Oslo fjord

Investigation of chemicals released from the Malmøkalven dumping area.

Polycyclic aromatic hydrocarbons

ExposMeter AB

Tavelsjö

2007 06 21

Project report 2006N-003

Investigation of chemicals released from Malmøkalven dumping area.

Polycyclic aromatic hydrocarbons

Project report 2006N-003

ExposMeter AB
Tavelsjö
2007 06 21

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

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

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 cm^2 or 100 cm^2 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.

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

Legends

List of Tables.

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.

The investigation has shown that:

1. Elevated levels of PAHs are found outside the (of SFT marked) dumping area compared to the background site.
2. The levels are lower when further away from the dumping area.
3. Elevated levels (compared to background site) of individual PAH compounds are found at one sampling period from bottom up to 40 meters above sea bottom close to the dumping area compared to the reference site. This is based on one sample and one analysis, since it is outside the scope of this investigation to study this question. For total PAH measurements this can not be seen.
4. Several compounds are thus decreasing in concentration when comparing levels at 3 meter from bottom with 10 and 25 meter from bottom (site 5, 6, 7 and 8).
5. Levels of alkylated PAHs (R-PAHs) were difficult to evaluate due to relatively similar levels at all sampling sites except sites in Oslo harbor.
6. Fingerprinting is unclear for PAH and R-PAH since these compounds is more unstable in the environment and also possess large differences in the particle binding properties. Bottom samples from site 5, 6, 7, 12 are similar and all harbor sites (1, 2, 17, 18) are similar.

This report is the third 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)

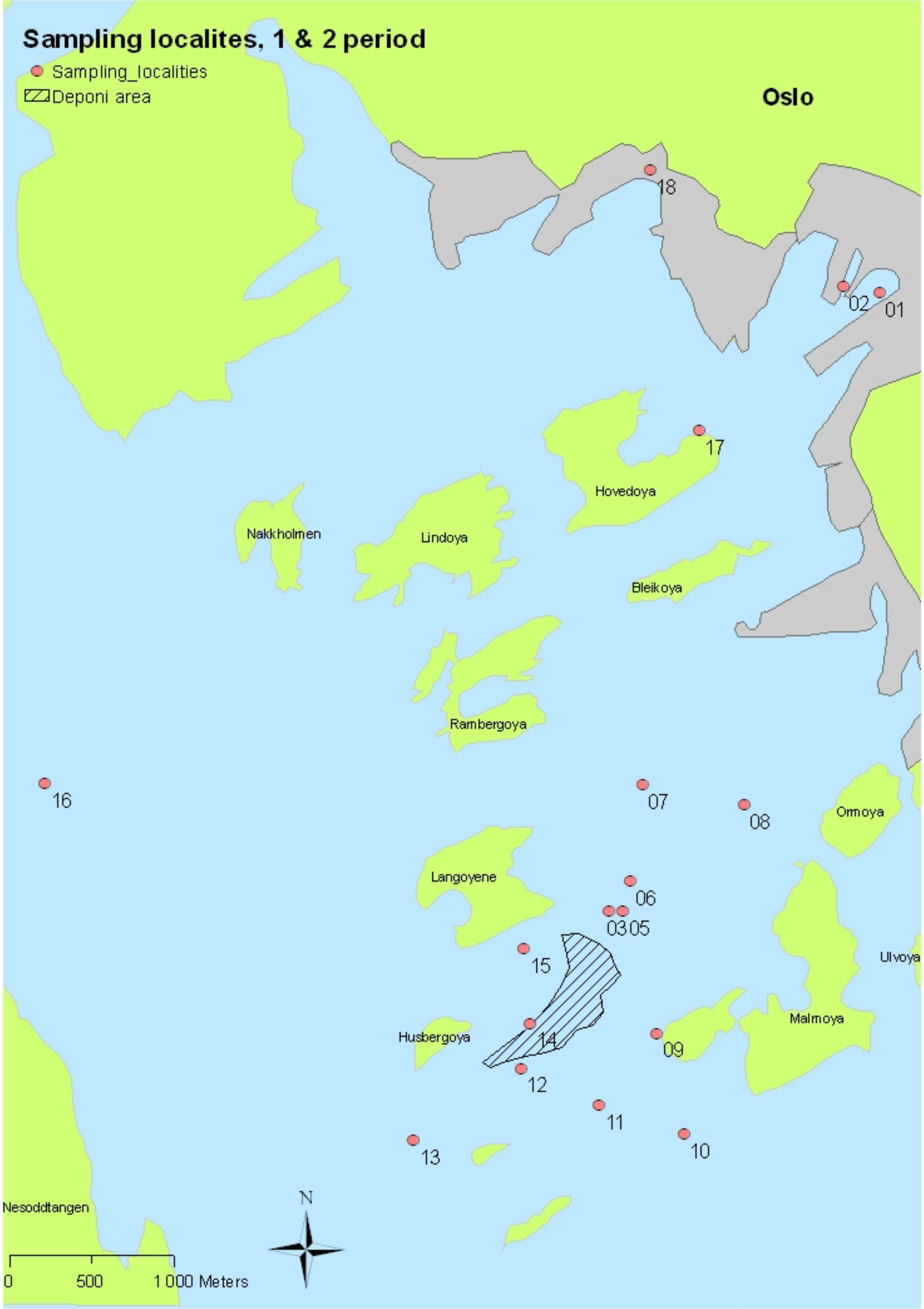

Figure 2. Sampling places in Oslo Fjord during the period 30.10 – 12.12 2006 except site 04.

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 $3 < \log K_{ow} < 8$ and molecular masses lower than ca. 600 Daltons such as polyaromatic hydrocarbons (PAHs), non-polar pesticides, polychlorinated biphenyls (PCB), polychlorinated naphthalenes, 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.

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.

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 2) and a protective cage that prevents mechanical damage to the membranes, is used for deploying EHDs in the water (Figure 3).

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 4.

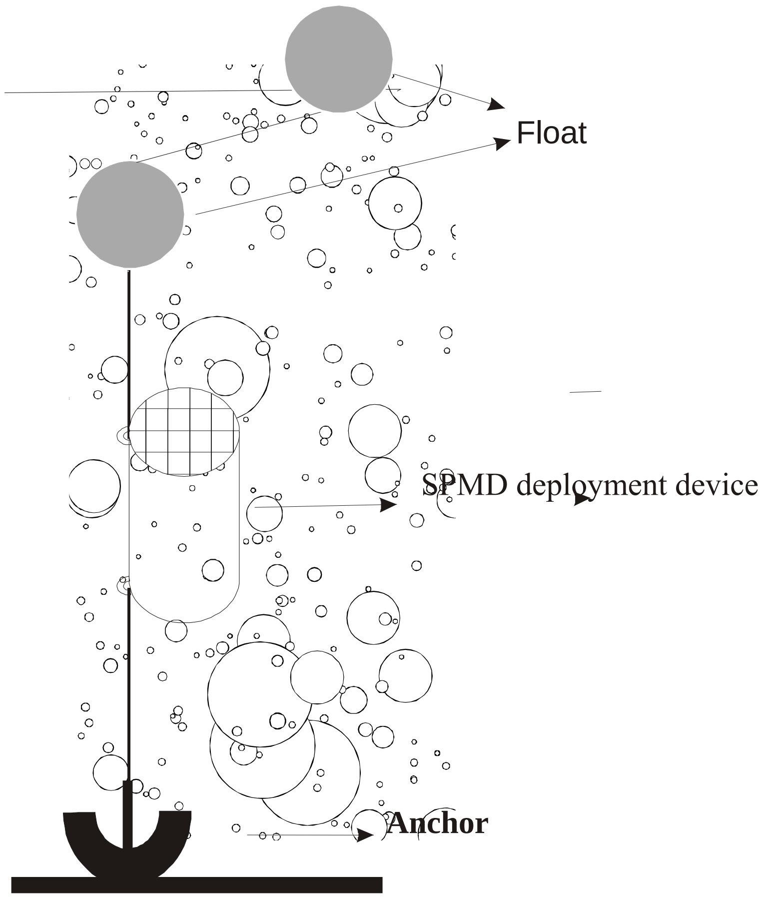

Figure 5. Deployment in water of protective cage with SPMDs inside. Heavy anchor on the bottom and floating devices lifting the rope to the surface. **

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 5.

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 formulae for calculations were (from Huckins et al. 2006):

$$C_w = \frac{N}{V_s \cdot K_{sw}\left(1 - \exp\left(-\frac{R_s \cdot t}{V_s \cdot K_{sw}}\right)\right)} \left[ng \cdot L^{-1}\right]$$

In the analysis both polyaromatic hydrocarbons (PAHs) and alkylated polyaromatic hydrocarbons (R-PAHs). The PAHs represent the 16 by US EPA selected PAHs, which is commonly measured in city air and used as indicators for PAH pollution. The origins of these compounds are mainly from combustion processes and are thus often called “pyrogenic PAHs”. The other group of compounds are a selection of R-PAHs which is also commonly referred to as “petrogenic PAHs” since one major source is petroleum products. A simplified graphical representation of the main analytical steps is presented in figure 6.

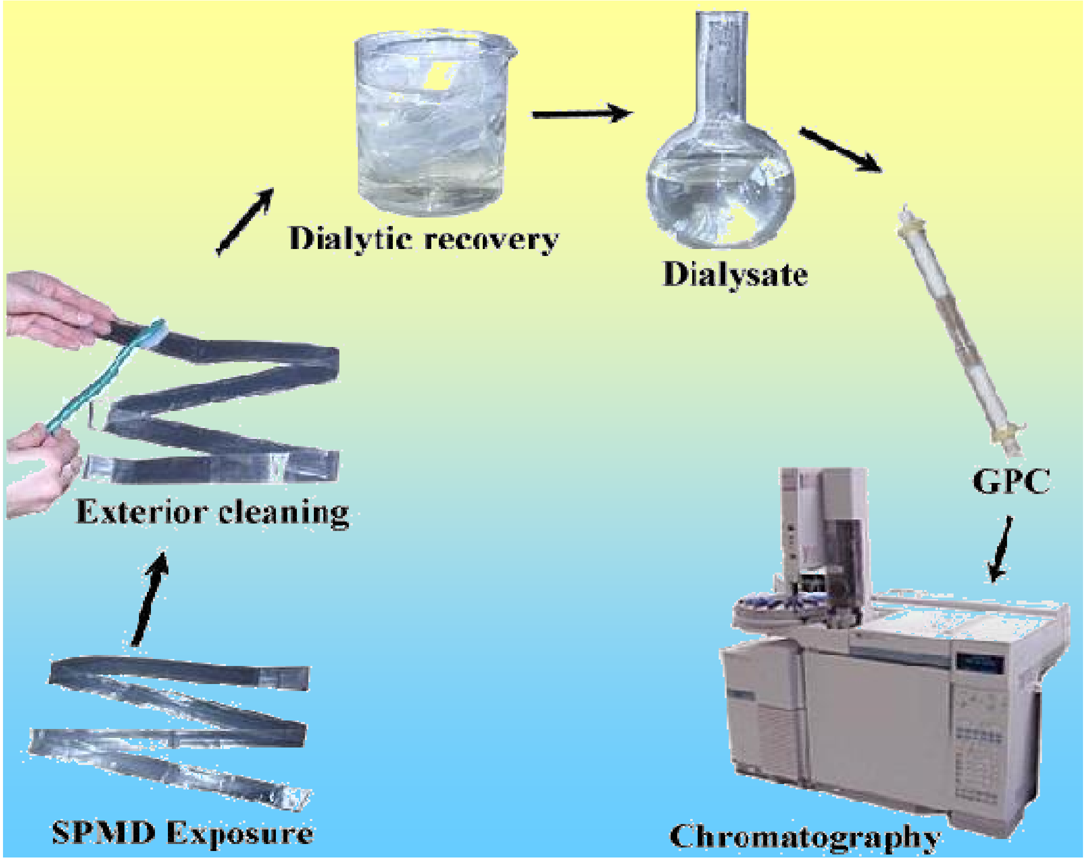

Figure 7. Schematic representation of SPMD treatment

Table 1. PAHs analyzed in the EHD extracts.

Naphthalene
Acenaphthylene
Acenaphtene
Fluorene
Phenantrene
Anthracene
Fluoranthene
Pyrene
Benzo(a)anthracene
Chrysene
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(a)pyrene
Benzo(g,h,i)perylene
Dibenzo(a,h)anthracene
Indeno(1,2,3-c,d)pyrene

2MeNaphtalene
1MeNaphtalene
2+1EtNaphtalene
26DiMeNaphtalene
17DiMeNaphtalene
14+23DiMeNaphtalene
18DiMeNaphtalen
235TriMeNaphtalen
1MeAnthracene
2MeAnthracen
1+2MePhenanthrene

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 coordinates		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 measured nd - not deployed							

Results

The results from the PAH and R-PAH investigation are presented below. The difference in behaviour due to e.g. physical and chemical properties, vary between the different compounds. These cause larger changes in pattern due to time, temperature, mixing, oxidation, photolysis etc and make the situation difficult to interpret.

