Oslo Fjord

Investigation of chemicals released from Malmøkalven dumping area.

Polychlorinated biphenyls

ExposMeter AB

Tavelsjö

2007 03 24

Project report 2006N-001

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Definitions

The following terms and definitions are used in the 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) – Sampling membrane consisting of a standard Semipermeable Membrane Device (Standard SPMD)

ExposMeter Metal Devise – Sampling membrane consisting of a standard Diffusive Gradient in Thin film Device (DGT)

Standard SPMD - 2.5-cm wide (layflat) by 92-cm-long LDPE tubes (70-95 µm wall thickness and surface area is $\cong$ 450 cm^2 or $\cong$ 100 ,cm^2/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 and used for EHD.

Field control EHDs - quality control EHD to record any chemical accumulated in sampling devices during production, transportation, deployment, retrieval and analysis.

Performance reference compounds (PRCs) - compound that has low to moderate fugacity to the EHD, and which does not interfere with the sampling and analytical processes. It is spiked to EHD triolein during assembly of EHD in the laboratory.

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

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Summary

During autumn 2006 ExposMeter AB were contacted by the foundation Neptun in Norway regarding an investigation of pollutants transported to the surroundings of the dumping area in Oslo fjord. The task given were to investigate if chemicals can be found outside the dumping area, which originate from the dumping area itself, i.e. from the excavated sediment which is pumped down to the bottom close to Malmøkalven. The investigation should start as soon as possible

Other agreements were that after ExposMeter AB presented the investigation strategy and Neptun accepted it, no-one will interfere with ExposMeters work, sampling plan, analysis, evaluation and reporting of the results. The conclusions should be solely ExposMeter AB opinions. Neptun encourage the publishing of obtained results in open scientific literature and gave the full rights to ExposMeter AB to do so.

The use of passive samplers as ExposMeter Hydrophobic allow the sampling of only in water truly dissolved compounds, which means that the measured concentrations is readily available for bioaccumulation in biota. It also means that compounds have been released from the sediment particles during the remediation process and thus increasing the toxic potency of the chemicals.

The investigation has shown that:

1. Elevated levels of PCBs are found outside the dumping area.
2. The levels decrease with the distance from the dumping area.
3. Elevated levels of PCB are found from bottom up to 40 meters above sea bottom close to the dumping area.
4. The PCB “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.

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

Introduction

Passive monitors, **ExposMeter Hydrophobic Device** (EHD, based on SPMD technology) and **ExposMeter Metal device** (EMD, based on DGT technology), were used to detect transport of chemicals from dumping area. The installations are easy to perform. Without battery and electricity they can measure a 21 day time weighted average value of dissolved individual chemical compounds and they can also integrate toxicity in the water. EHD as a monitor of dissolved concentrations has advantage over measurement of particles in the water (turbidity) as a pollution spreading indicator, since it can detect specific compounds and mixtures/fingerprints. During the sampling no metabolism/degradation of the chemicals occurs and it is no differentiation of sampling depending on pollution level or water condition. By a proper design of sampling locations and good chemical analysis an EHD can suggest pollution sources and serve as an efficient tool for risk assessment.

Results from the analysis of extracts from EHDs with performance reference compounds give us the opportunity to calculate time weight average concentration (TWA) of pollutants in the water during whole deployment time [1]. EHDs are usually deployed for 3- 4 weeks. Longer time of deployment can lead to the equilibrium sampling of some of the compounds by the sampler. According to theory of the uptake of pollutants by EHD described by Huckins et. al. only kinetic uptake phase of the compounds give us possibility to calculate the integrated water concentrations from the amount accumulated in the SPMDs. We have combined two deployments following one after each other which gave us the knowledge about TWA concentrations of the compounds in water during 3+3 weeks from October 30 till December 12 2006.

In addition to the sampling performed in the vicinity of the marked dumping area, we also sampled water close to the excavation are in order to receive a basis for the fingerprinting when tracing to origin of the water pollution (see figure 1). The sampling at Hovedøya and Akers brugge were done due to public discussions in these areas and an additional sampling during this intense sampling period might give some more insight into the situation at these areas as well.

Following considerations were applied in the design of the sampling program:

- sampling points were chosen in the different depths with the lowest 3 m from the bottom of the water;
- monitors were deployed in the places of bottom water flows;
- sampling points reflected gradient of the pollutant spreading from the dumping area.
- monitors was placed near the sediment excavation area to get a finger print of pollution.
- deployment locations also considered possible influence from other pollution sources.

Figure 1. Sampling places in Oslo Fjord during the period 30.10 – 12.12 2006. Location 15 missing in the map.

Method description

From the first scientific articles published two decades ago, passive monitors have developed into the world wide accepted and standardized method for:

- screening of presence of pollutants
- monitoring of temporal and spacial pollution trends
- toxicity assessment
- investigative monitoring

SPMDs (also EHDs) is the most established passive monitor in the world for hydrophobic organic compounds ($\lg K_{ow} > 3$) with over 200 scientific publications and 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 approx. <600 Daltons such as polyaromatic hydrocarbons (PAHs), non-polar pesticides, polychlorinated biphenyls (PCB), polychlorinated naphthalenes, polychlorinated dibenzofurans, polychlorinated dibenzodioxins, polybrominated diphenyl ethers, polychlorinated benzenes, alkyl phenols (nonyl phenols) etc.

Standard commercially available SPMDs (EHDs) are modeled after original USGS (United States Geological Service) design. Use of standard SPMD design ensures that the sampling rate calibration data and theory are applicable for estimating ambient water concentration of analytes. Use of standard SPMDs gives possibility to compare data between studies, since standard configuration is used globally in most SPMD applications (Figure 2).

Figure 2. 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. Cans are opened and SPMD exposed to the air just before deployment in the water. The time in air should be minimized and UV light should be avoided. A stainless steel protective device is used for deployment of EHDs in the water. The device consists of spiders for mounting of EHDs (figure 2) and the protective cage which avoid mechanical damage of the membranes (Figure 3).

Figure 3. 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.

For keeping the devices in place during the whole sampling period heavy anchors are used, and the anchor is connected to a floating and indicating device on the surface of the water. On the rope between the anchor and the floating device, the EHD can be attached to different specific depth. A deployment scheme of the EHD device in Oslo fjords is presented in Figure 4.

