqueous-phase hydrophobic organic contaminants (HOCs) with 3<logK<sub>ow</sub><8 and molecular masses lower than ca. 600 Daltons such as polyaromatic hydrocarbons (PAHs), non-polar pesticides, polychlorinated biphenyls (PCB), polychlorinated naphthalenes PCN), polychlorinated dibenzofurans, polychlorinated dibenzodioxins, polybrominated diphenyl ethers, polychlorinated benzenes, and alkyl phenols (nonyl phenols).



Standard commercially available SPMDs (EHDs) are modelled on the original USGS (United States Geological Service) design. Use of a standard SPMD design ensures that published sampling rate calibration data and theory can be used to estimate the ambient water concentrations of analytes from the data acquired. Furthermore, the data obtained in different studies can be readily compared, since the standard configuration is used in most SPMD applications globally (Figure 2). The ExposMeter Hydrophobic device (EHD) used in this study is modelled on the original design.

#### Sampling methodology

EHDs are transported to the field in air tight-cans. The cans are opened and the SPMD is exposed to the air just before deployment in the water. The time in air should be minimized and exposure of the SPMD to UV light should be avoided. A stainless steel protective device, consisting of spiders for mounting the EHDs (figure 3) and a protective cage that prevents mechanical damage to the membranes, is used for deploying EHDs in the water (Figure 4).





FIGURE 3. STANDARD SPMD CONFIGURATION BEFORE DEPLOYMENT. A 92 CM MEMBRANE IS APPLIED TO THE STAINLESS STEEL SPIDER BEFORE PLACEMENT IN THE PROTECTIVE STAINLESS STEEL DEVICE.



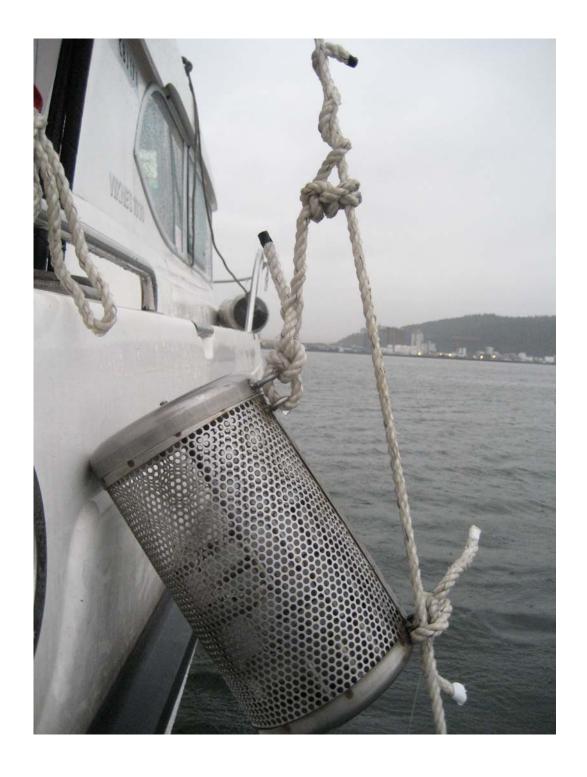


FIGURE 4. COMMERCIALLY AVAILABLE STAINLESS STEEL SPMD DEPLOYMENT APPARATUS: ON THE PICTURE IS A PROTECTIVE STAINLESS STEEL CAGE FOR FIVE SPMD SPIDERS ATTACHED TO ROPES FOR BEING SUBMERGED INTO THE OSLO FJORD.



To keep the devices in place during the sampling period a heavy anchor and buoy, connected by a rope, are used which keep them in position and mark their location. EHDs can be attached to the rope at specific, selected depths. A schematic diagram of an EHD device deployed in Oslo fjord is presented in Figure 5.

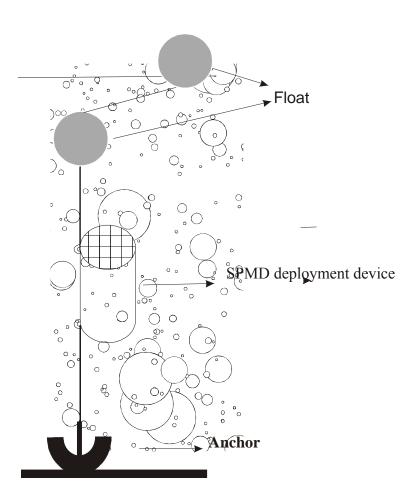


FIGURE 5. DEPLOYMENT IN WATER OF PROTECTIVE CAGE WITH SPMDs INSIDE. HEAVY ANCHOR ON THE BOTTOM AND FLOATING DEVICES LIFTING THE ROPE TO THE SURFACE. \*\*



After 21 days deployment, the samplers were retrieved and the membranes were replaced in their airtight tin cans. During this time, the membranes were protected from sunlight and both water and fouling (external biotic material or other material attached to the outer surface of the membrane) on the surface of the membrane was gently removed physically. An example of a retrieved membrane is shown in figure 6.



FIGURE 6. EXAMPLE ON EHD MEMBRANE RETRIEVED FROM THE OSLO FJORD AFTER 21 DAYS OF EXPOSURE.



### Analysis of compounds

Analyses of the compounds accumulated by the SPMDS were performed in a laboratory accredited for analysis of SPMD samples targeting many different compounds. As yet, official accreditation for calculating water dissolved concentrations is not available, but there are plans to include this essential part of monitoring programs in the accreditation scheme in the near future. Compounds analyzed in the second stage of the analysis are listed in Table 1.

Briefly, the analytical procedures were as follows. The outer surfaces of the retrieved membranes were gently physically and chemically cleaned. The target compounds were transferred to the solvent by dialysis for 40-72 hours. Appropriate labelled compounds were added to the dialysate for quality control and quantification purposes. After concentration of the dialysate, the compounds were cleaned using appropriate liquid chromatography columns. The samples were again concentrated and labelled recovery standards were added to adjust for losses during cleanup.

The target compounds were then analyzed using a Finnigan ion trap HRGC/LRMS in MS/MS mode. Individual response factors for each of the quantified compounds were applied and the results were then corrected for blank levels and adjusted for recovery values. Performance reference compounds were analyzed in three separate field control samples (as well as in all samples) and appropriate conversion factors were derived from



mean values obtained in the three analyses to calculate water concentrations of the target analytes. The formulas for calculations were (from Huckins et al. 2006):

$$C_{w} = \frac{N}{V_{s} \cdot K_{sw} \left(1 - \exp\left(-\frac{R_{s} \cdot t}{V_{s} \cdot K_{sw}}\right)\right)} [ng \cdot L^{-1}]$$

A simplified graphical representation of the main analytical steps is presented in figure 7.