In order of simplifying the interpretation of the results we will visualize them in three ways. First the levels of the sum of PAH and R-PAH substances is shown, then the distribution of PAHs and R-PAHs around the Oslo fjord is shown on maps and finally the relationship in “finger prints” between the different sampling locations.

PAH 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 140 ng/L and all other sites has levels at or below 40 ng/L. During the second sampling period (figure 9) the overall levels is a factor of 2 lower than during the first sampling period except that site 1 and 2 is nearly at the same level as compared to the first period. The only time the background site 16 has been higher than any other site were for R-PAHs during second sampling period (figure 11). It can also be seen that the samples from harbors areas do contain elevated levels of the R-PAHs probably partly due to boat traffic.

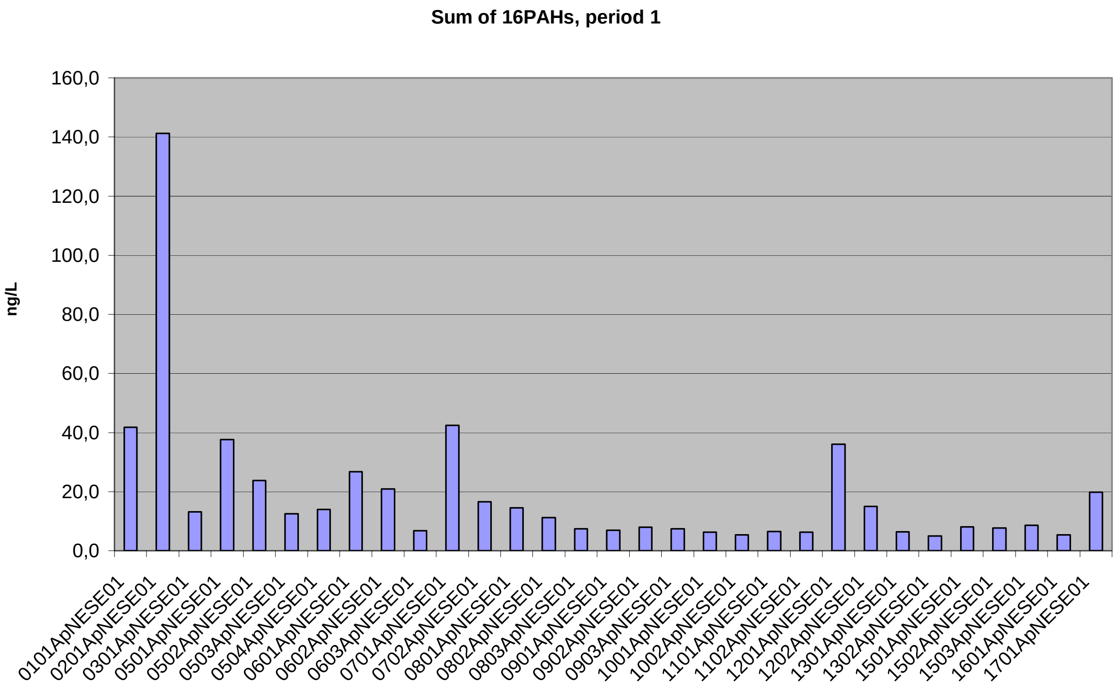

Figure 8. Sum of 16PAHs sampled in period 1 at the different sites, ng/L

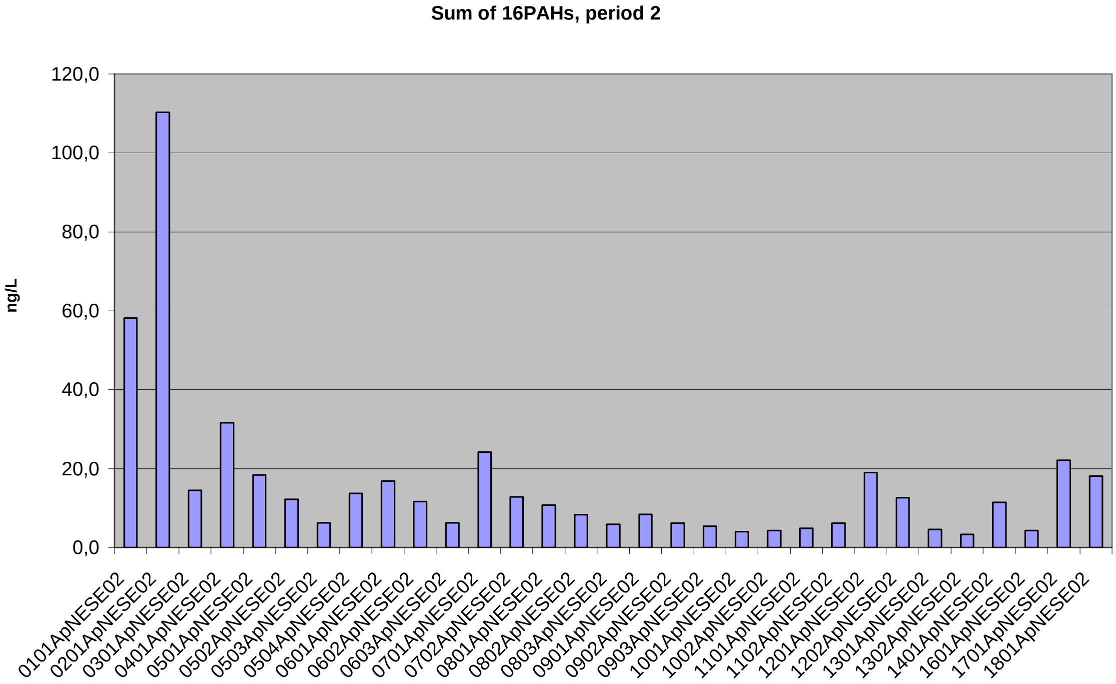

Figure 9. Sum of 16PAHs sampled in period 2 at the different sites, ng/L

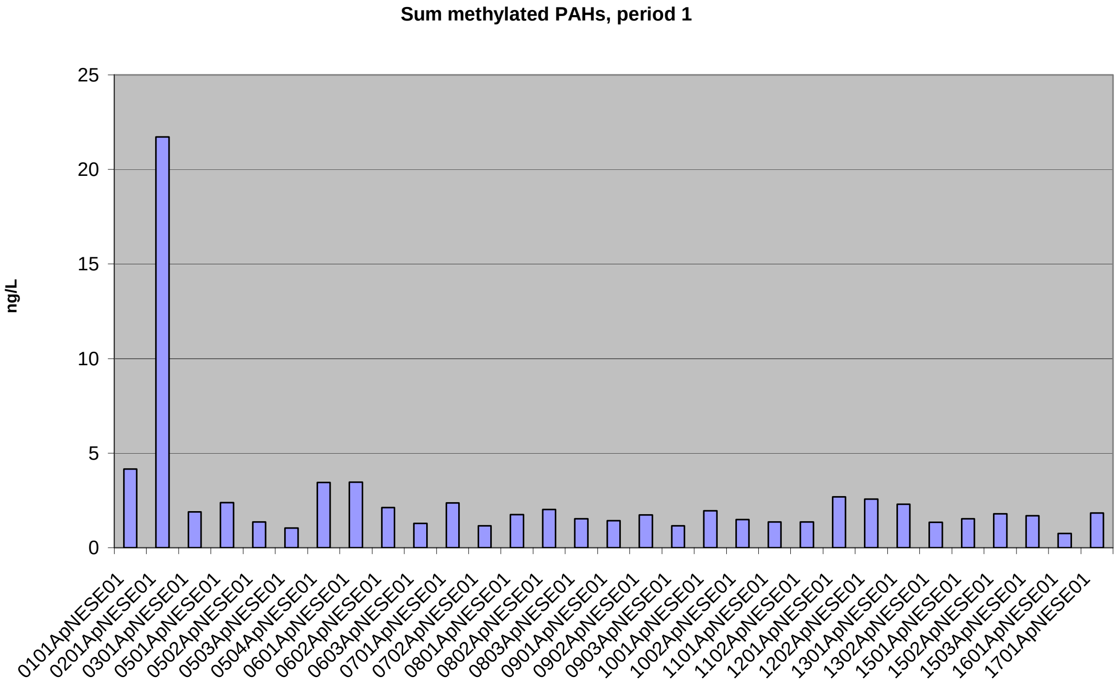

Figure 10. Sum of all methylated PAHs sampled in period 1 at the different sites, ng/L

……………………………………………………….

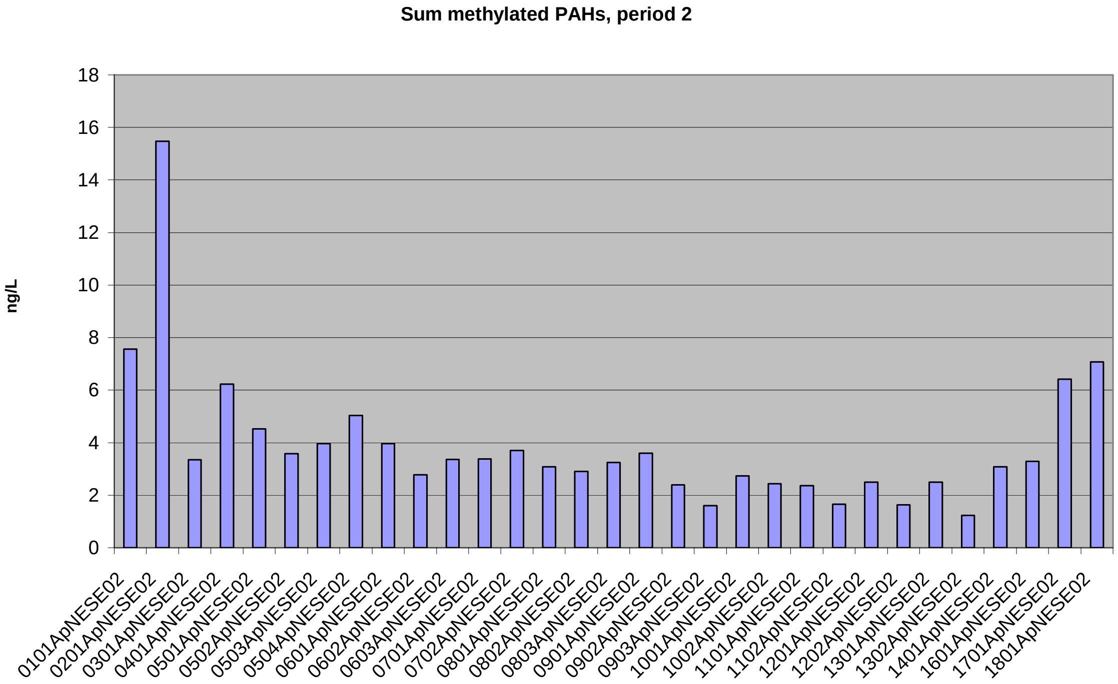

Figure 11. Sum of all methylated PAHs sampled in period 2 at the different sites, ng/L

The concentration for selected compounds of PAHs with 3-4 aromatic rings and with 2, 5, 6 rings from first and second sampling period are presented in figures 12, 13, 14 and 15, respectively. Selected alkylated PAHs (R-PAHs) are presented in figure 16 and 17. All compounds are not presented due to low levels and/or for increasing the readability of the graphs, but in total level figures all compounds are included.

For R-PAHs a decrease with distance to the sediment floor can bee seen for i.e. sites 5, 6, 7, 12 where also the 3 meter from bottom sample represents the highest values when studying acenaphthene. This is valid for both sampling periods.