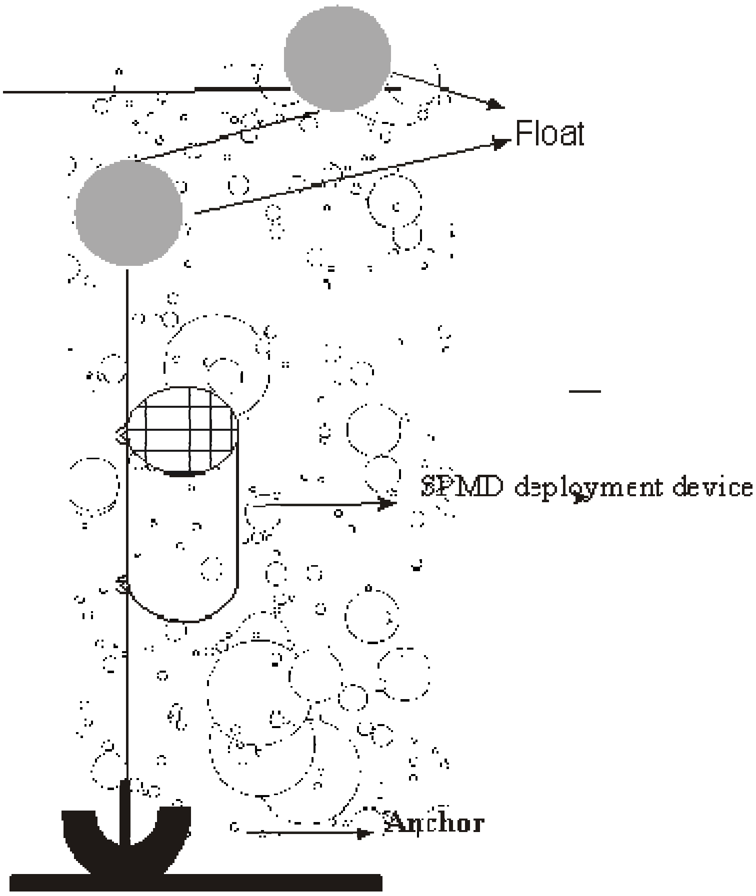

Figure 4. Deployment in water of protective cage with SPMDs inside. Heavy anchor on the bottom and floating devices lifting the rope to the surface.

After 21 days deployment, the samplers wee retrieved and membranes put back in the airtight tin cans. During this time, the membranes were protected from sun light and also mechanically slightly dried from water and the fouling on the surface of the membrane. In figure 5 an example of retrieved membrane is shown.

Figure 5. Example on EHD membrane retrieved from the Oslo fjord after 21 days of exposure.

Analysis of compounds

Compounds analyzed in the first analysis stage are presented in Table 1. Analyses were performed in accredited laboratory. The laboratory has accreditation for analysis of SPMD samples targeting many different compounds. The calculation of water dissolved concentration is still not under accreditation, but the intention is to include also this part into the accreditation.

In short the analytical method is as follow. Obtained membranes are mechanically and chemically cleaned on the outer surface. The target compounds are dialyzed during 40-72 hours. Many labeled compounds are added to the dialysate for quality control and quantification purposes. After concentration of the dialysate, the compounds were cleaned on different liquid chromatography columns. The samples were again concentrated and labeled recovery standards were added for adjusting the losses during cleanup.

The analysis were performed on a Finnigan ion trap HRGC/LRMS running in MS/MS mode. Individual response factors for each of the quantified PCB congeners were applied. Results were corrected for blank levels of PCBs and adjusted for recovery values. Performance reference compounds were analyzed in three separate samples and suitable factors were applied in the calculation of water concentration based on a mean value of these three analysis. Necessary physical factors concerning each of the PCB congener were found in the scientific literature. In figure 6 a short graphical explanation of the analytical work is shown.

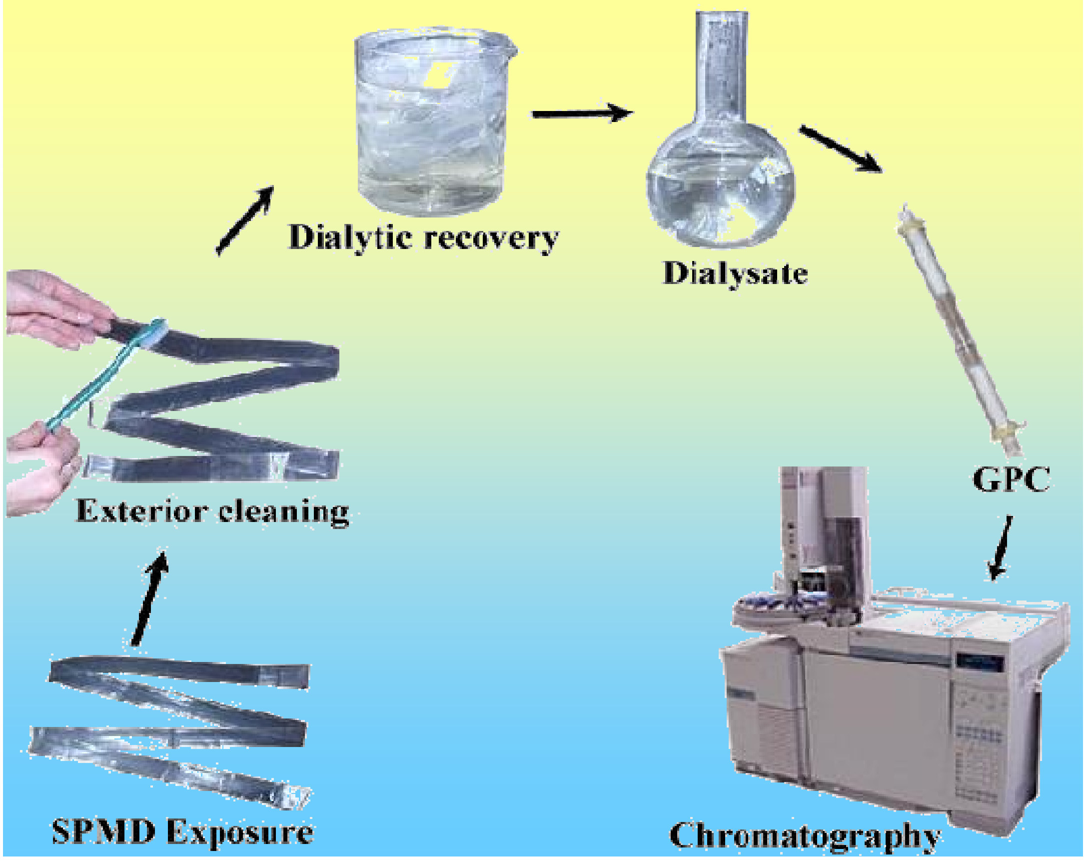

Figure 6. Schematic representation of SPMD treatment

In order to track sources and to do “fingerprinting” work we decided to analyze a large number of PCB congeners. In total 79 peaks (Table 1) were quantified. The lower chlorinated congeners are most common in water sampling, but also the larger molecules could sometimes be found in detectable quantities. Usually the difference between duplicate samples is below 20% including both sampling and analysis.