FIGURE 7. SCHEMATIC REPRESENTATION OF SPMD TREATMENT



#### TABLE 1. PCNs analyzed in the EHD extracts.

1+2MonoCN	1467TetraCN	12478PentaCN		
14+16+15+27DiCN	1368+1256TetraCN	12358PentaCN		
26+17DiCN	1235+1358TetraCN	12458PentaCN		
12DiCN	1237+1234+1267TetraCN	12345PentaCN		
136TriCN	1245TetraCN	12378PentaCN		
146TriCN	1248TetraCN	123467+123567HexaCN		
125TriCN	1268TetraCN	123457+123568HexaCN		
126TriCN	1458TetraCN	123578HexaCN		
127TriCN	12357+12467PentaCN	124568+124578HexaCN		
123TriCN	12457PentaCN	123456HexaCN		
145TriCN	12468PentaCN	123458HexaCN		
1357TetraCN	12346+12356			
1257+1246+1247TetraCN	12456PentaCN			

One way to present the data, in order to visualize relationships between samples from different locations, is to use PCA (Principal Component Analysis)-based statistical analysis and presentation). In this statistical approach the patterns of all analyzed and quantified compounds at all locations are simultaneously compared, and the data are "projected" from a multidimensional space to a two-dimensional plane, allowing the patterns to be visualized on paper, or other two-dimensional display medium (e.g. a computer screen). The original data were auto scaled, the variables were mean centered and scaled to unit variance. Sampling sites are described in table 2.



TABLE 2. SAMPLING SITES AND SAMPLING TIMES DURING THE TWO SAMPLING PERIODS ARE DESCRIBED.

Site number	GIS cool	rdinates	Depth	Sampling I		Sampling II	
				start	end	start	end
01	6653622	1217614	nm	30.10.2006	21.11.2006	21.11.2006	11.12.2006
02	6653661	1217396	nm	30.10.2006	21.11.2006	21.11.2006	16.12.2006
03	6649850	1215969	60	31.10.2006	22.11.2006	22.11.2006	12.12.2006
04	6649512	1216225	66.6	31.10.2006	27.11.2006	28.11.2006	11.12.2006
05	6649855	1216056	66	31.10.2006	27.11.2006	27.11.2006	12.12.2006
06	6650034	1216100	63.7	30.10.2006	21.11.2006	21.11.2006	12.12.2006
07	6650623	1216172	65.7	30.10.2006	22.11.2006	22.11.2006	12.12.2006
08	6650499	1216790	61.8	30.10.2006	22.11.2006	22.11.2006	11.12.2006
09	6649109	1216261	49.3	30.10.2006	21.11.2006	21.11.2006	11.12.2006
10	6648493	1216424	69.9	30.10.2006	21.11.2006	21.11.2006	11.12.2006
11	6648668	1215910	31.1	30.10.2006	21.11.2006	21.11.2006	11.12.2006
12	6648896	1215435	63.9	30.10.2006	21.11.2006	21.11.2006	11.12.2006
13	6648458	1214782	62.0	30.10.2006	21.11.2006	21.11.2006	11.12.2006
14	6649087	1215541	55.9	30.10.2006	lost	28.11.2006	11.12.2006
15	6649625	1215453	46.7	30.10.2006	21.11.2006	21.11.2006	lost
16	6650631	1212541	41.4	30.10.2006	21.11.2006	21.11.2006	11.12.2006
17	6652781	1216516	nm	31.10.2006	21.11.2006	21.11.2006	11.12.2006
18	6654368	1216222	nm	nd	nd	22.11.2006	11.12.2006
nm not		·					·

nm - not measured nd - not

deployed



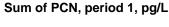
#### **Results**

The results from the PCN investigation are clear and show an elevated concentration in the vicinity of the dumping area. In order of simplifying the interpretation of the results we will visualize them in three ways. First the levels of the sum of PCN congeners is shown, then the distribution of PCNs around the Oslo fjord is shown on maps and finally the relationship in "finger prints" between the different sampling locations.

#### PCNs amounts at different sites

The highest levels were usually found at site 2, which is Bjørvika, and this sampler were very close to the excavation operation leading to that a extremely turbid water were sampled. This sample should be considered as an exception and therefore we also have the other sampler in Bjørvika at site 1. I figure 8 the levels at site 1 are 1300 pg/L and all other sites has levels below 250 pg/L. During the second sampling period the overall levels is similar as during the first sampling period except that site 2 is lower compared to the first period. The lower levels at site 2 during second period might be due to differences in the excavation activity or active location.





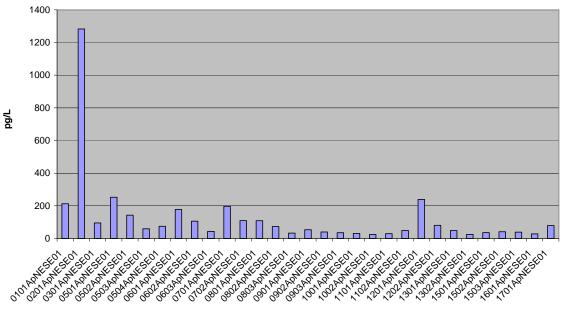
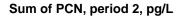


Figure 8. Sum of all PCNs sampled in period 1 at the different sites, pg/L



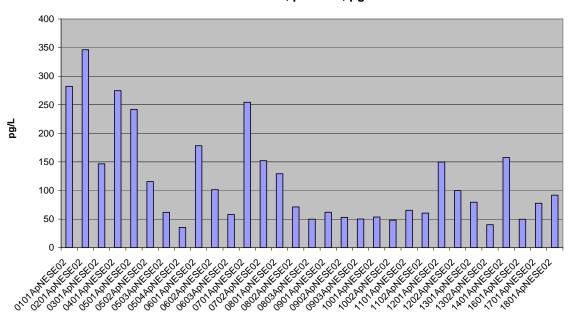


Figure 9. Sum of all PCNs sampled in period 2 at the different sites, pg/L



The sum of each congener group of PCN is shown in figure 10 and 11. All congener groups are the highest in sample from site 2, both at first and second sampling period.

During the first sampling period (but not during second sampling period) mono chlorinated PCNs are especially elevated at site 2, suggesting that during this time an area with a fresh PCN source were excavated. This could be studied further since the analysis of Mono-PCN is little more unstable than the rest of the congener groups.

The overall concentrations are similar between the two sampling periods, except for site 2.

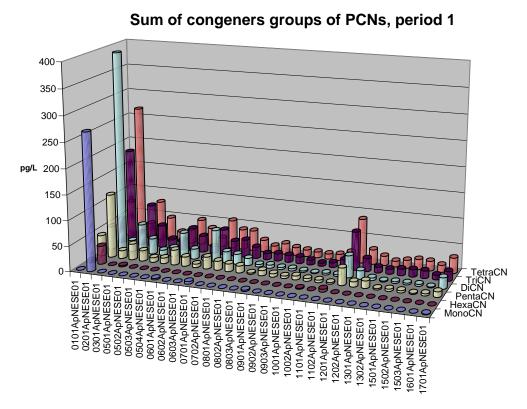


Figure 10. Sum of PCN for each congener group sampled in period 1 at the different sites, pg/L



# Sum of congeners groups of PCNs, period 2

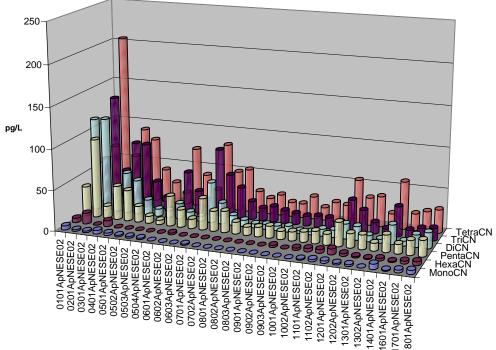


Figure 11. Sum of PCN for each congener group sampled in period 2 at the different sites, pg/L

Di and tri- chlorinated PCNs are presented in figure 12 and 13.