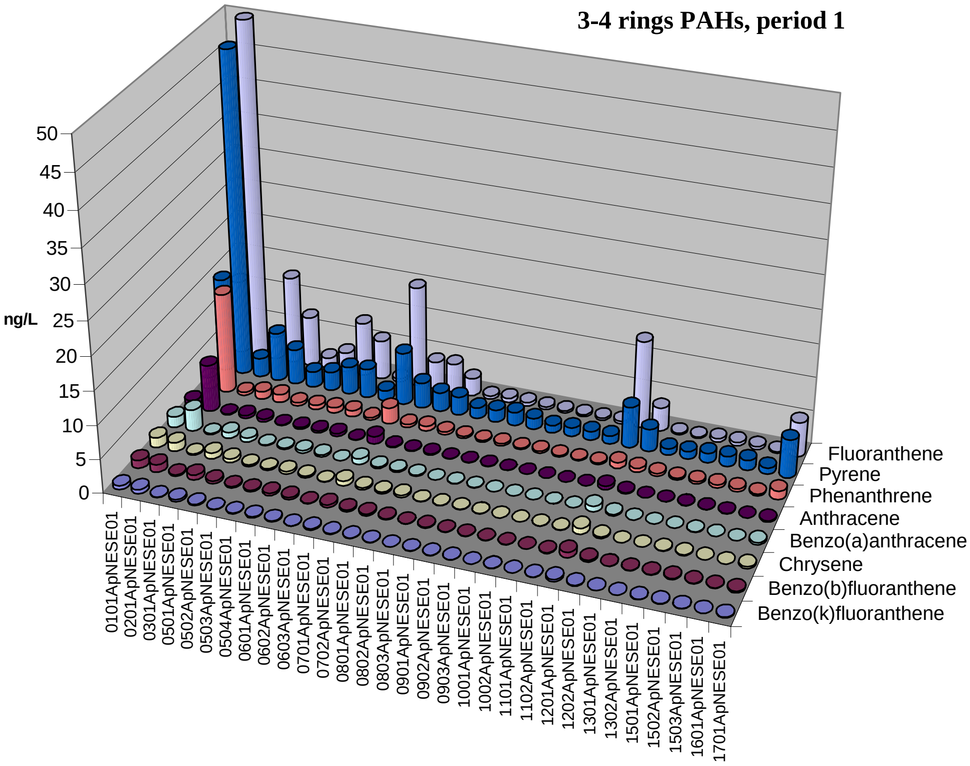

Figure 12. 3-4 rings PAHs in period 1 from different sites in the Oslo fjord study, ng/L.

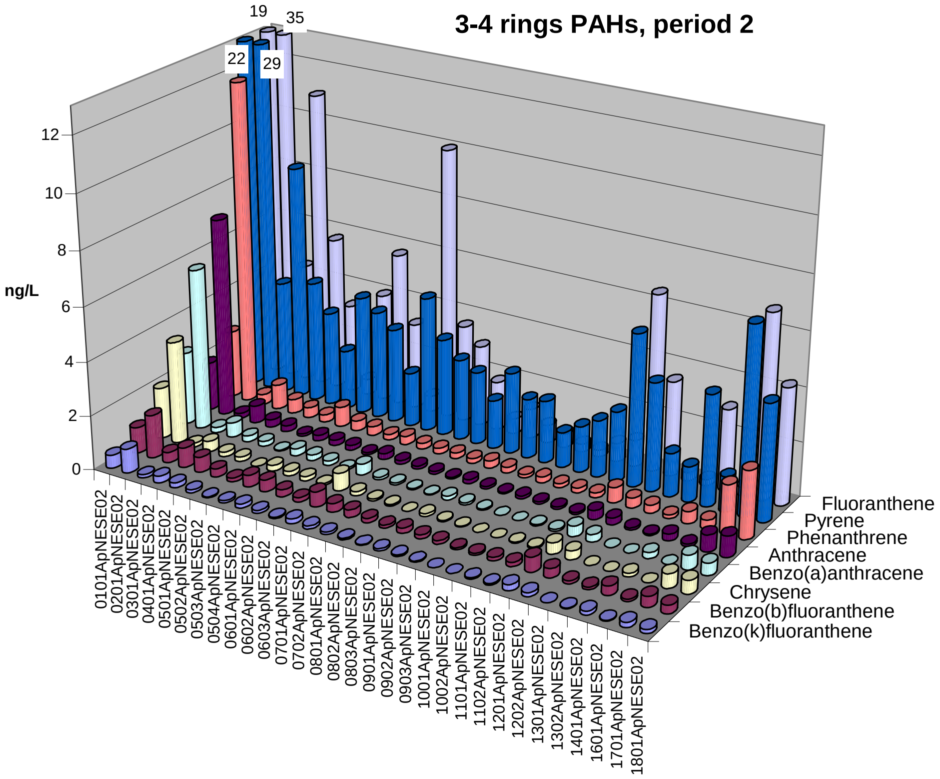

Figure 13. 3-4 rings PAHs in period 2 from different sites in the Oslo fjord study, ng/L.

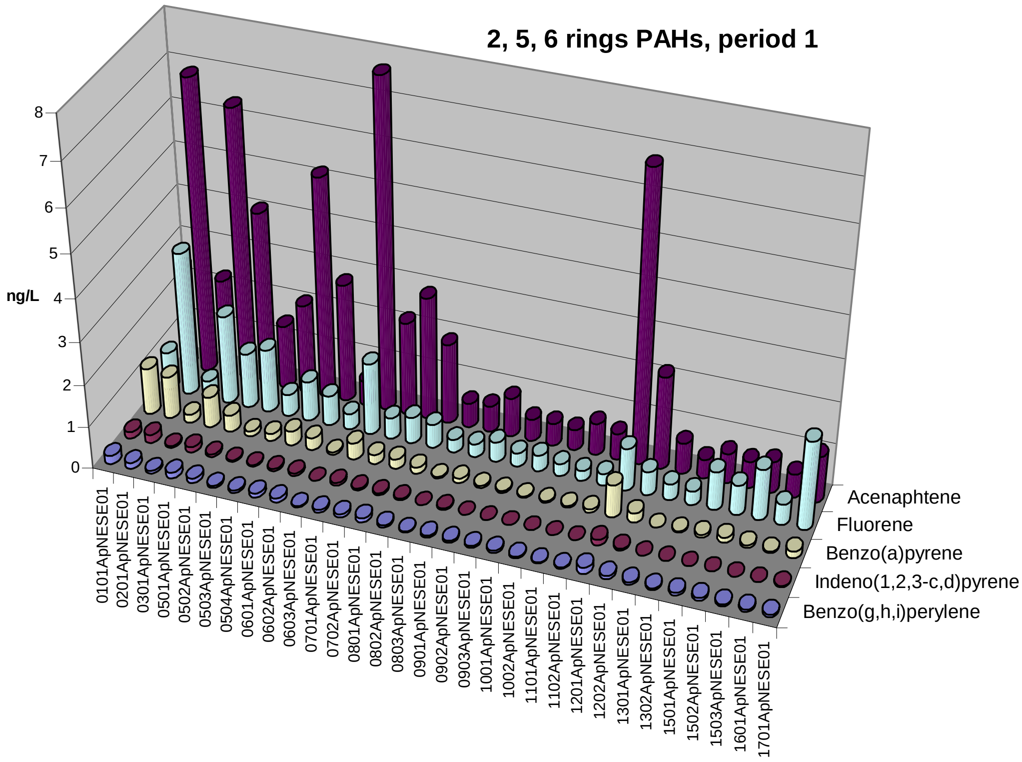

Figure 14. 2, 5, 6 rings PAHs in period 1 from different sites in the Oslo fjord study, ng/L.

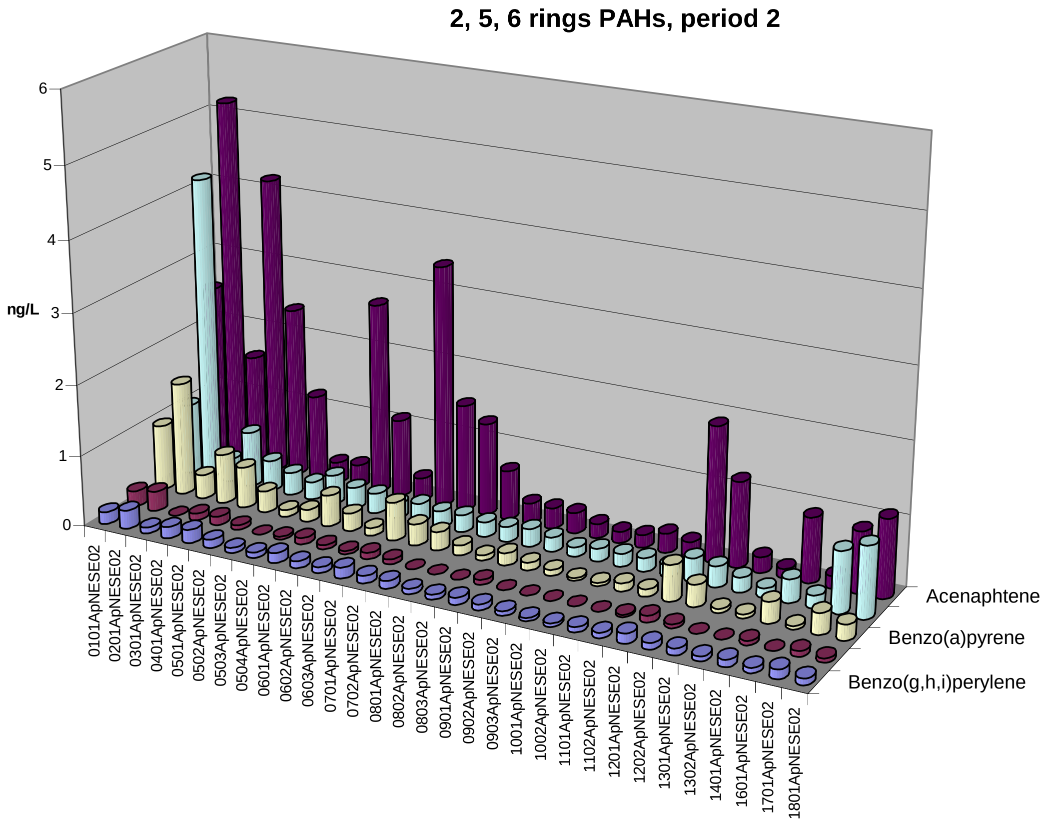

Figure 15. 2, 5, 6 rings PAHs in period 2 from different sites in the Oslo fjord study, ng/L.

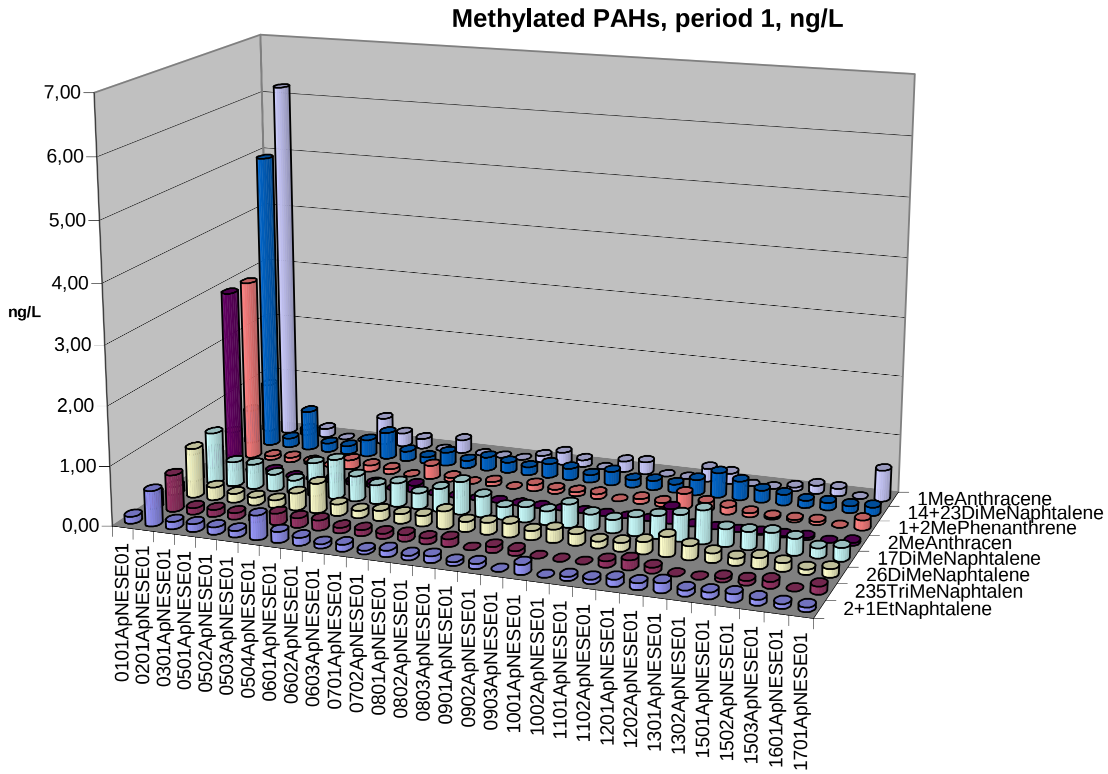

Figure 16. Alkylated PAHs in period 1 from different sites in the Oslo fjord study, ng/L.