Table 1. PCBs congeners analyzed in the extract from EHDs.

TriCBs
PCB19
PCB18
PCB17
PCB27+24
PCB16+32
PCB26+25
PCB28+31
PCB33
PCB22
PCB37
TetraCBs
PCB54
PCB53
PCB51
PCB45
PCB46
PCB52
PCB49
PCB48+47
PCB44
PCB42
PCB41+64+71+72
PCB74
PCB70
PCB80+66
PCB60+56
PCB81
PCB77
PentaCBs

PCB104
PCB95
PCB84+89+92
PCB101
PCB99+113
PCB119
PCB97
PCB87
PCB110
PCB123
PCB118
PCB114
PCB105
PCB126
HexaCBs
PCB155
PCB148
PCB151
PCB135+144
PCB149
PCB153+168
PCB130
PCB163+164
PCB138
PCB158
PCB128
PCB167
PCB156
PCB157
PCB169

HeptaCBs
PCB188
PCB179
PCB176
PCB178
PCB187
PCB183
PCB174
PCB177
PCB171
PCB180
PCB191
PCB170
PCB189
OctaCBs
PCB202
PCB201
PCB199
PCB203+196
PCB194
PCB205
Nona CBs
PCB208
PCB206
PCB207
DecaCBs
PCB209

One way to present the data, in order to see the relationship between samples from different locations, is to use PCA (Principal componenet analysis, statistical analysis and presentation). This statistical method compare the pattern of all analyzed and quantified

PCBs at all locations at the same time. The presentation will be done by projection from a multidimensional space down to a two-dimensional plane on the paper.

Results

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

PCB 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 7 the levels at site 1 are 3500 pg/L and all other sites has levels below 1100 pg/L. To make the picture clearer we have magnified the y-axis in figure 8, so the difference between the other sites can be visible. 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.

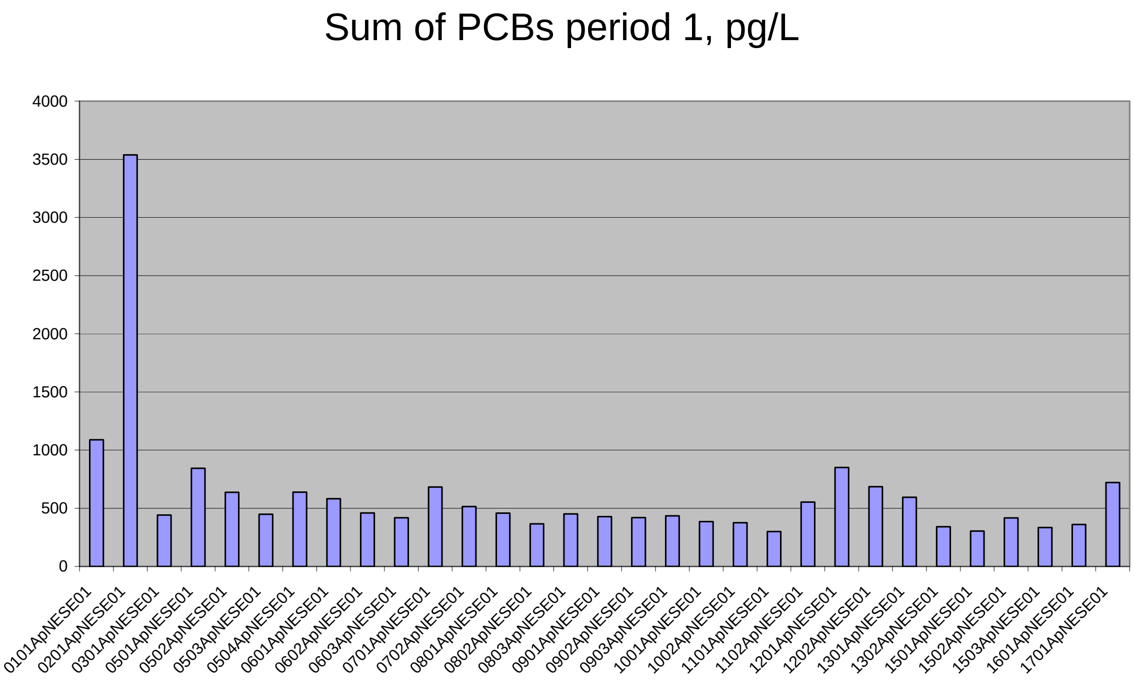

Figure 7. Sum of all PCB congeners sampled during period 1 at the different sites in pg/L.