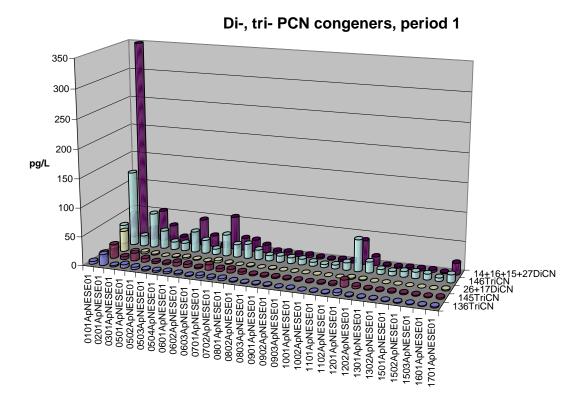


FIGURE 12. DI-, TRI-PCN IN PERIOD 1 FROM DIFFERENT SITES IN THE OSLO FJORD STUDY, PG/L.



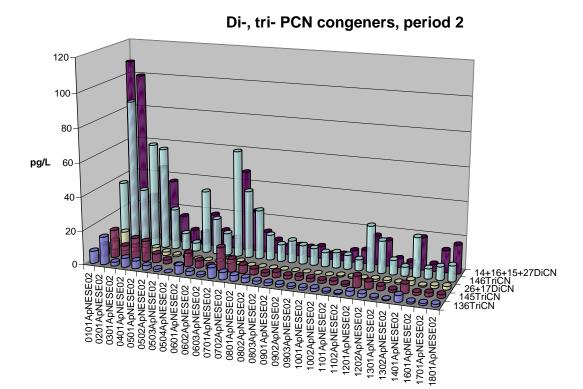


Figure 13. Di-, Tri- PCN in period 2 from different sites in the Oslo fjord study, pg/L.

Tetra, penta and hexa-chlorinated PCNs are presented in figure 14 and 15.



### tetra-, penta-, hexa- PCN congeners, period 1

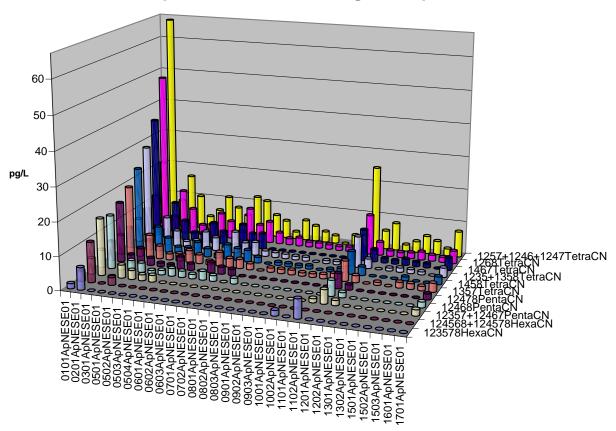


Figure 14. Tetra-, penta-, hexa- PCN in period 1 from different sites in the Oslo fjord study, Pg/L.



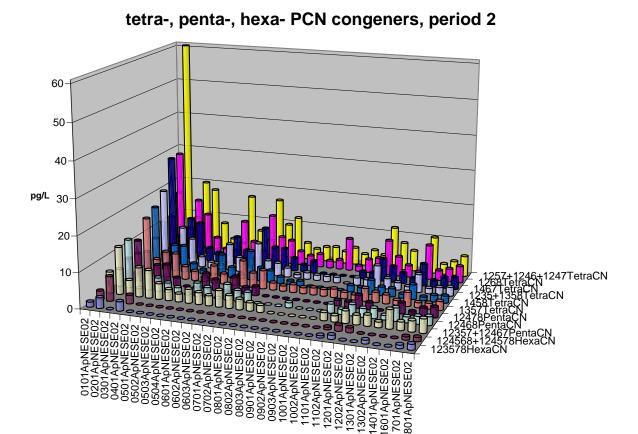


FIGURE 15. TETRA-, PENTA-, HEXA- PCN IN PERIOD 2 FROM DIFFERENT SITES IN THE OSLO FJORD STUDY, PG/L.

### Water mixing

The spread of pollutants in water is affected by mixing processes in the water, for obvious reasons, so these processes need to be considered in a monitoring program such as this. The currents in the area where the "deep sea" dumping is taking place are complex and not easy to describe. Between the islands the current shifts for many different reasons, and the bottom current has measured velocities of ca. 2 cm/second in the area. Variations in

## Investigation of chemicals released from Malmøkalven dumping area. Polychlorinated naphthalenes

salinity with depth can also affect mixing and pollutant dispersal parameters, and they are affected by various factors (including sea currents, river runoff and wind). Therefore, salinity profiles were obtained in both of the sampling periods. The mixing areas 25 meters from the sea bottom can be seen in figure 16, where the darker areas show larger changes in salinity during our study. In the northern part of the study area the sea seems to be fairly stable and mixing appears to be minor, suggesting that there may have been a steady northward flow north in this area during the study.

In figure 16 the variations in salinity at and between several depths are shown (some of which are substantial). Three sites (5, 7 12) are chosen to represent the area (data for up to 30 sites in the area exist in file) for depths profiles of salinity and are presented in figures 18, 19, 20.



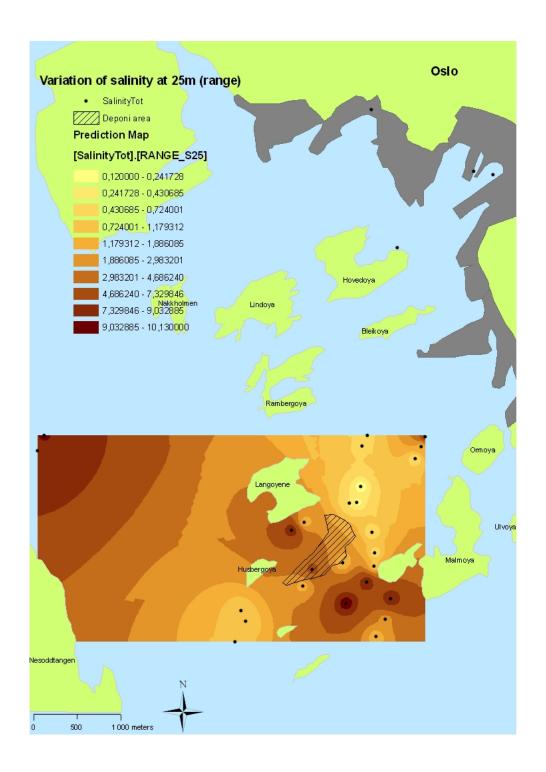


Figure 16 Variation of salinity at 25 meter from sea bottom.