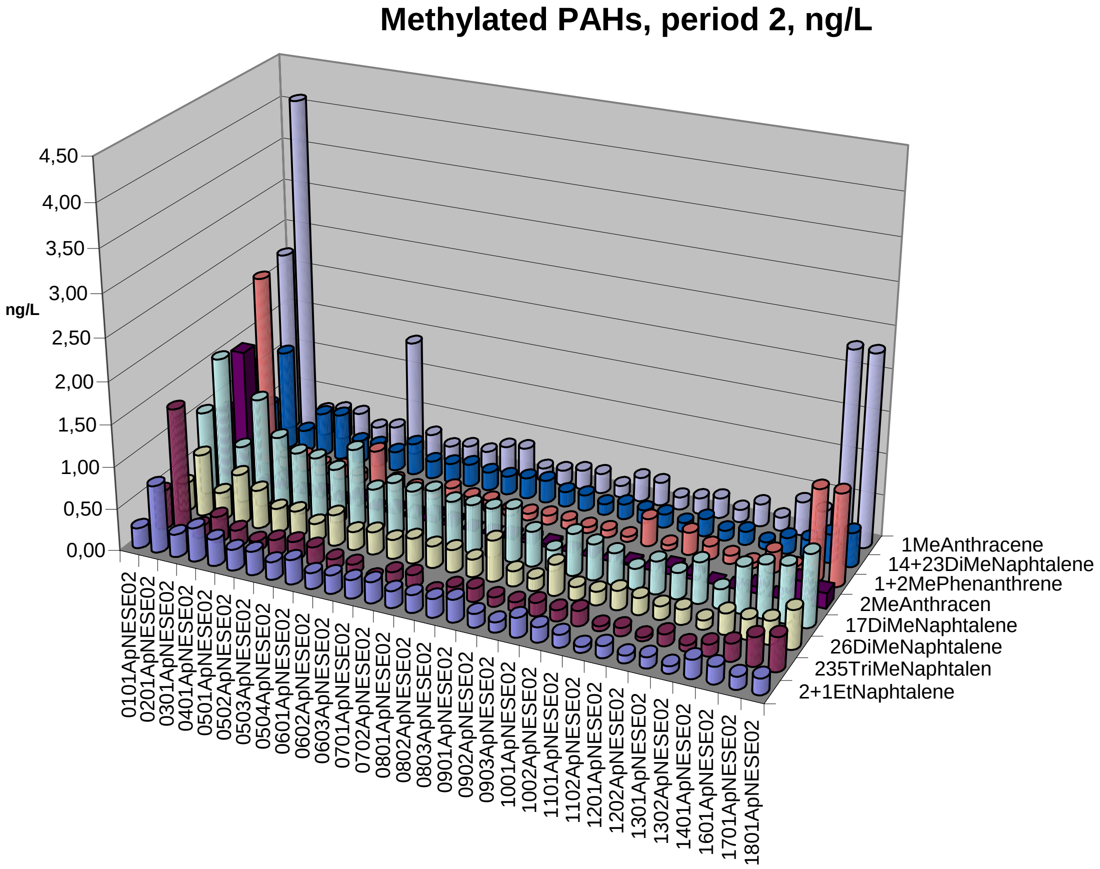

Figure 17. Alkylated PAHs in period 2 from different sites in the Oslo fjord study, ng/L.

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 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 17, 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 18 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 19, 20, 21.

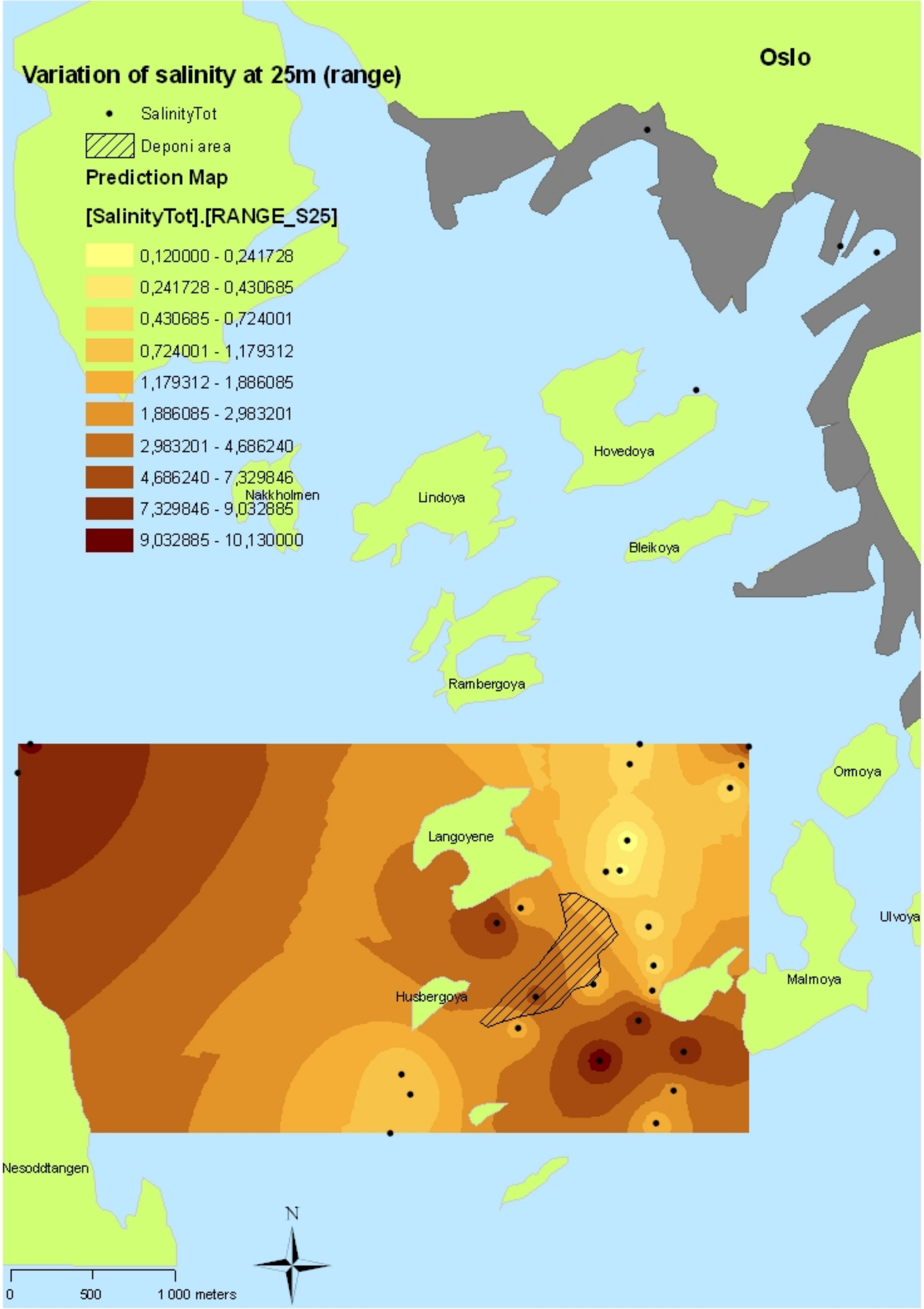

Figure 18. Variation of salinity at 25 meter from sea bottom.

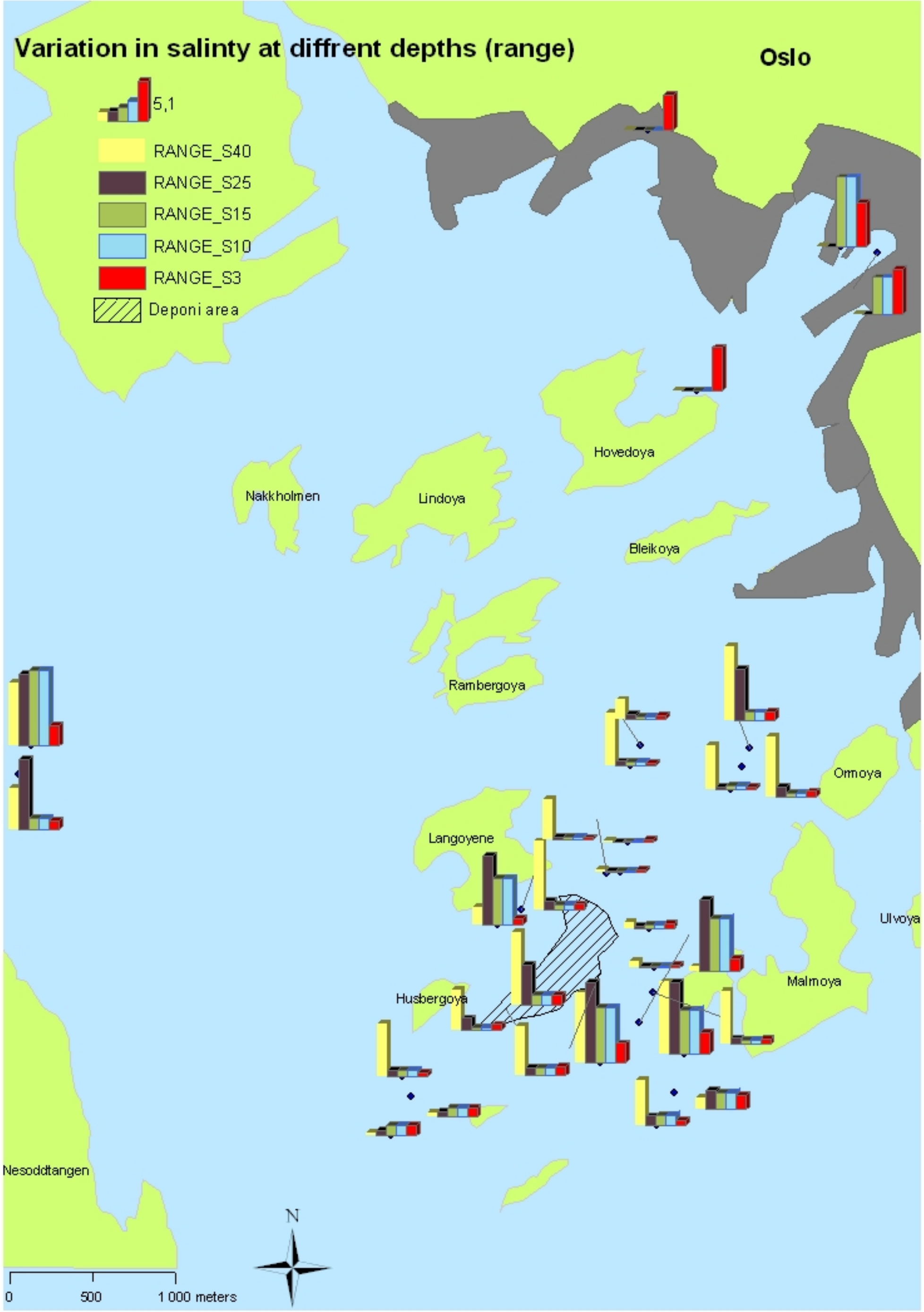

Figure 19. Variation of salinity at different depths during the study.

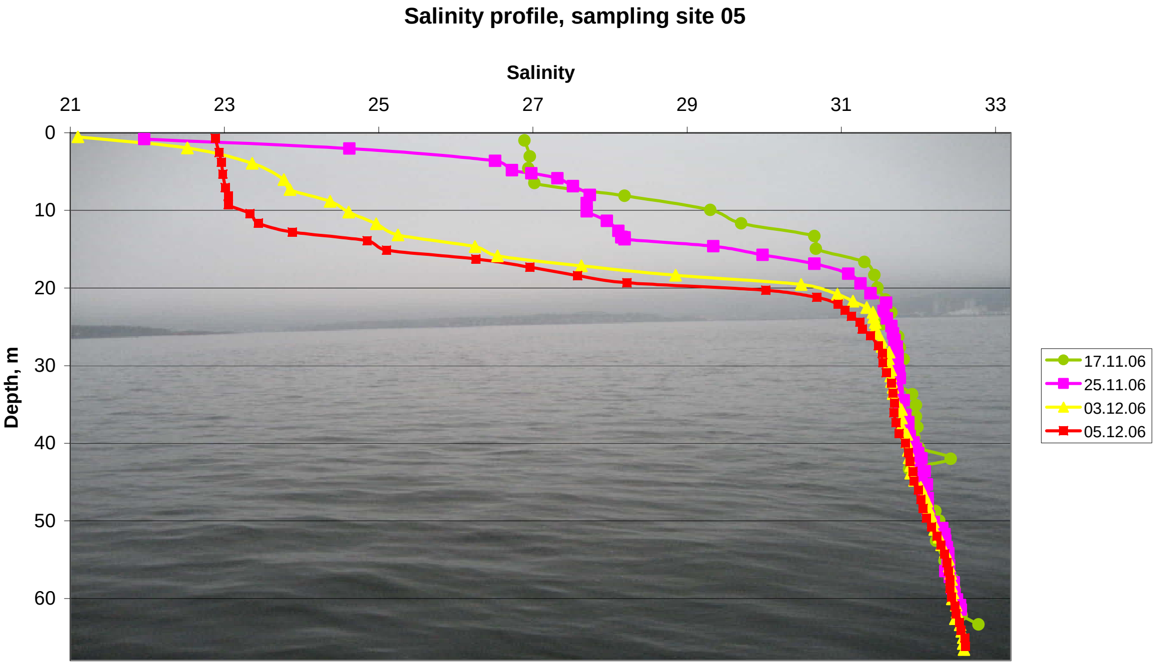

Figure 20. Salinity profile at site 05, from surface to bottom at four different dates during the two sampling periods.