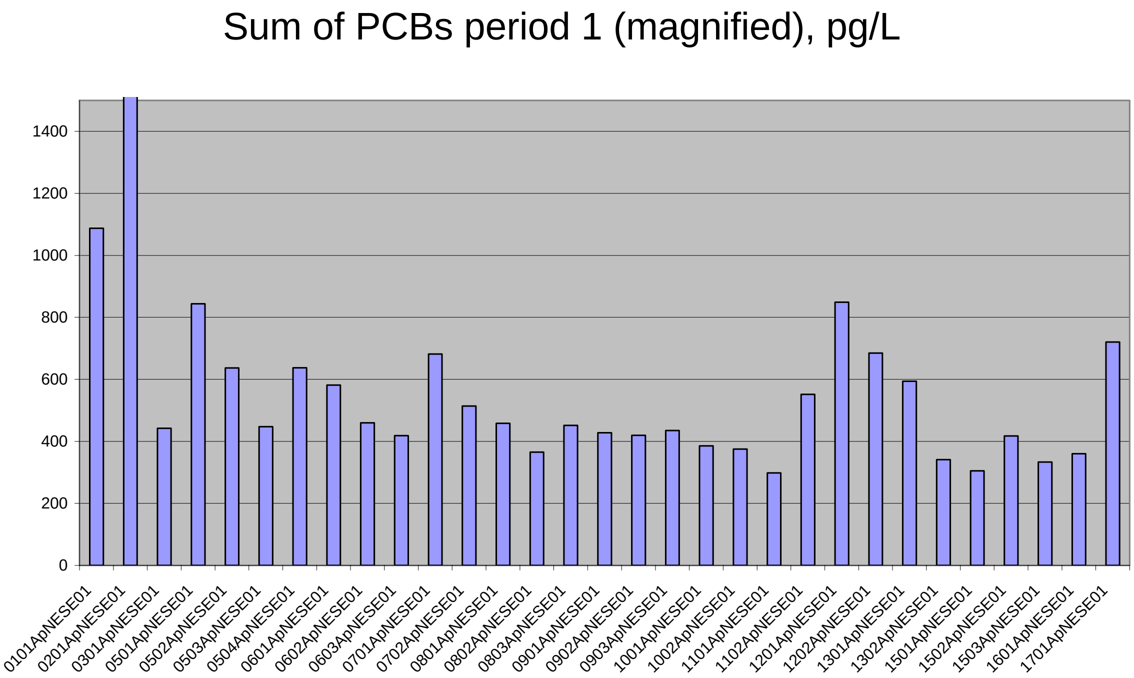

Figure 8. Sum of all PCB congeners sampled during period 1 at the different sites in pg/L. The y-axis is magnified.

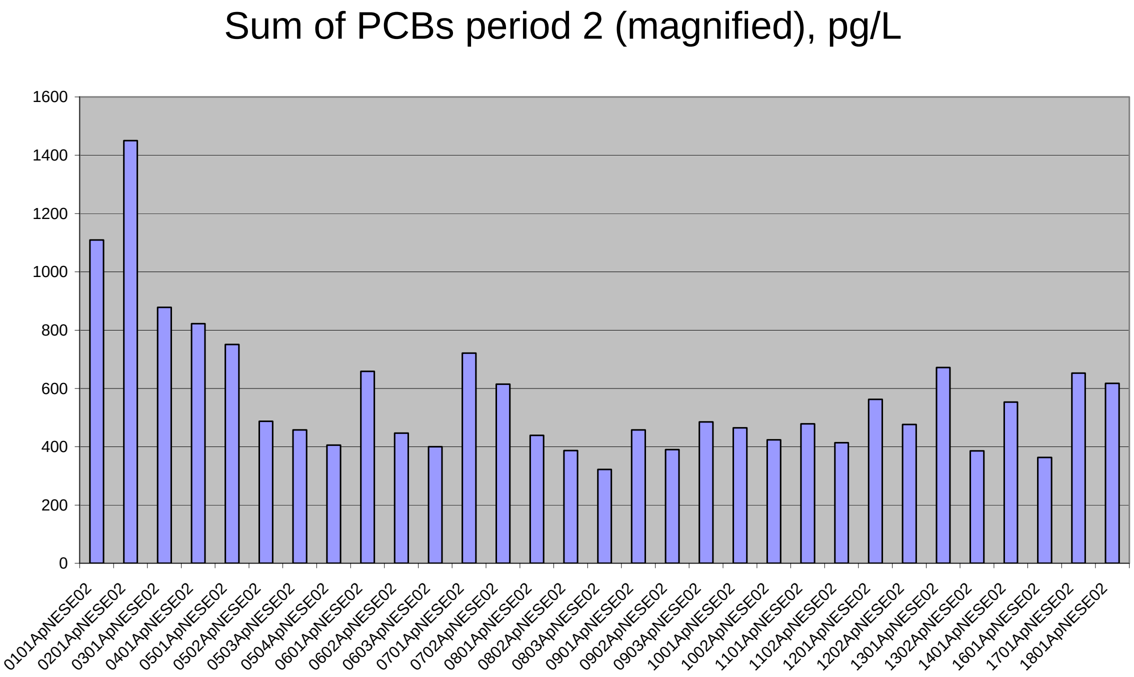

Figure 9. Sum of all PCB congeners sampled during period 2 at the different sites in pg/L.

The sum of each congener group of PCB is shown in figure 10. The y-axis is magnified due to the high level of tetra-CB at site 2. The levels of tri-CB are always lower in the samples compared to the tetra-CB, suggesting that the origin is a weathered source rather than a source of fresh technical PCB. This is also true for the extreme sample at site 2.

It can also be seen a small difference in especially samples from site 13, where hexa- and hepta-CB is elevated in relationship to the other congener groups. The same can be seen in figure 14, representing the sampling sites from period 2.

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

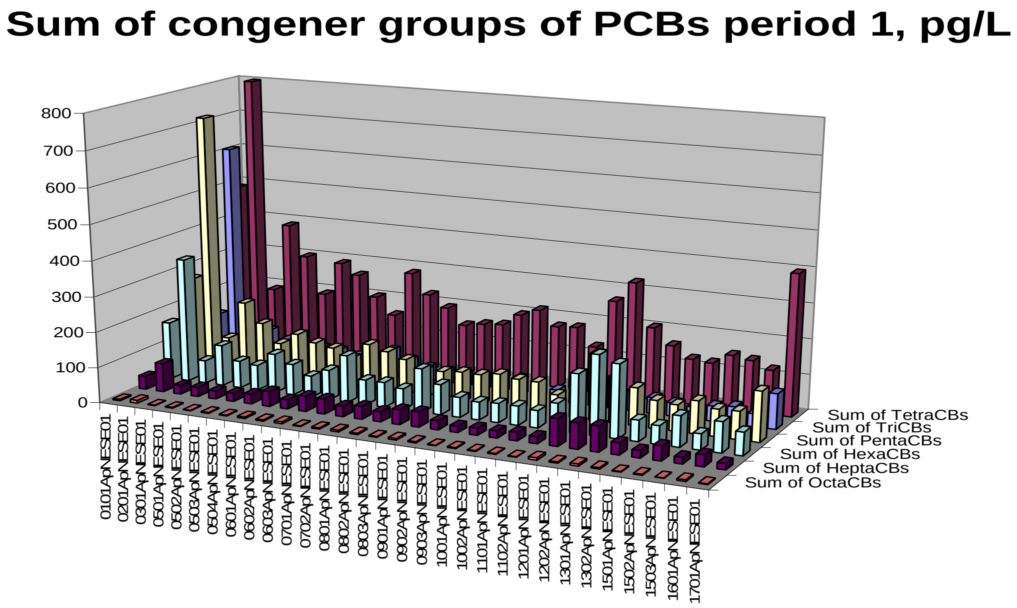

Figure 10. The sum of PCB for each congener group is shown in pg/L. The y-axis is magnified. For visibility Tri-CB is moved in z-axis.