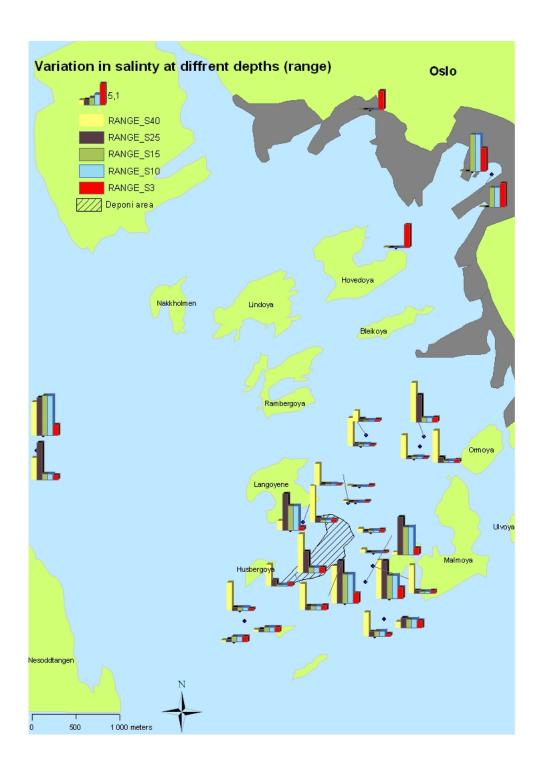
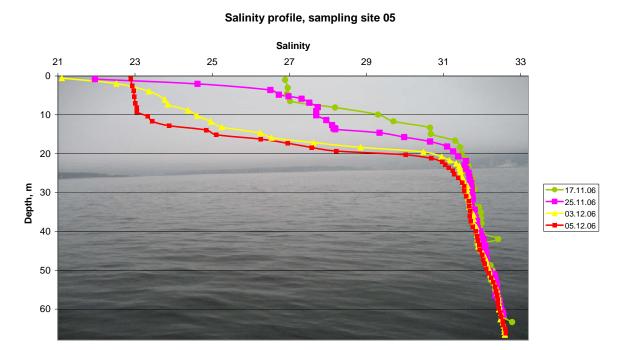
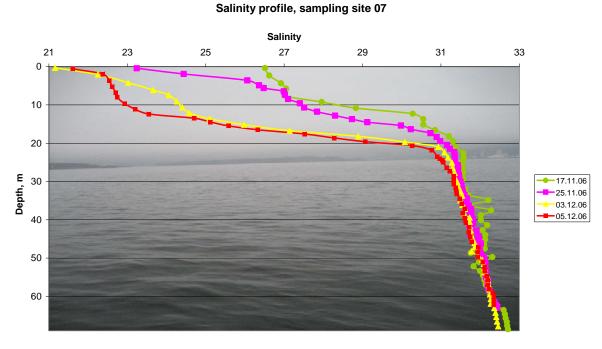


Figure 17 Variation of salinity at different depths during the study.



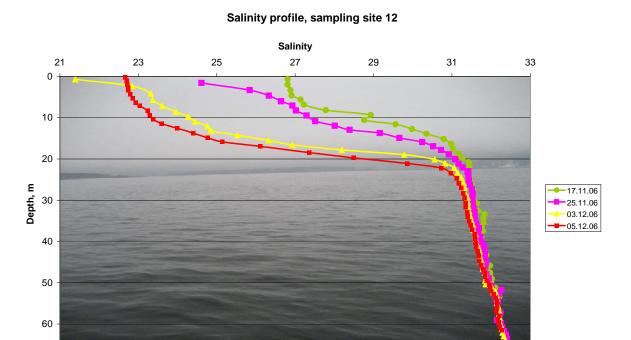


**Figure 18** Salinity profile at site 05, from surface to bottom at four different dates during the two sampling periods.



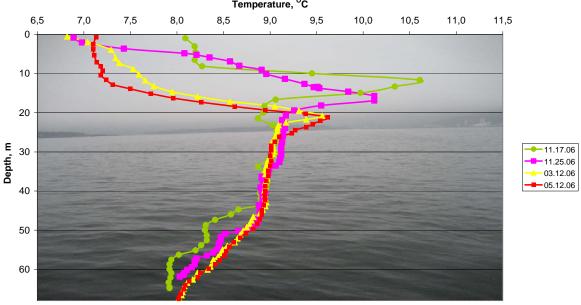
**Figure 19** Salinity profile at site 07, from surface to bottom at four different dates during the two sampling periods.





**Figure 20**. Salinity profile at site 12, from surface to bottom at four different dates during the two sampling periods.

# Temperature profile, sampling place 05 Temperature, °C





**Figure 21**. Temperature profile at site 05, from surface to bottom at four different dates during the two sampling periods.

#### Temperature profile, sampling place 12 Temperature, <sup>0</sup>C 6,5 7,0 7,5 8,0 8,5 9,0 10,0 10,5 11,0 11,5 0 10 20 Depth, m <del>---</del>11.17.06 30 11.25.06 03.12.06 **-**05.12.06 40 50 60

FIGURE 22. TEMPERATURE PROFILE AT SITE 12, FROM SURFACE TO BOTTOM AT FOUR DIFFERENT DATES DURING THE TWO SAMPLING PERIODS.



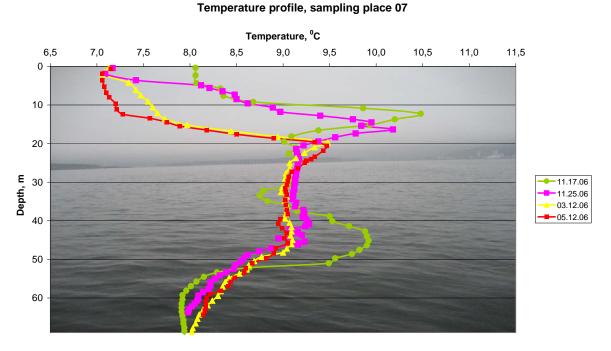


FIGURE 23 TEMPERATURE PROFILE AT SITE 07, FROM SURFACE TO BOTTOM AT FOUR DIFFERENT DATES DURING THE TWO SAMPLING PERIODS.

### Mapped concentrations of PCNs

As mentioned above, the PCN concentrations found at the different sites have also been displayed on maps, on which the size of the dots reflects the detected concentrations. Figure 24 shows a map of sum PCN levels from period 1 found at 3 meter from the sea bottom. The highest levels were found at site 5 and 12 but elevated levels were also found at site 6, 7 and 8. Concentrations were lowest at the background site 16, but also several other sites exhibit concentrations similar to the background. Decreasing levels can be found to the north-east and the south-west from the dumping area.

## Investigation of chemicals released from Malmøkalven dumping area. Polychlorinated naphthalenes

In figure 25, 26 and 27 are the PCN levels presented for 10 meter, 25 meter and 40 meter from the bottom. The number of sites measured decreased with the distance from the bottom. At 40 meter from the bottom only one site were measured. For the 10 meter samples (figure 25) the concentrations were lower than at 3 meter but the north-east and south-west directions were again the highest. At both 25 meter and 40 meter from bottom elevated concentrations of PCNs were detected at site 5.

The same general trend can be seen for the second sampling period (figure 28, 29, 30 and 31), except that the only sample from 40 meter from bottom do not show any elevated level.