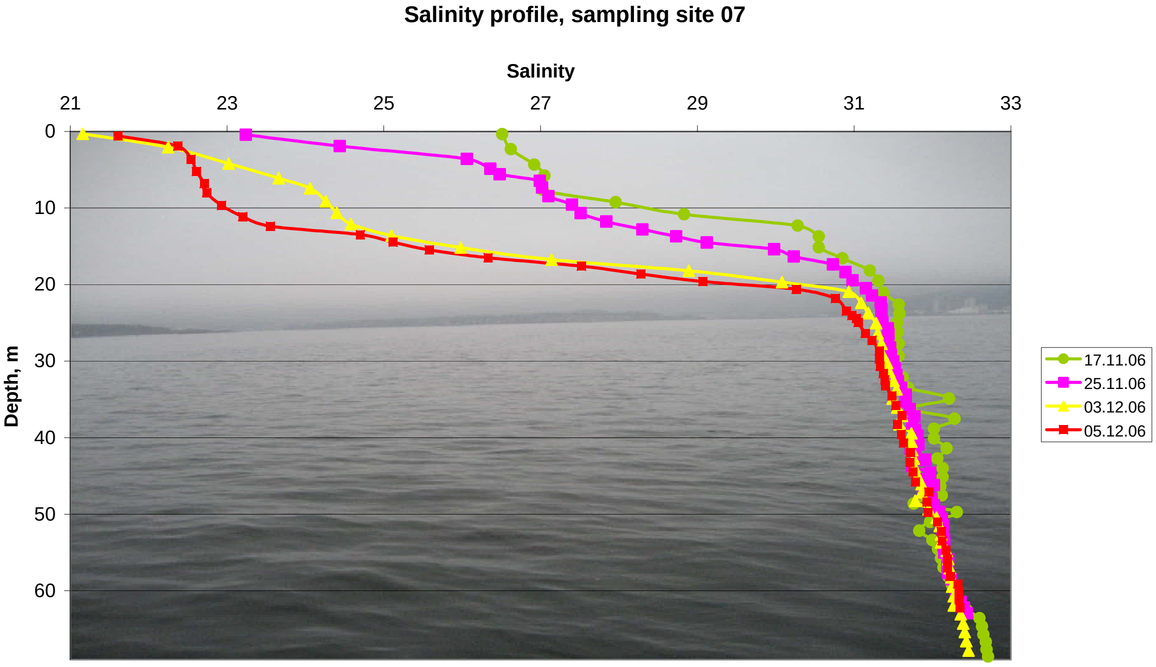

Figure 21. Salinity profile at site 07, from surface to bottom at four different dates during the two sampling periods.

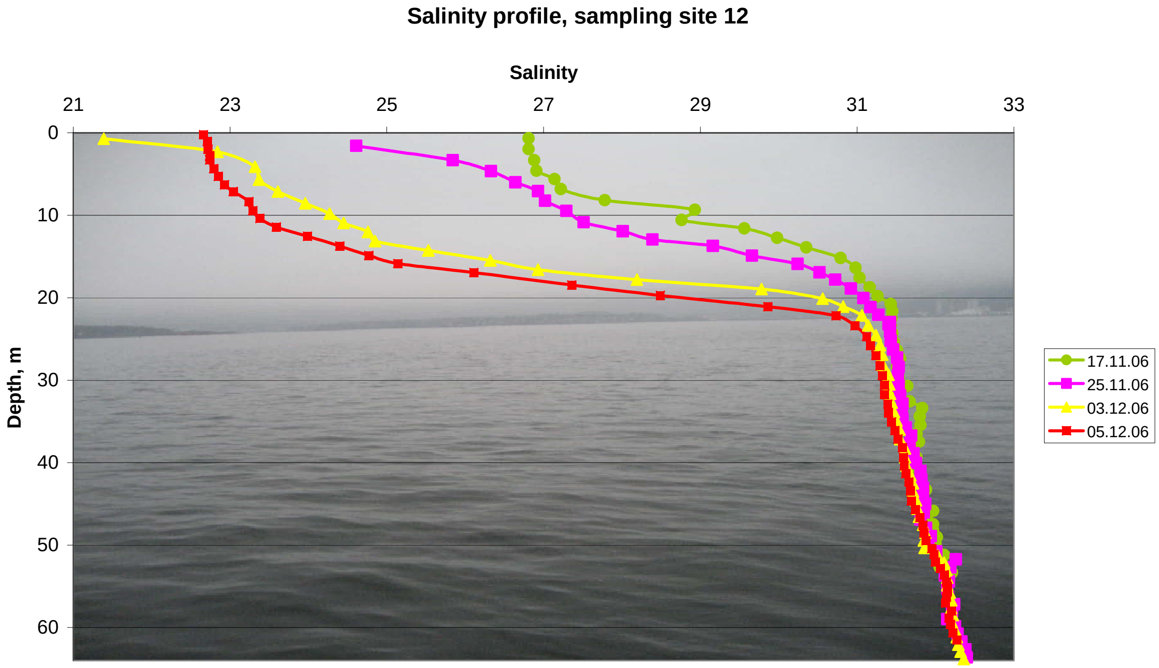

Figure 22. Salinity profile at site 12, from surface to bottom at four different dates during the two sampling periods.

Mapped concentrations of PAHs

As mentioned above, the PAH concentrations found at the different sites have also been displayed on maps, on which the size of the dots reflects the detected concentrations. Figure 23 shows a map of sum PAH levels from period 1 found 3 metres from the sea bottom. The highest levels were found at site 5, 7 and 12 and during second sampling period also at site 4. Concentrations were lowest at the background site (Näsudden). Most of the sampling sites close to the dumping area are located at a depth of 60-70 meters.

Most sampling was performed at 3 meters from the bottom, while fewer samples were taken from 10 meter and 25 meter from bottom. At 40 meter from bottom only one sample were taken, which is the reason that on these maps only one dot is marked. In an attempt to increase visibility the scale between the dot sizes is changing.

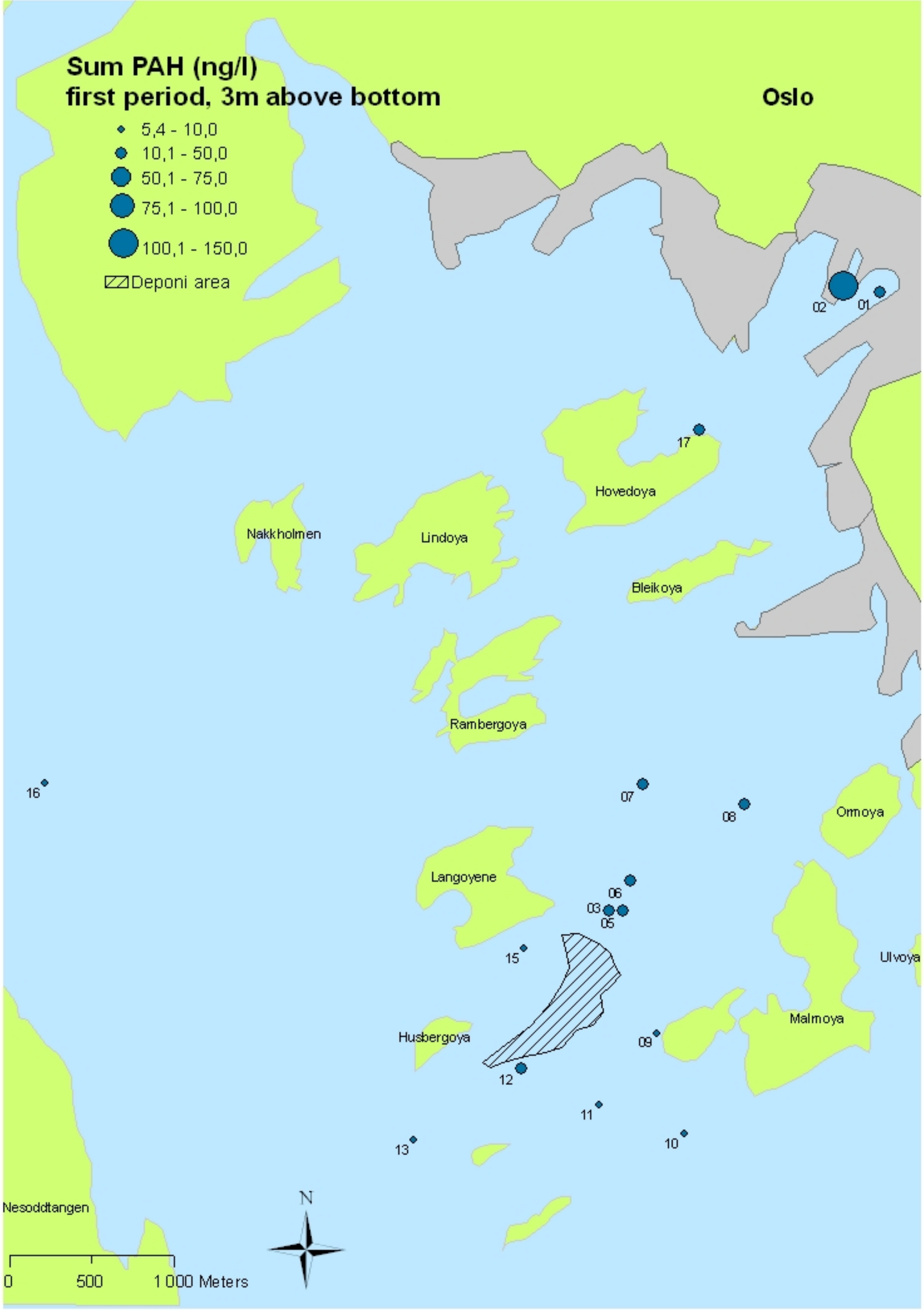

Figure 23. Map showing sum of PAH water concentrations at 3 meter from the bottom in the inner Oslo fjord and especially around the Malmøkalven dumping area from the first sampling period.

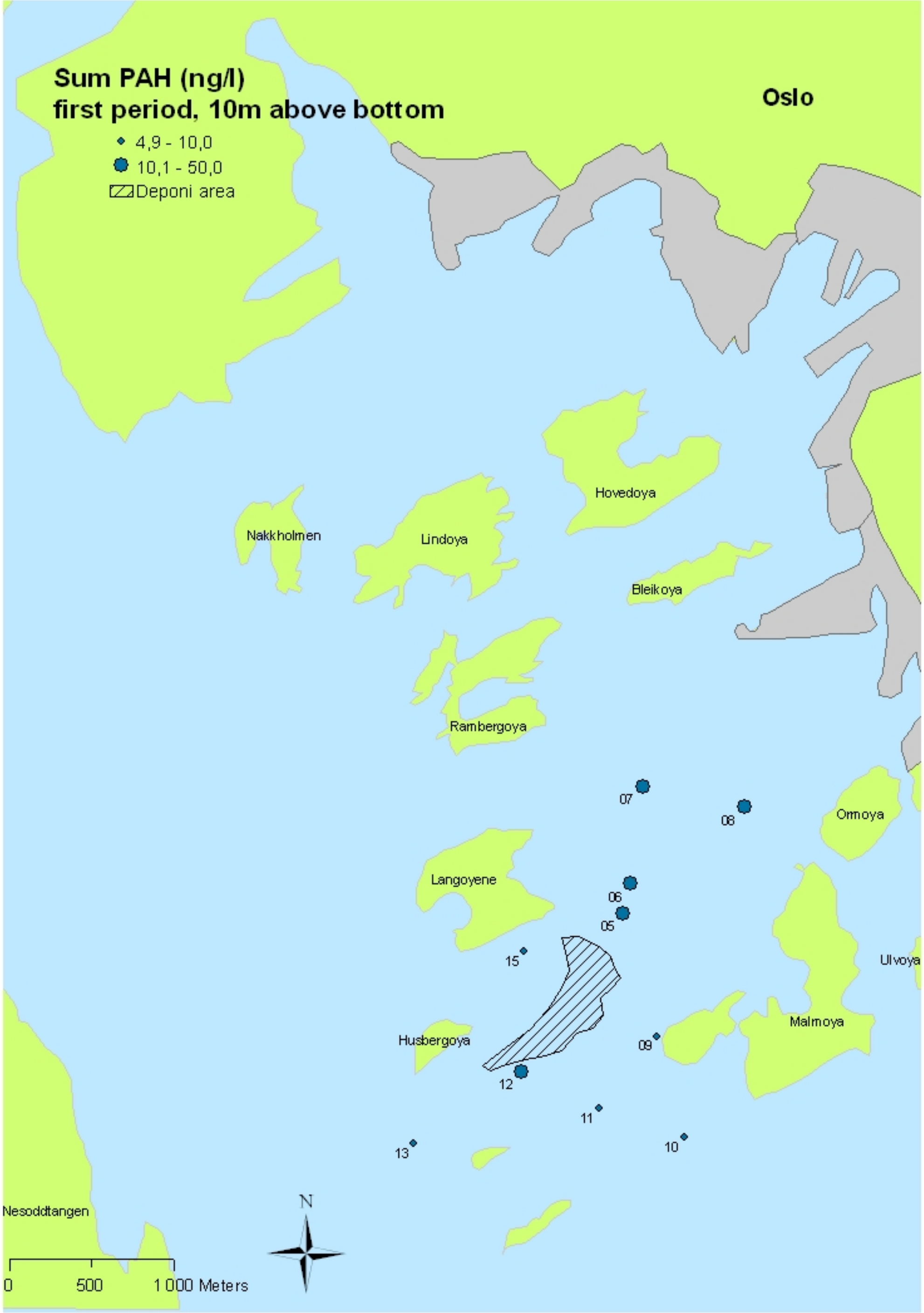

Figure 24. Map showing sum of PAH water concentrations at 10 meter from the bottom in the inner Oslo fjord and especially around the Malmøkalven dumping area from the first sampling period.