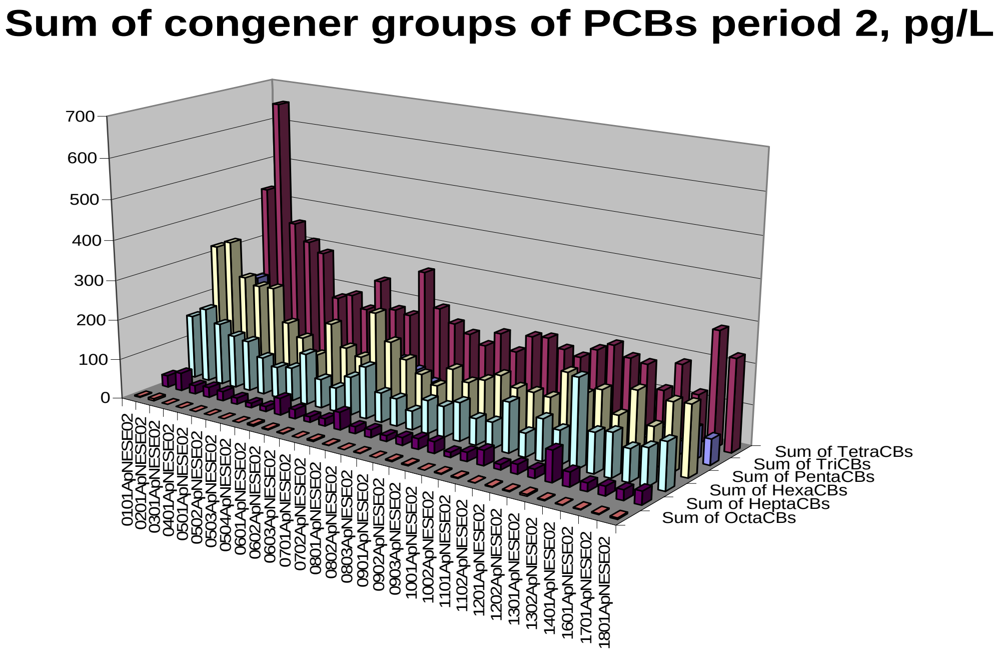

Figure 11. The sum of PCB for each congener group is shown in pg/L. For visibility Tri-CB is moved in z-axis.

As an example the tetra-CB isomer pattern is presented in figure 12 for period 1 and in figure 13 for period 2.

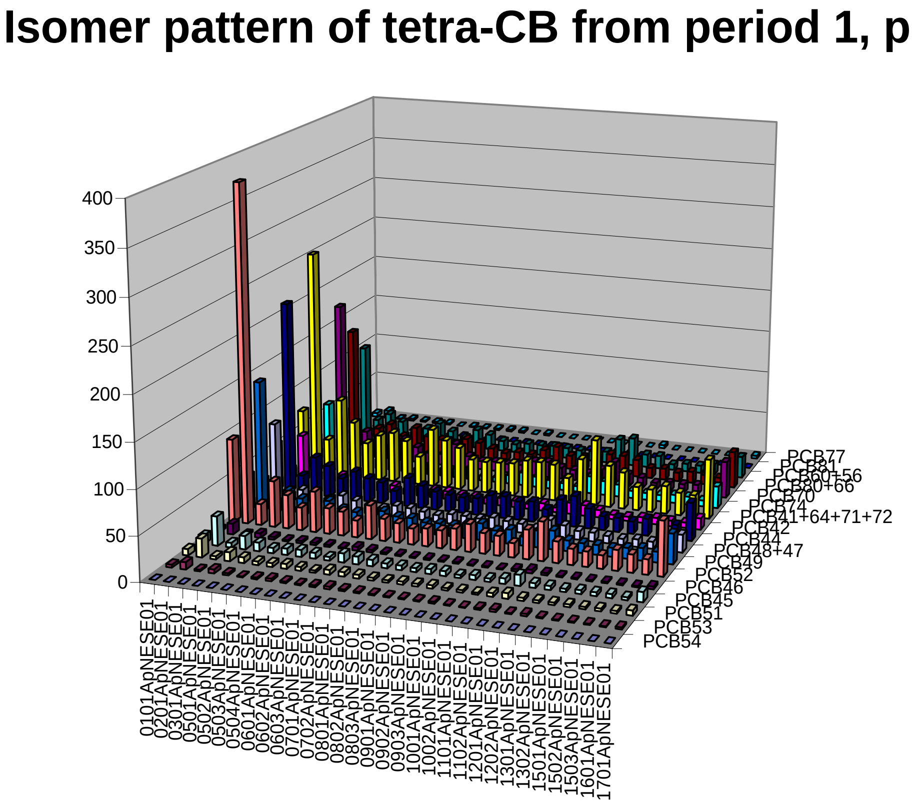

Figure 12. Isomer pattern of tetra-CB from period 1from different sites in the Oslo fjord study, pg/L.