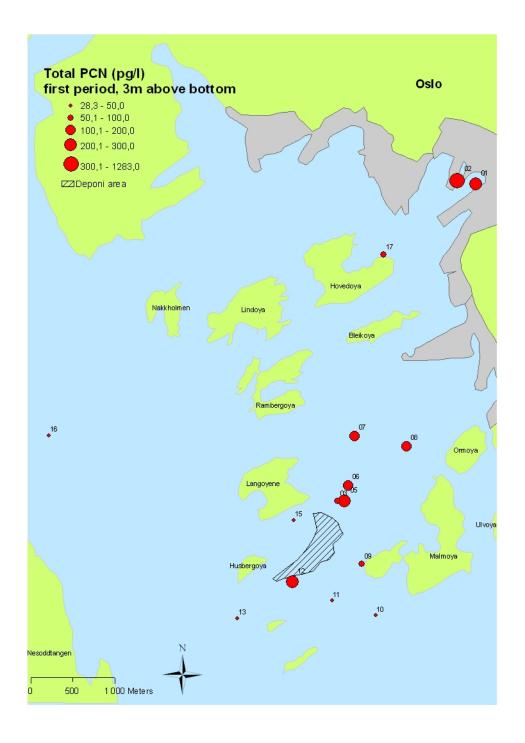


FIGURE 24. MAP SHOWING SUM OF PCN WATER CONCENTRATIONS AT 3 METER FROM THE BOTTOM IN THE INNER OSLO FJORD AND ESPECIALLY AROUND THE MALMØKALVEN DUMPING AREA FROM THE FIRST SAMPLING PERIOD.



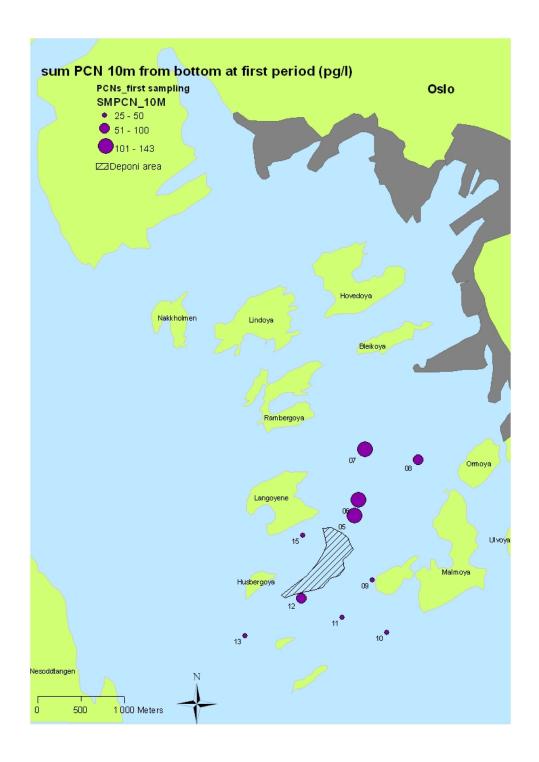


FIGURE 25. MAP SHOWING SUM OF PCN WATER CONCENTRATIONS AT 10 METER FROM THE BOTTOM IN THE INNER OSLO FJORD AND ESPECIALLY AROUND THE MALMØKALVEN DUMPING AREA FROM THE FIRST SAMPLING PERIOD.



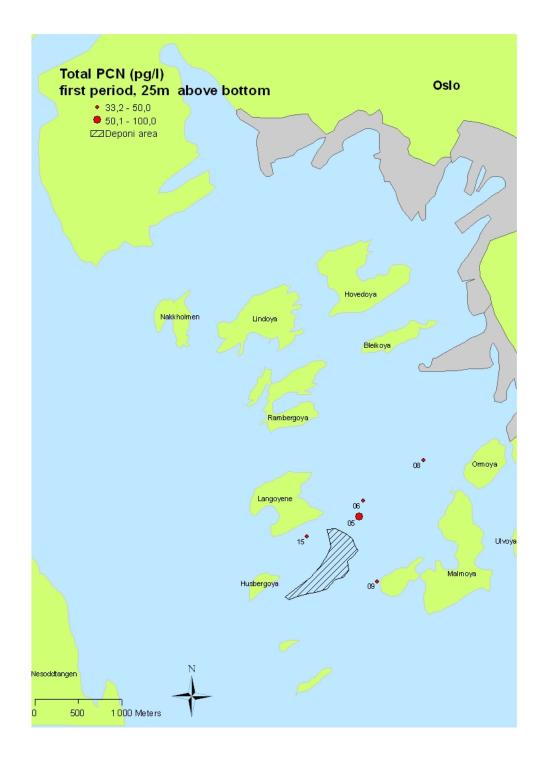


FIGURE 26. MAP SHOWING SUM OF PCN WATER CONCENTRATIONS AT 25 METER FROM THE BOTTOM IN THE INNER OSLO FJORD AND ESPECIALLY AROUND THE MALMØKALVEN DUMPING AREA FROM THE FIRST SAMPLING PERIOD.



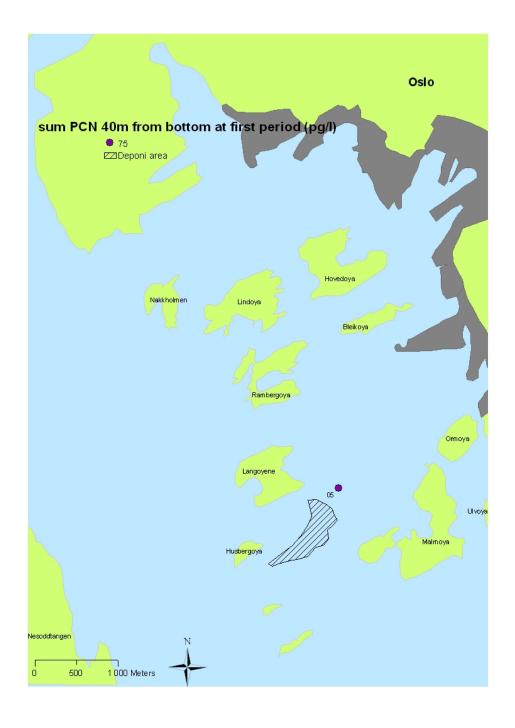


FIGURE 27. MAP SHOWING SUM OF PCN WATER CONCENTRATIONS AT 40 METER FROM THE BOTTOM IN THE INNER OSLO FJORD AND ESPECIALLY AROUND THE MALMØKALVEN DUMPING AREA FROM THE FIRST SAMPLING PERIOD.