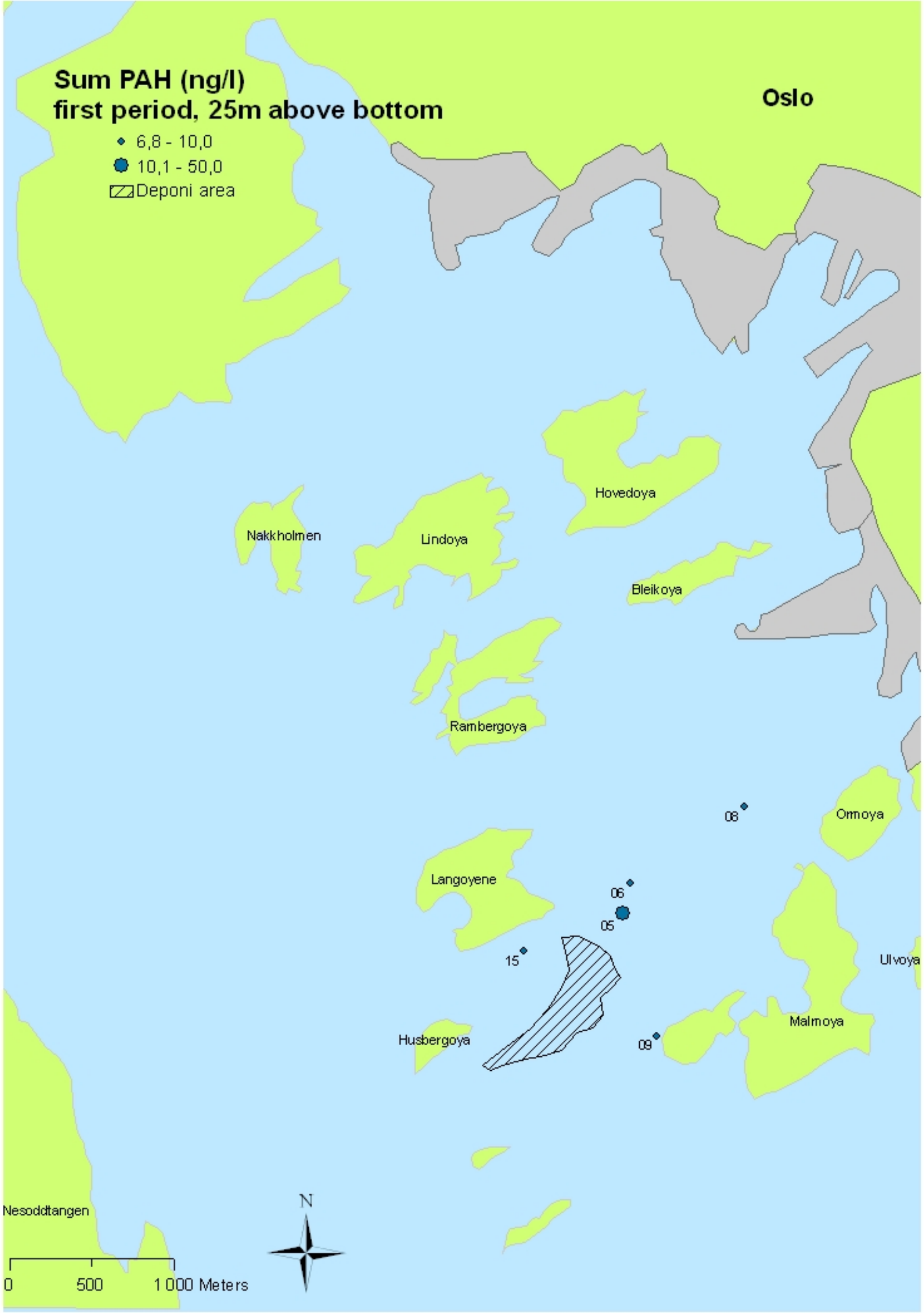

Figure 25. Map showing sum of PAH water concentrations at 25 meter from the bottom in the inner Oslo fjord and especially around the Malmøkalven dumping area from the first sampling period.

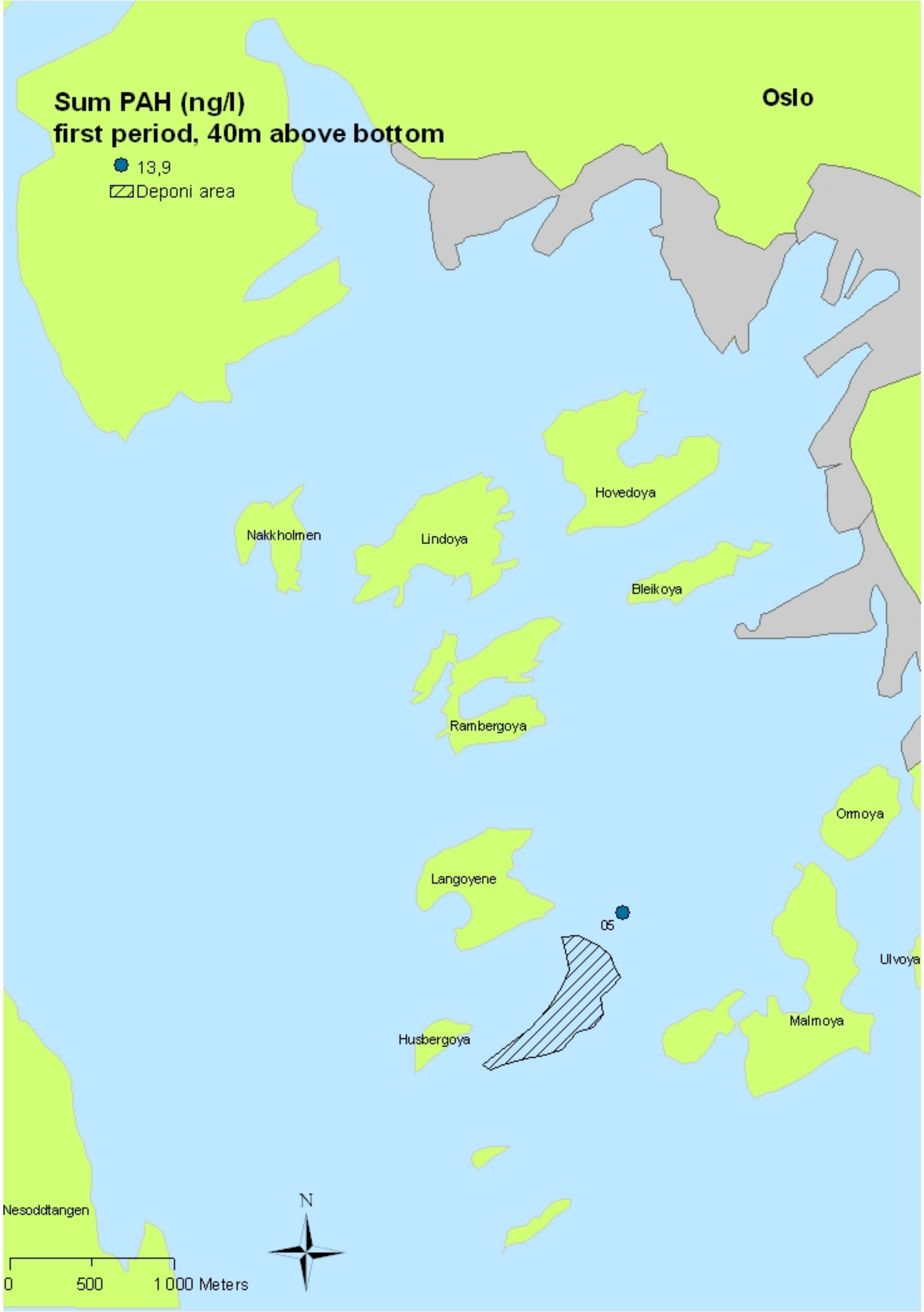

Figure 26. Map showing sum of PAH water concentrations at 40 meter from the bottom in the inner Oslo fjord and especially around the Malmøkalven dumping area from the first sampling period.

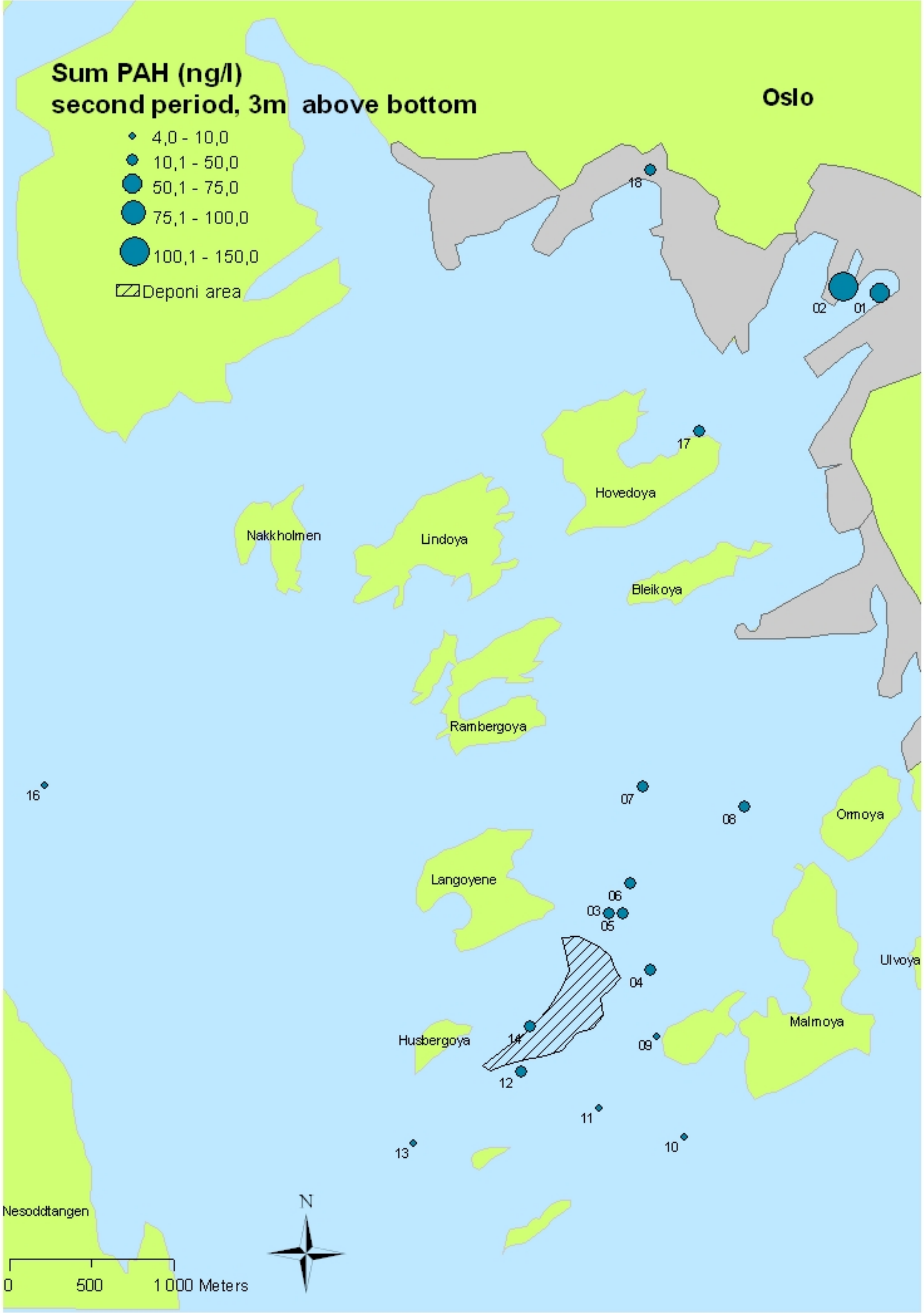

Figure 27. Map showing sum PAH water concentrations at 3 meter from the bottom in the inner Oslo fjord and especially around the Malmøkalven dumping area from the second sampling period.