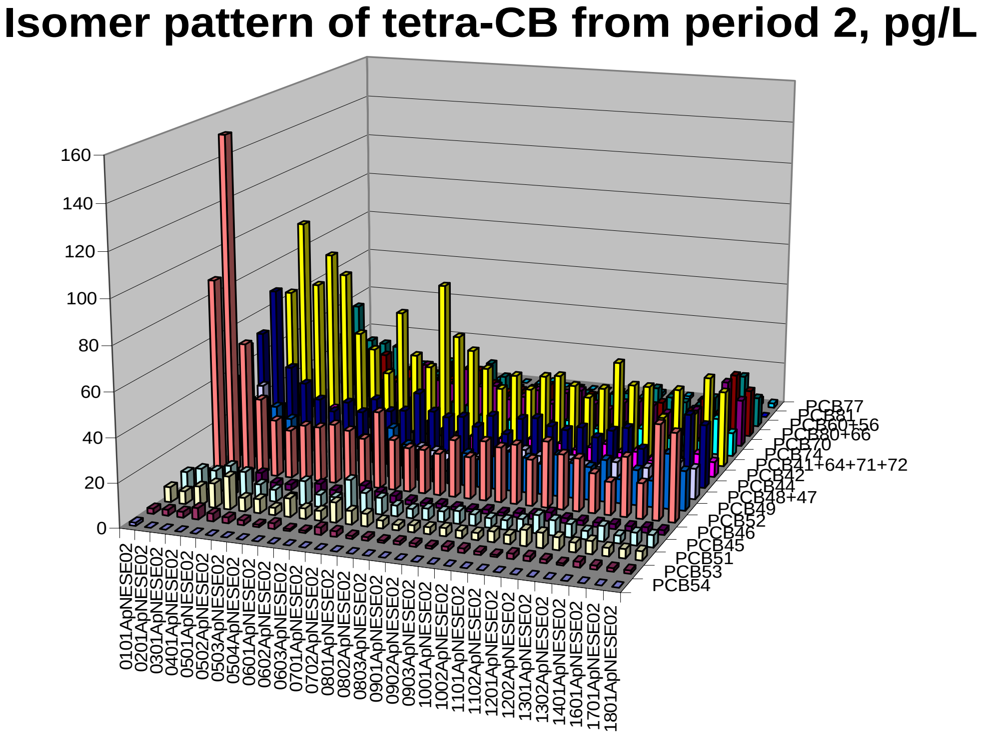

Figure 13. Isomer pattern of tetra-CB from period 2 from different sites in the Oslo fjord study, pg/L.

Mixing of water

The area where the "deep sea" dumping is performed is very difficult to explain from a sea current perspective. Between the islands the current is shifting due to many different reasons. Bottom current velocity is measured to be around 2 cm/second in the area. The salinity was measured during both of the sampling periods. One reason for changes in salinity at different depths can be the sea current, but also river runoff and wind can cause differences. This will change the mixing and spreading of pollutants in the area during the sampling time as well as changing the dilution factors of the chemicals. The mixing areas at 25 meter from sea bottom can be seen in figure 14, where the darker areas show larger changes of the salinity during our study. To the north the sea mixing seems to be rather stable and small, which con suggest a steady flow north at this point during the study.

In figure 15 this variation are described at several depths showing large variation also with depth.

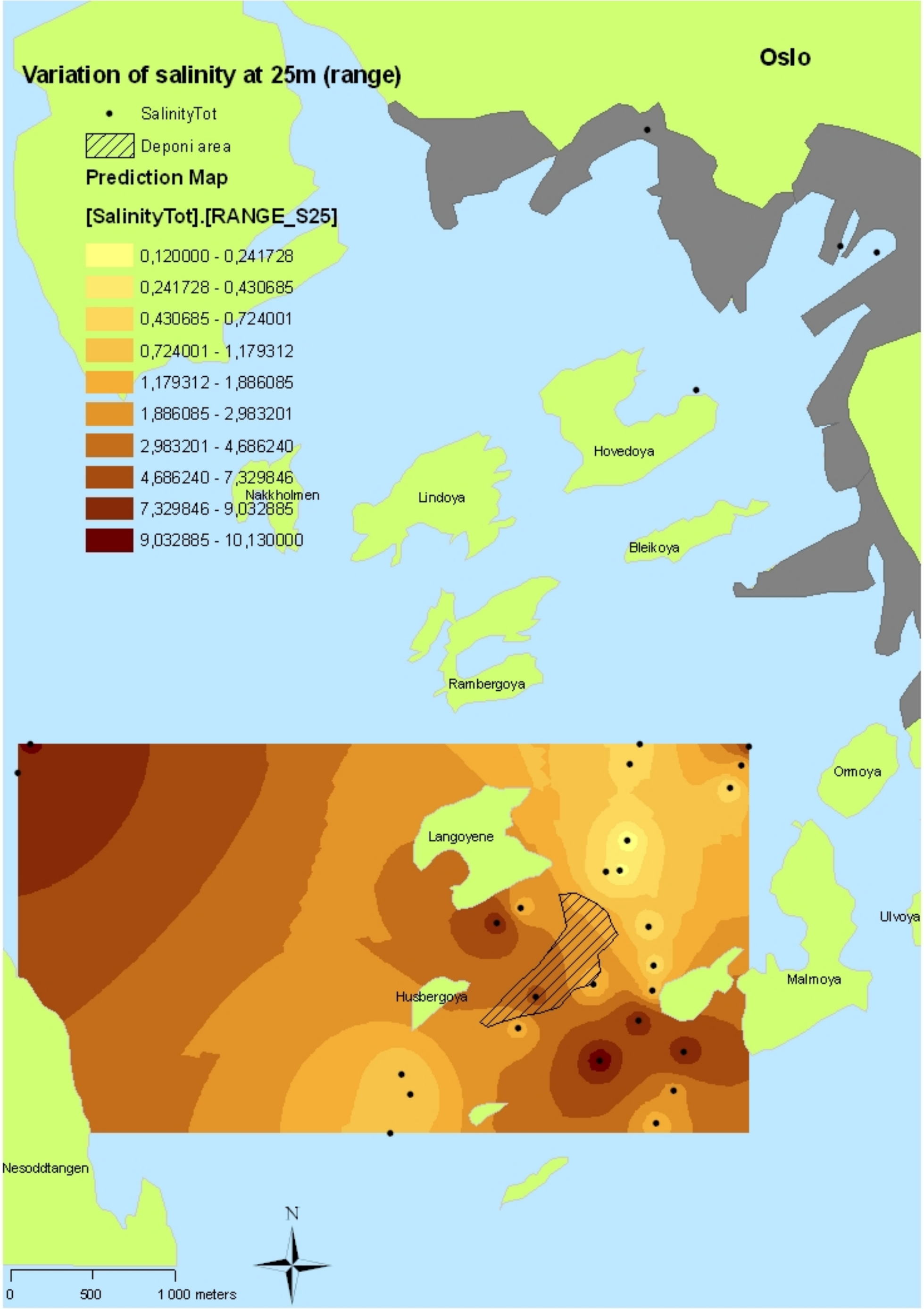

Figure 14. Variation of salinity at 25 meter from sea bottom.