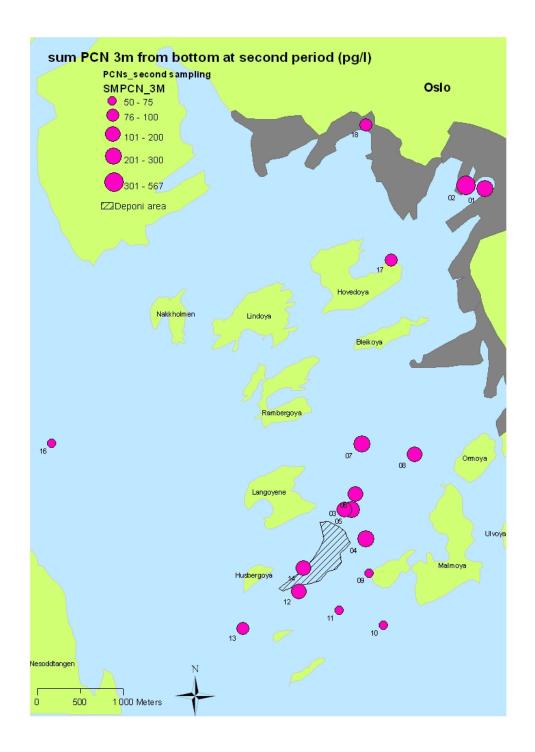


FIGURE 28. MAP SHOWING SUM OF PCN WATER CONCENTRATION AT 3 METER FROM THE BOTTOM IN THE INNER OSLO FJORD AND ESPECIALLY AROUND THE MALMØKALVEN DUMPING AREA FROM THE SECOND SAMPLING PERIOD.



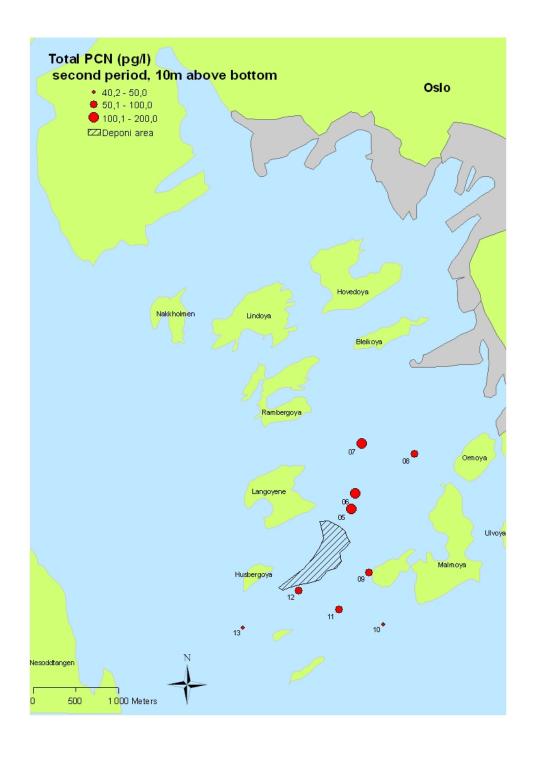


FIGURE 29. MAP SHOWING SUM OF PCN WATER CONCENTRATIONS AT 10 METER FROM THE BOTTOM IN THE INNER OSLO FJORD AND ESPECIALLY AROUND THE MALMØKALVEN DUMPING AREA FROM THE SECOND SAMPLING PERIOD.



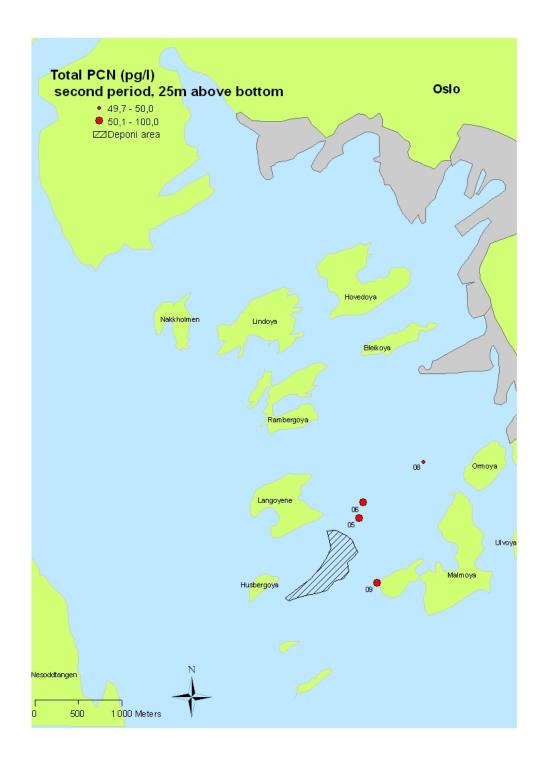


FIGURE 30. MAP SHOWING SUM OF PCN WATER CONCENTRATIONS AT 25 METER FROM THE BOTTOM IN THE INNER OSLO FJORD AND ESPECIALLY AROUND THE MALMØKALVEN DUMPING AREA FROM THE SECOND SAMPLING PERIOD.



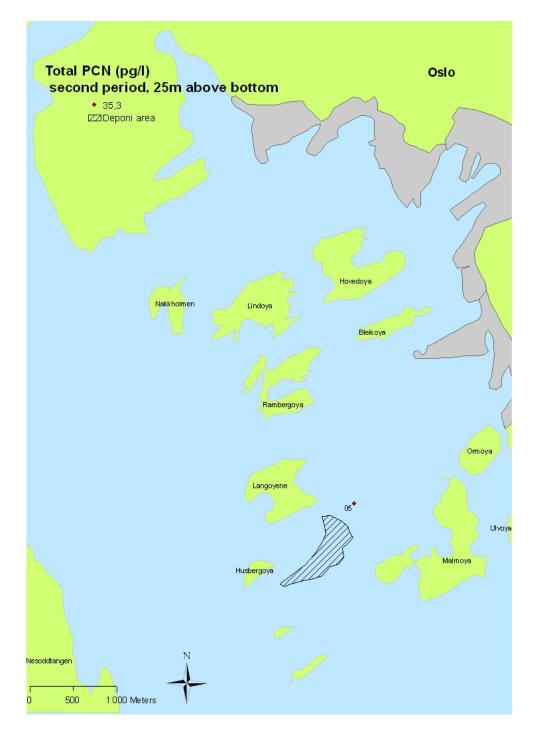


FIGURE 31. MAP SHOWING SUM OF PCN WATER CONCENTRATIONS AT 40 METER FROM THE BOTTOM IN THE INNER OSLO FJORD AND ESPECIALLY AROUND THE MALMØKALVEN DUMPING AREA FROM THE SECOND SAMPLING PERIOD. IT IS WRONG TEXT INSIDE FIGURE 31, SINCE THE DISTANCE FROM BOTTOM IS 40M.



### PCA "fingerprinting"

In order to visualize the relationships in PCN concentrations between the different sampling sites the statistical method PCA was used, whereby patterns in the levels of all PCN amongst the sampling sites were examined. Figures 32 and 33 present comparisons of data obtained from the sites in the first sampling period. The first two digits in the numerical codes indicate the site and the second two the sampling depth. For instance, 0501 indicates data obtained from site 5, 3 meters from the bottom. The numbers ending with 02, 03, 04 indicate data acquired 10, 25 and 40 m from the bottom, respectively. Data for sampling site 2 are excluded since it is an extreme site, but the information acquired from this site showed similar patterns to site 1, but much stronger. Excluding the data from site 2 allows the differences between the other sites to be visualized more readily. In figure 34 and 35 the same data are presented for the second sampling period.

During the first sampling period the samples from 3 meter depth at site 5 and 7 were most similar to the reference site 1 at the excavation area. Also the sample at site 5 at 10 meters showed large similarity to the site 1 pattern. The background station were very different compared to the above mentioned sites and several of the low concentration sites were closely related with the background site.