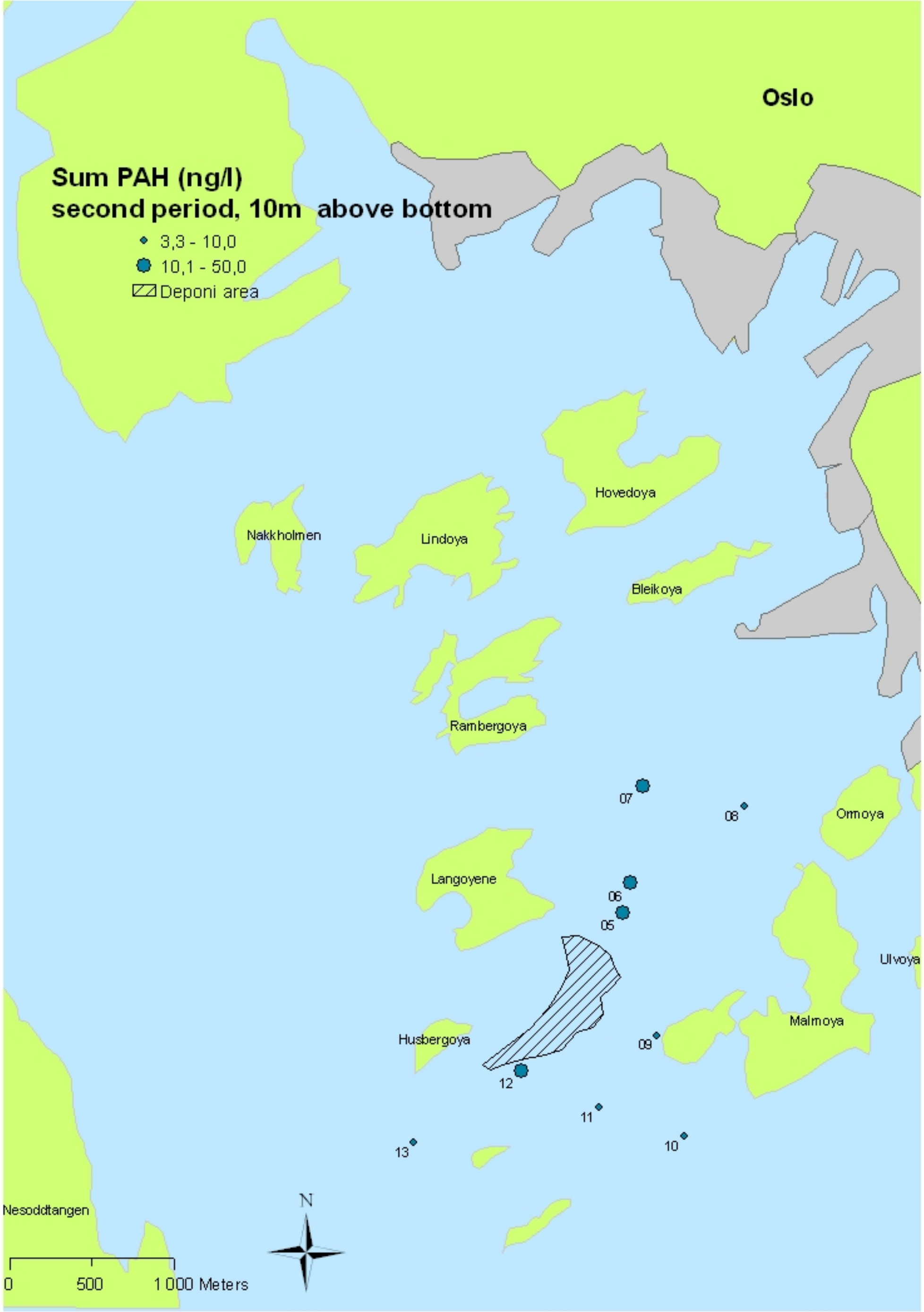

Figure 28. Map showing sum PAH water concentrations at 10 meter from the bottom in the inner Oslo fjord and especially around the Malmøkalven dumping area from the second sampling period.

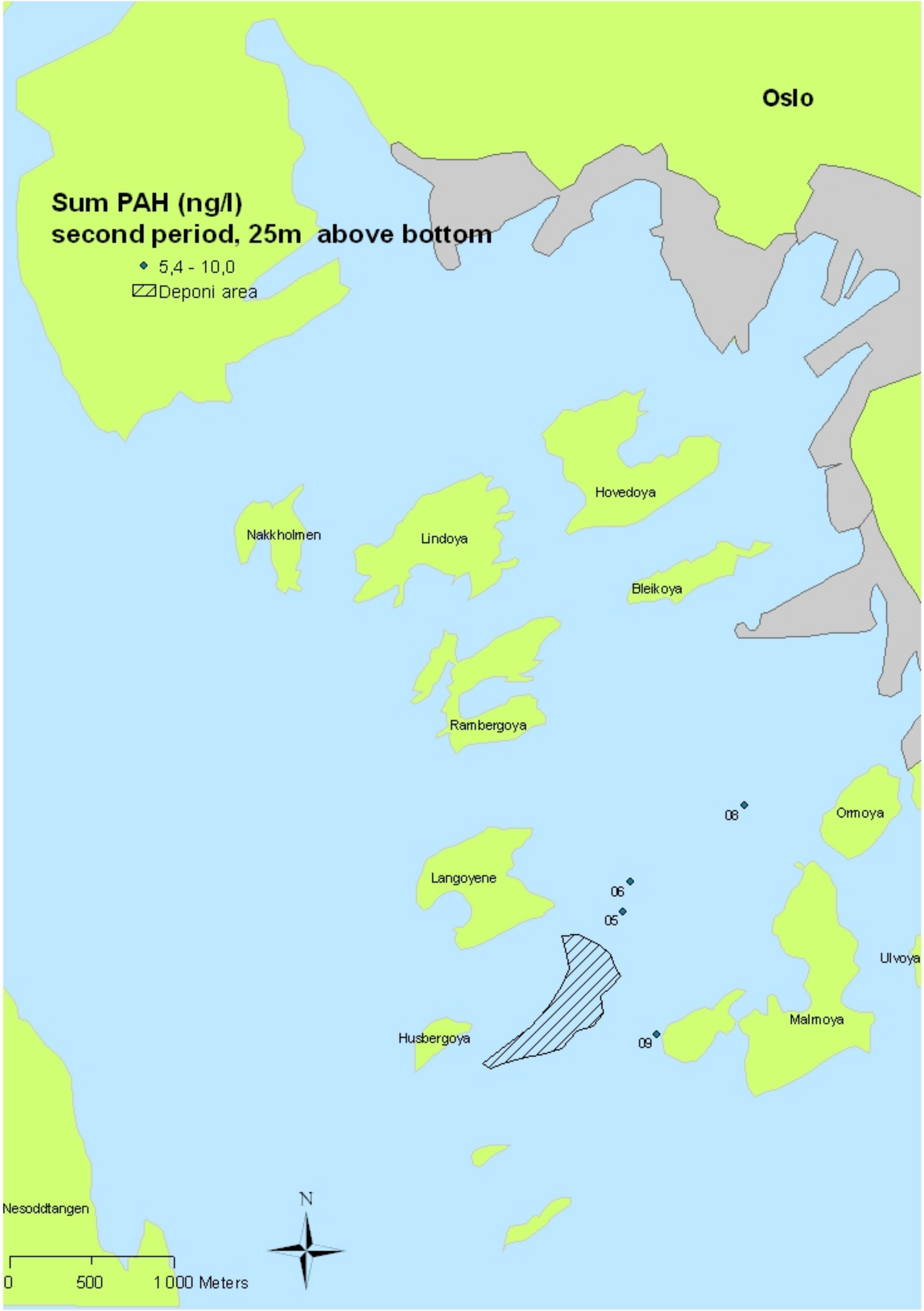

Figure 29. Map showing sum PAH water concentrations at 25 meter from the bottom in the inner Oslo fjord and especially around the Malmøkalven dumping area from the second sampling period.

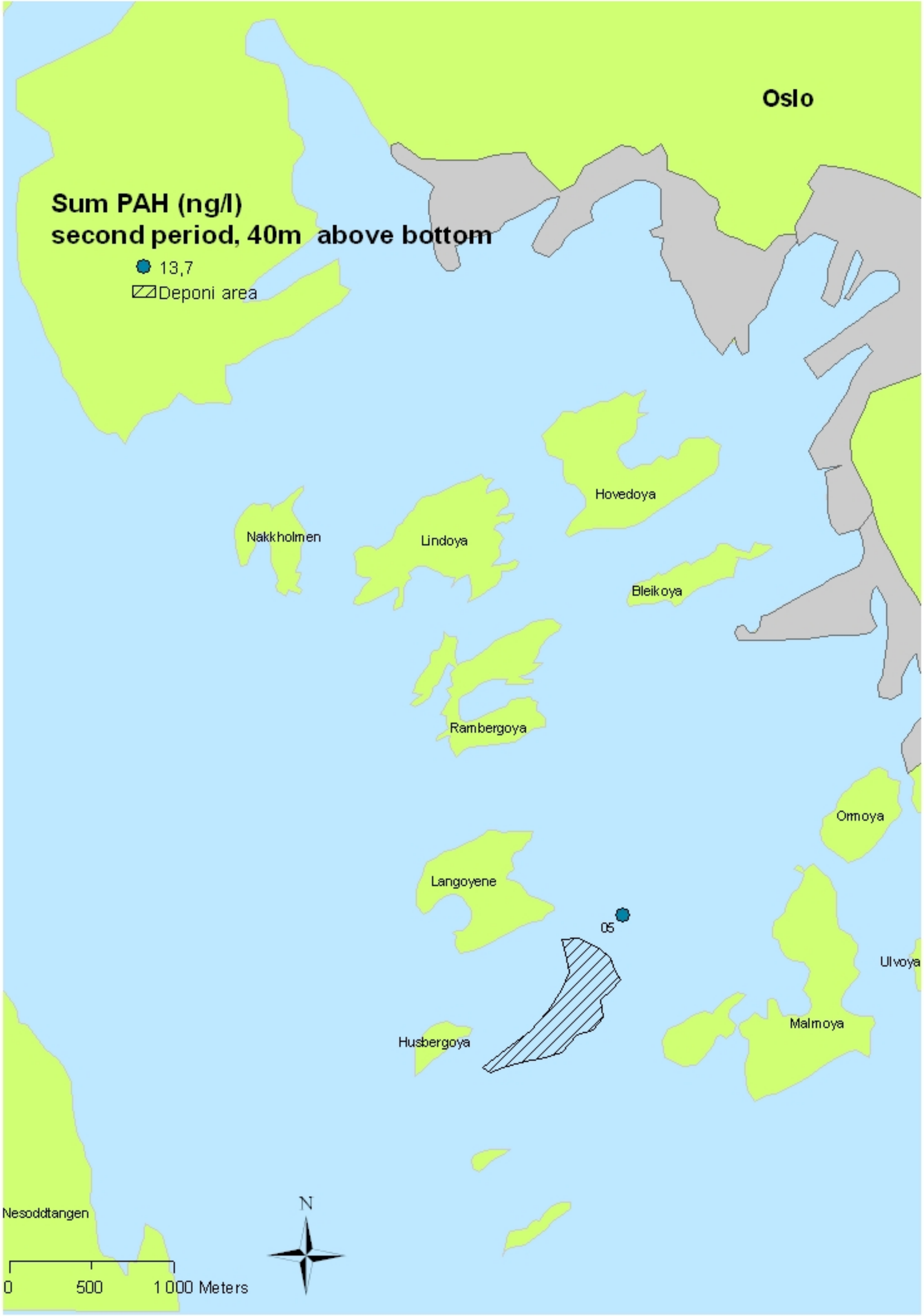

Figure 30. Map showing sum PAH water concentrations at 40 meter from the bottom in the inner Oslo fjord and especially around the Malmøkalven dumping area from the second sampling period.

PCA "fingerprinting"

In order to visualize the relationships in PAH concentrations between the different sampling sites the statistical method PCA was used, whereby patterns in the levels of all PAH amongst the sampling sites were examined. Figures 31 and 32 present comparisons of data obtained from the sites in the first sampling period and in figures 33 and 34 are the data for sampling period 2. 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.

A more deep evaluation will be performed in the summary report. The data looks different between sampling period 1 and 2. The evaluation will continue and also separate PAHs and R-PAHs data.