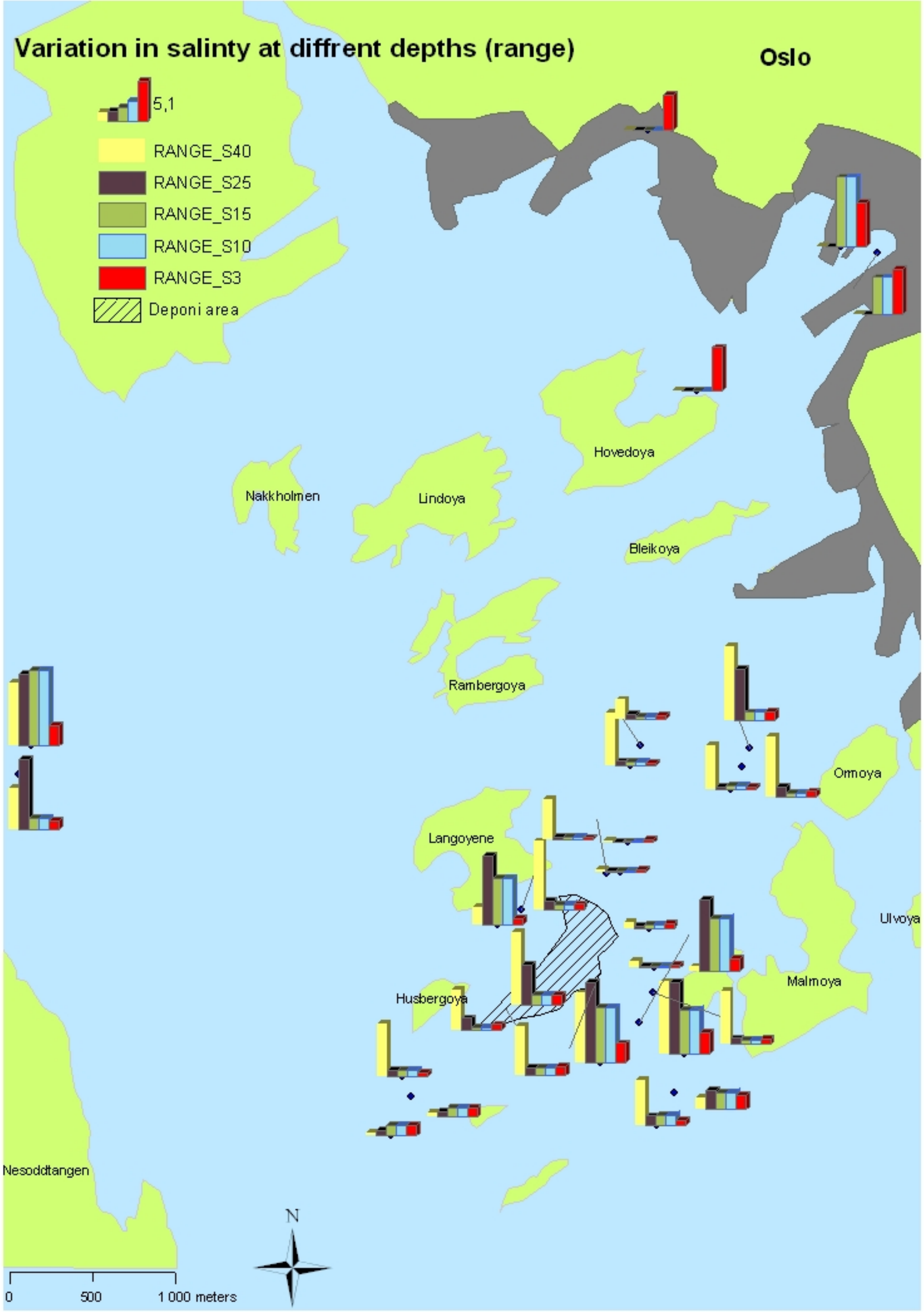

Figure 15. Variation of salinity at different depths during the study.

Concentrations of PCBs on maps

The concentration levels at different sites can also be explained on maps. The larger a dot is the higher is the concentration. In figure 16 the sum PCB levels from period 1 at 3 meter from sea bottom is shown. The highest levels were found in the Bjørvika sampling sites and then the sites 5 and 12 which are in the vicinity of the dumping area. The reference site 16, which is located outside the tip of Näsudden showed the lowest concentration. Decreasing levels can be found to the north where site 6 and 7 is located. Surprisingly elevated levels can also be found at site 13, which is outside the shallow part to the southwest. As pointed out earlier the PCB pattern were also little different at this site.