During the second sampling, the reference pattern from site 1 is regarded as a slight outlyer (since site 2 pattern is already taken out from the PCA calculation. Still we se a relationship with site 5 at 3 meter and the background site 16 is very distant from both site 1 and 5 (at 3 meter depth). The main components causing the difference between sites are some tetra and penta congeners

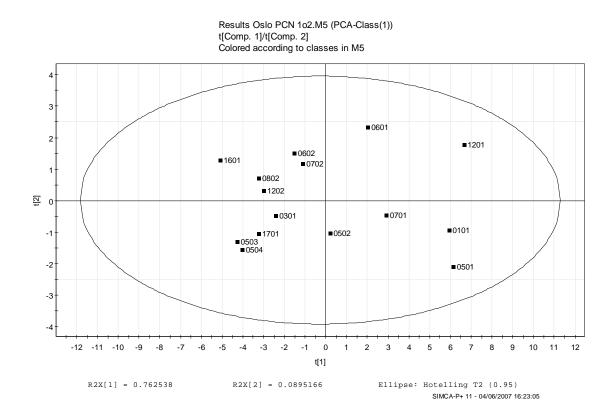


FIGURE 32. T1/T2 SCATTER PLOT OF ALL PCN DATA FROM THE FIRST SAMPLING PERIOD.

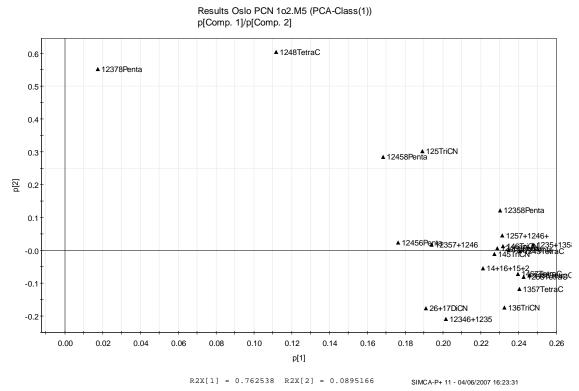


FIGURE 33. P1/P2 SCATTER PLOT OF ALL PCN DATA FROM THE FIRST SAMPLING PERIOD.

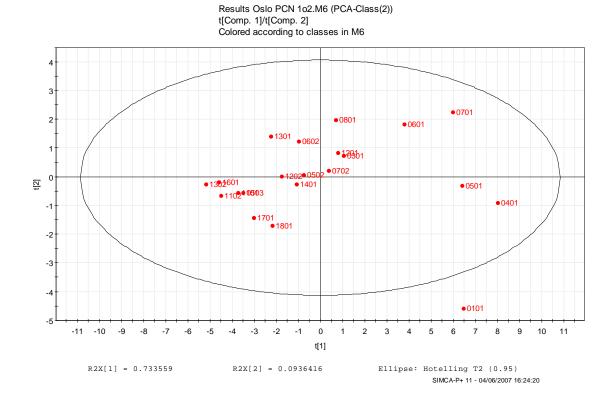


FIGURE 34. T1/T2 SCATTER PLOT OF ALL PCN DATA FROM THE SECOND SAMPLING PERIOD.

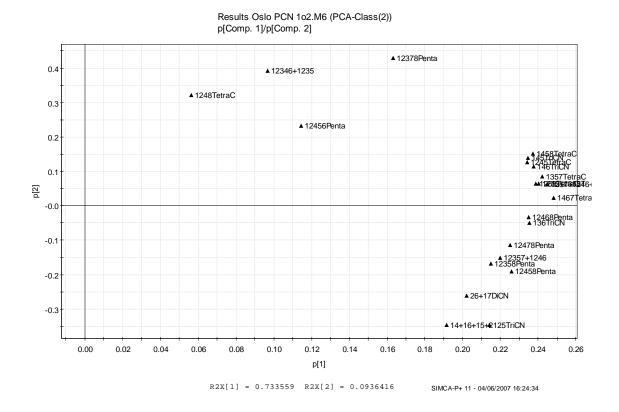


FIGURE 35. P1/P2 SCATTER PLOT OF ALL PCN DATA FROM THE SECOND SAMPLING PERIOD.

Below is a reference list including suggestions for further reading.



#### References

Baumard P, Budzindki H, Garrigues P. 1998. PAHs in Arcachon Bay, France: origin and biomonitoring with caged organisms, *Mar Pollut Bull*, 36: 577-586.

Bergqvist P-A., Jegorova I, Kauneliene V, Zaliauskiene A. 2007 Dissolved organochlorine and PAH pollution profiles in Lithuanian and Swedish waters. Bull of Environ Contam and Toxicol, Published on web.

Bergqvist P-A., Zaliauskiene A. Field Study Considerations in the Use of Passive Sampling Devices in Water Monitoring. 2007. Passive sampling techniques in environmental Monitoring. Editors: Greenwood R, Mills G, Vrana B. Comprehensive analytical chemistry, Vol. 48, Elsevier B.V., ISBN:978-0-444-52225-2

Bergqvist P-A., Zaliauskiene A. SPMD and DGT as integrative tools for measuring pollutants in runoff water, fresh water and in air. 1st senspol workshop, university of Alcala, Alcala De Henares, Spain, 9/11 May, 2001.

Bergqvist P-A, Augulyte L, Zaliauskiene A. Persistent organic pollutants (POP) in wastewater treatment plants sampled by semipermeable membrane devices (SPMD). 12th Annual Meeting SETAC Europe. Vienna, Austria. 13-17 May, 2002.

Bergqvist P-A., Ulciniene L., Zaliauskiene A. Storm water sampling of oil products using Semipermeable membrane devices (SPMD). 12th Annual Meeting SETAC Europe. Vienna, Austria. 13-17 May, 2002.

Bergqvist P-A, Augulyte L., Zaliauskiene A. Budget of water dissolved POPs in municipal wastewater treatment plant. 13th Annual Meeting SETAC Europe. Hamburg, Germany. 27 April -1 May, 2003.

Bergqvist P-A, Jegorova I., Augulyte L., Zaliauskiene A. Search for unidentified PCB sources in Swedish stream using semi permeable membrane devices. 14<sup>th</sup> Annual Meeting SETAC Europe. Prague, Czech Republic. 18-22 April, 2004.

Bergqvist P-A., Jegorova I., Kauneliene V., Zaliauskienė A. 2007. Dissolved organochlorine and PAH pollution profiles in Lithuanian and Swedish waters, *Bulletin of Environmental Contamination and Toxicology*, published on web.



Booij, K., Zegers, B.N., Boon, J.P. 2002. Levels of some polybrominated diphenyl ether (PBDE) flame retardants along the Dutch coast as derived from their accumulation in SPMDs and blue mussels (*Mytilus edulis*), *Chemosphere* 46: 683-688.

Booij, K.; Hoedemaker, J.R.; and Bakker, J.F.; 2003. Dissolved PCBs, PAHs, and HCB in pore waters and overlying waters of contaminated harbor sediments, *Environ. Sci. Technol.* 37: 4213-4220.