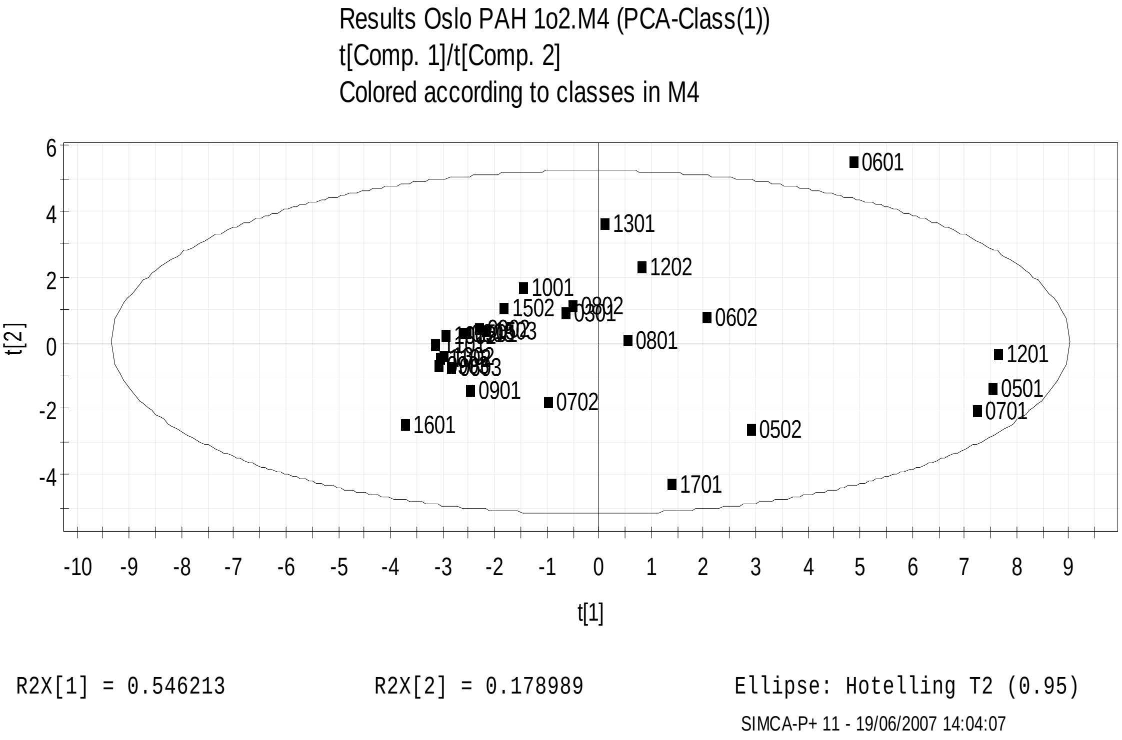

Figure 31. t1/t2 Scatter plot of PAH data from the first sampling period.

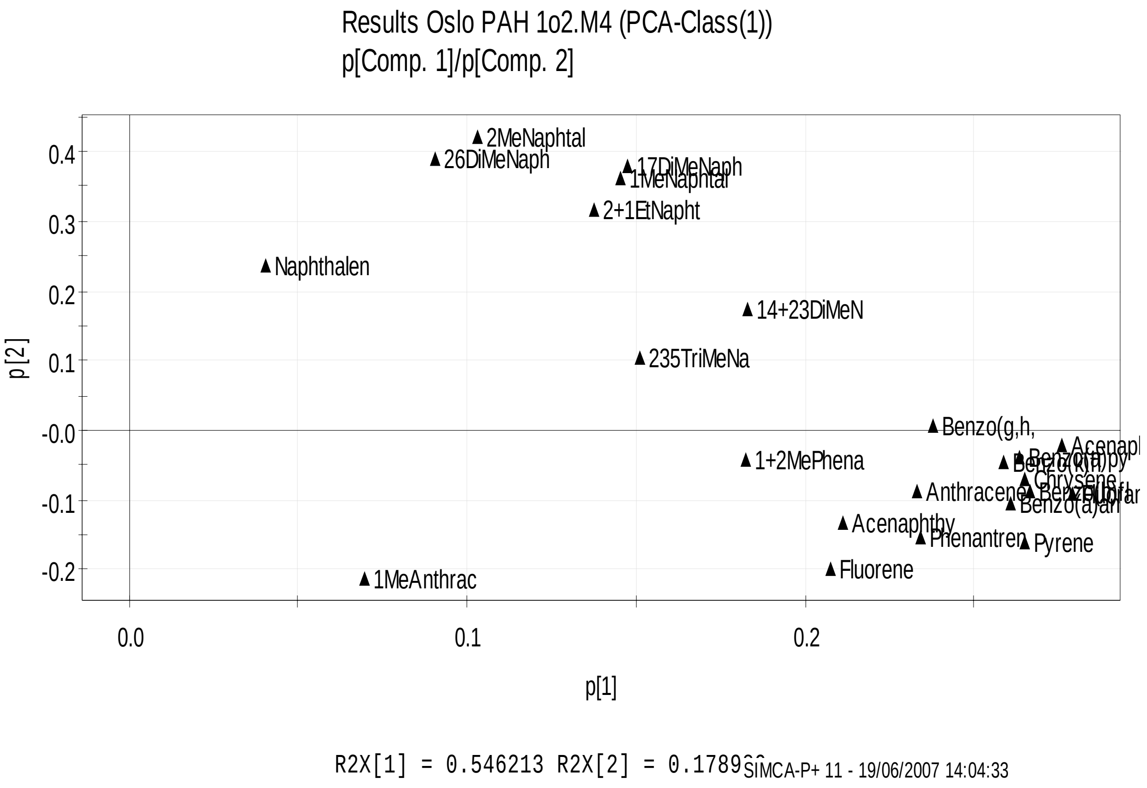

Figure 32. p1/p2 Scatter plot of PAH data from the first sampling period.

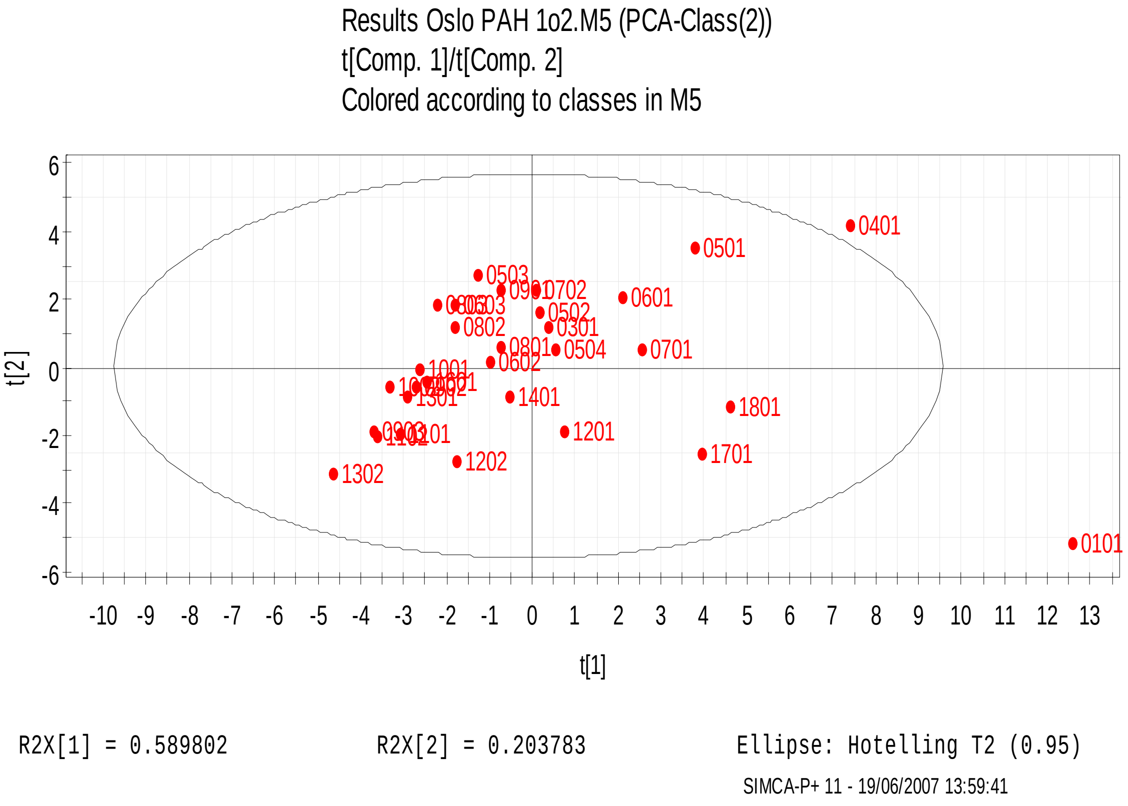

Figure 33. t1/t2 Scatter plot of PAH data from the second sampling period.

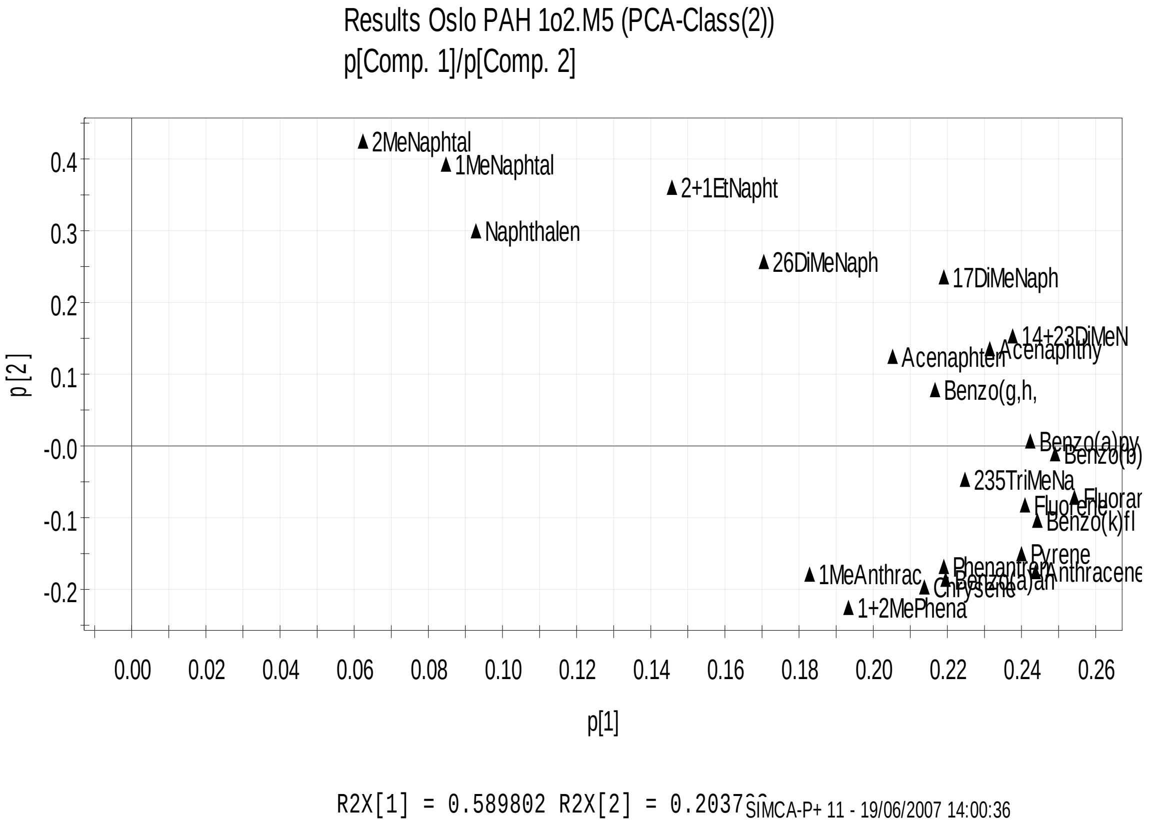

Figure 34. p1/p2 Scatter plot of PAH data from the second sampling period.

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., Zaliauskiene A. *Passive sampling techniques in environmental monitoring.* Field Study Considerations in the Use of Passive Sampling Devices in Water Monitoring. Comprehensive analytical chemistry, Vol. 48, Elsevier B. V., 2007: 311 – 328.

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. 14th 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., Petty, J.D., Lebo, J.A., Almeida, F.V., Booij, K., Alvarez, D.A., Cranor, W.L., Clark, R.C., Mogensen, B.B. 2002. Development of the permeability/performance reference compound (PRC) approach for in situ calibration of semipermeable membrane devices (SPMDs), *Environ. Sci. Technol.* 3: 85-91.

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.

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.

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 , Jegorova I , Bergqvist P-A. Dissolved organochlorine and PAH pollution profiles in Lithuanian and Swedish waters. 12th Annual Meeting SETAC Europe, Vienna, Austria 13-17 May, 2002.

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