Booij, K.; and van Drooge, B.L.; 2001. Polychlorinated biphenyls and hexachlorobenzene in atmosphere, sea-surface microlayer, and water measured with semi-permeable membrane devices (SPMDs), *Chemosphere* 44: 91-98.

Davison, W. and Zhang, H. *In situ* speciation measurements of trace components in natural waters using thin-film gels. *Nature*, 367: 546-548.

Ellis, G.S., Huckins, J.N., Rostad, C.E., Schmitt, C.J., Petty J.D., MacCarthy, P. 1995. Evaluation of lipid-containing semipermeable membrane devices (SPMDs) for monitoring organochlorine contaminants in the Upper Mississippi River, *Environ. Toxicol. Chem.* 14: 1875-1884.

Følsvik N, Brevik EM, Berge JA. 2002. Organotin compounds in a Norwegian Fjord. A comparison of concentration levels in semipermeable membrane devices (SPMDs), Blue mussels (*Mytilus edulis*) and water samples, *Jour Environ Monitor* 4: 280-283.

Granmo Å, Ekelund R, Berggren M, Brorström-Lunden E, Bergqvist PA. 2000. Temporal trend of organochlorine marine pollution indicated by concentrations in mussels, semipermeable membrane devices, and sediment, *Environ Sci Technol* 34: 3323-3329.

Huckins, J.N., Manuweera, G.K., Petty, J.D., Mackay, D., Lebo, J.A. 1993. Lipid-containing semipermeable membrane devices for monitoring organic contaminants in water, *Environ. Sci. Technol.* 27: 2489-2496.

Huckins, J.N., Tubergen, M.W., Manuweera, G.K. 1990. Semipermeable membrane devices containing model lipid: a new approach to monitoring the availability of lipophilic contaminants and estimating their bioconcentration potential, *Chemosphere* 20: 533-552.

Huckins J. N, Petty J. D. A Guide for the Use of Semipermeable Membrane Devices (SPMDs) as Samplers of Waterborne Hydrophobic Organic Contaminants, API, publication number 4690, March 2002.

Huckins, J.N., Prest, H.F., Petty, J.D., Lebo, J.A., Hodgins, M.M., Clark, R.C., Alvarez, D.A., Gala, W.R., Steen, A., Gale, R., Ingersoll, C.G. 2004. Overview and comparison of lipid-containing semipermeable membrane devices and oysters (*Crassostrea gigas*) for assessing organic chemical exposure. *Environ. Toxicol. Chem.* 23: 1617-1628.



Huckins, J.N.; Petty, J.D.; Lebo, J.A.; Almeida, F.V.; Booij, K.; Alvarez, D.A.; Cranor, W.L.; Clark, R.C.; and Mogensen, B.B.; 2002. Development of the permeability/performance reference compound approach for in situ calibration of semipermeable membrane devices. *Environ. Sci. Technol.* 36: 85-91.

Huckins, J.N., Petty, J.D., Booij, K. (2006) Monitors of organic chemicals in the environment: Semipermeable Membrane Devices. SpringerScience+Business Media, U.S.A., pp. 223.

Knutzen Jon, Bjerkeng Birger, Næs Kristoffer, Schlabach Martin. 2003 Polychlorinated dibenzofurans/dibenzo-p-dioxins (PCDF/PCDDs) and other dioxin-like substances in marine organisms from the Grenland fjords, S. Norway, 1975–2001: present contamination levels, trends and species specific accumulation of PCDF/PCDD congeners. Chemosphere 52 745–760

Lebo, J.A., Gale, R.W., Petty, J.D., Tillitt, D.E., Huckins, J.N., Meadows, J.C., Orazio, C.E., Echols, K.R., Schroeder, D.J., Inmon, L.E.. 1995. Use of the semipermeable membrane device (SPMD) as an in situ sampler of waterborne bioavailable PCDD and PCDF residues at sub-part-per-quadrillion concentrations. *Environ. Sci. Technol.* 29: 2886-2892.

Lebo, J.A., Zajicek, J.L., Huckins, J.N., Petty, J.D., and Peterman, P.H. 1992. Use of Semipermeable Membrane Devices of in Situ Monitoring of Polycyclic Aromatic Hydrocarbons in Aquatic Environments, Chemosphere 25, 697-718.

McCarthy, K.A., Gale, R.W. 2001. Evaluation of persistent hydrophobic organic compounds in the Columbia River Basin using semipermeable-membrane devices. *Hydrol. Process.* 15: 1271-1283.

Moring, J.B., Rose, D.R. 1997. Occurrence and concentration of polycyclic aromatic hydrocarbons in semipermeable membrane devices and clams in three urban streams of the Dallas-Fort Worth metropolitan area, Texas, *Chemosphere* 34: 551-566.

Rantalainen, A.-L.; Cretney, W.; and Ikonomou, M.G.; 2000. Uptake rates of semipermeable membrane devices (SPMDs) for PCDDs, PCDFs and PCBs in water and sediment. *Chemosphere* 40: 147-158.

Parrott, J.L., Backus, S.M., Borgmann, A.I., and Swyripa, M. 1999. The Use of Semipermeable Membrane Devices to Concentrate Chemicals in Oil Refinery Effluent on the Makenzie River. *Arctic* 52: 125-138.

Persson N. Johan, Gustafsson Örjan,. Bucheli Thomas D, Ishaq Rasha, Næs Kristoffer, Broman Dag. 2005. Distribution of PCNs, PCBs, and other POPs together with soot and



## Investigation of chemicals released from Malmøkalven dumping area. Polychlorinated naphthalenes

other organic matter in the marine environment of the Grenlandsfjords, Norway. Chemosphere 60, 274–283

Prest, H.F., Jarman, W.M., Burns, S.A., Weismuller, T., Martin, M., Huckins, J.N. 1992. Passive water sampling via semipermeable membrane devices (SPMDs) in concert with bivalves in the Sacramento/San Joachin River Delta. *Chemosphere* 25: 1811-1824.

Prest, H.F., Richardson, B.J., Jacobson, L.A., Vedder, J. 1995. Monitoring organochlorines with semipermeable membrane devices (SPMDs) and Mussels (*Mytilus edulis*) in Corio Bay, Victoria, Australia. *Mar. Pollut. Bull.* 30: 543-554.

Sabaliunas, D., Lazutka, J., Sabaliuniene, I., and Södergren, A 1998. Use of Semipermeable Membrane Devices for Studying Effects of Organic Pollutants: Comparison of Pesticide Uptake by Semipermeable Membrane Devices and Mussels. *Environ. Toxicol. Chem.* 17: 1815-1824.

Utvik, TIR, Durell, GS, Johnsen, S. 1999. Determining produced water originating polycyclic aromatic hydrocarbons in North Sea waters: comparison of sampling techniques. *Mar Pollut Bull* 38: 977-989.

Vladimir Koci. Toxicological Evaluation of exposed SPMD membranes. 2003, *CEJC* 1: 28-34.

Zaliauskiene A., Bergqvist P-A. Contamination of former industrial site in K-Holmen, Sweden. 14<sup>th</sup> Annual Meeting SETAC Europe, Prague. Czech Republic. 18-22 April, 2004.