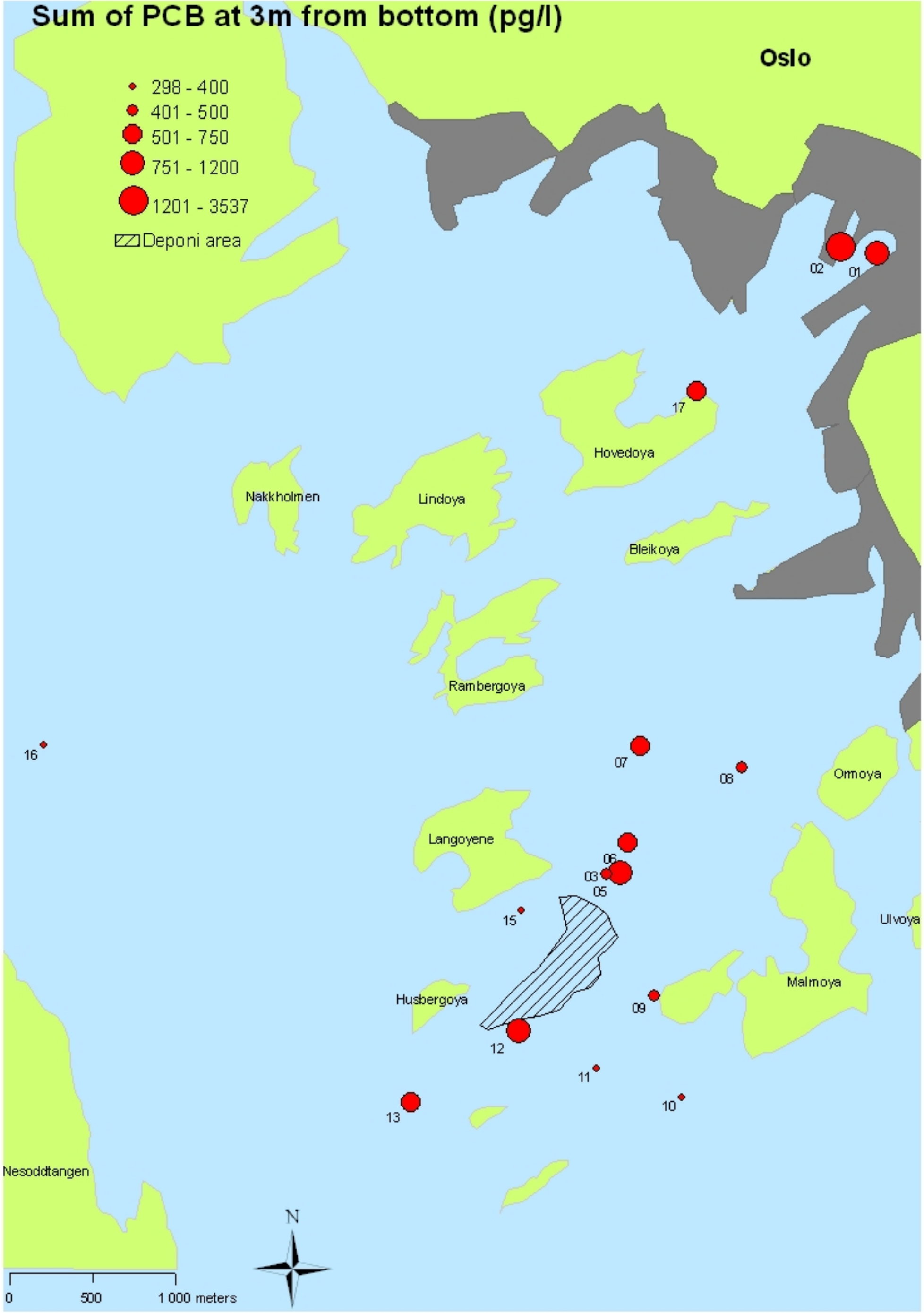

Figure 16. Map showing sum of PCB water concentrations at 3 meter from the bottom in the inner Oslo fjord and especially around the Malmøkalven dumping area from the first sampling period.

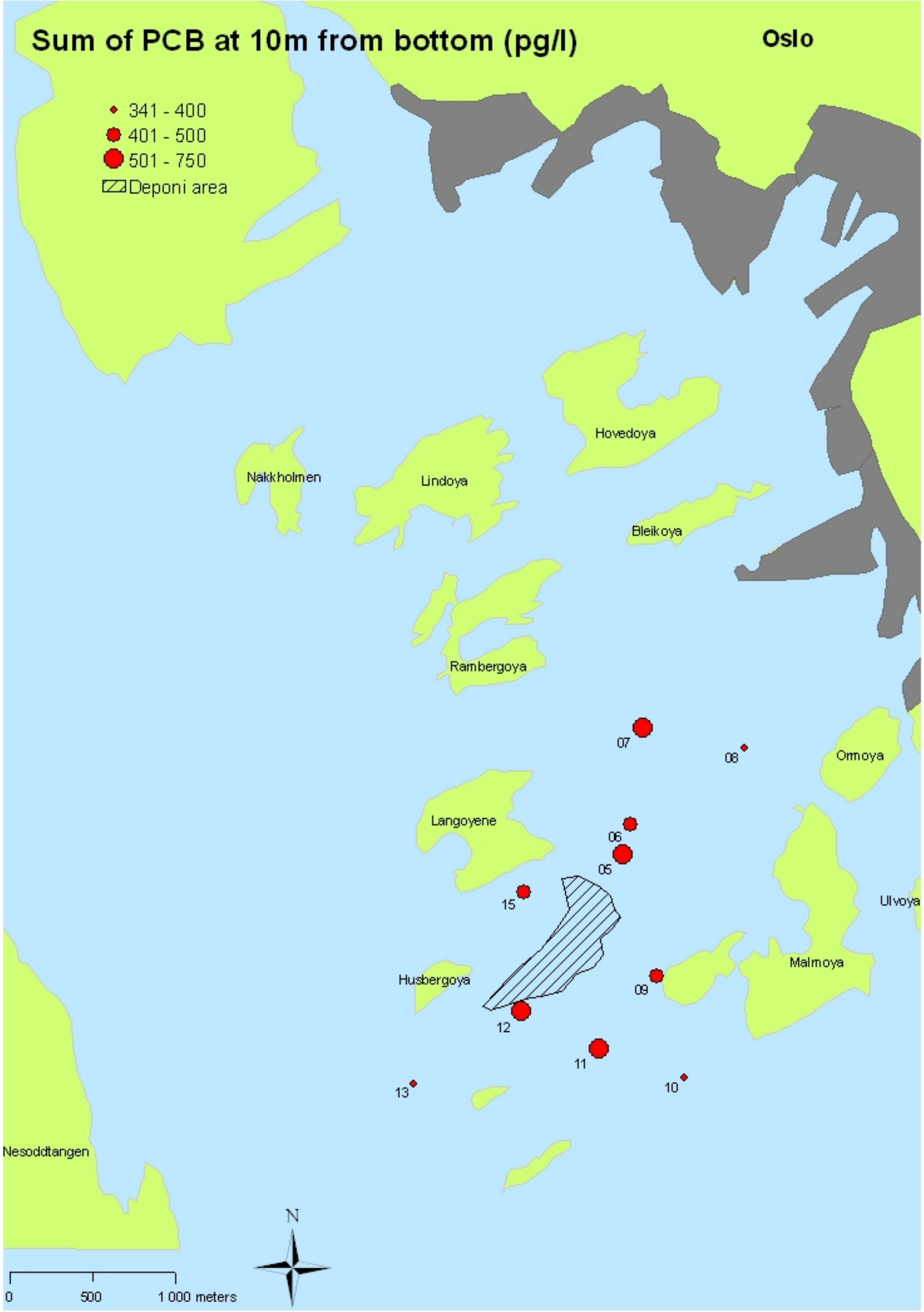

Figure 17. Map showing sum of PCB water concentrations at 10 meter from the bottom in the inner Oslo fjord and especially around the Malmøkalven dumping area from the first sampling period.

In figure 17 are the concentrations of sum PCB showed from the 10 meter from the bottom samples. All sites were not sampled on all distances from the bottom. Again elevated levels can be seen to the north at site 5 and 7, and to the south at site 12 and also at site 11.

To the north are the water concentrations of sum PCB over 400 pg/L at site 5, 6, 8 and 9. Figure 18 show the distribution of PCB still going to the north. In figure 19 elevated concentrations of sum PCB over 500 pg/L can be seen even at 40 meter from the sea bottom at site 5.

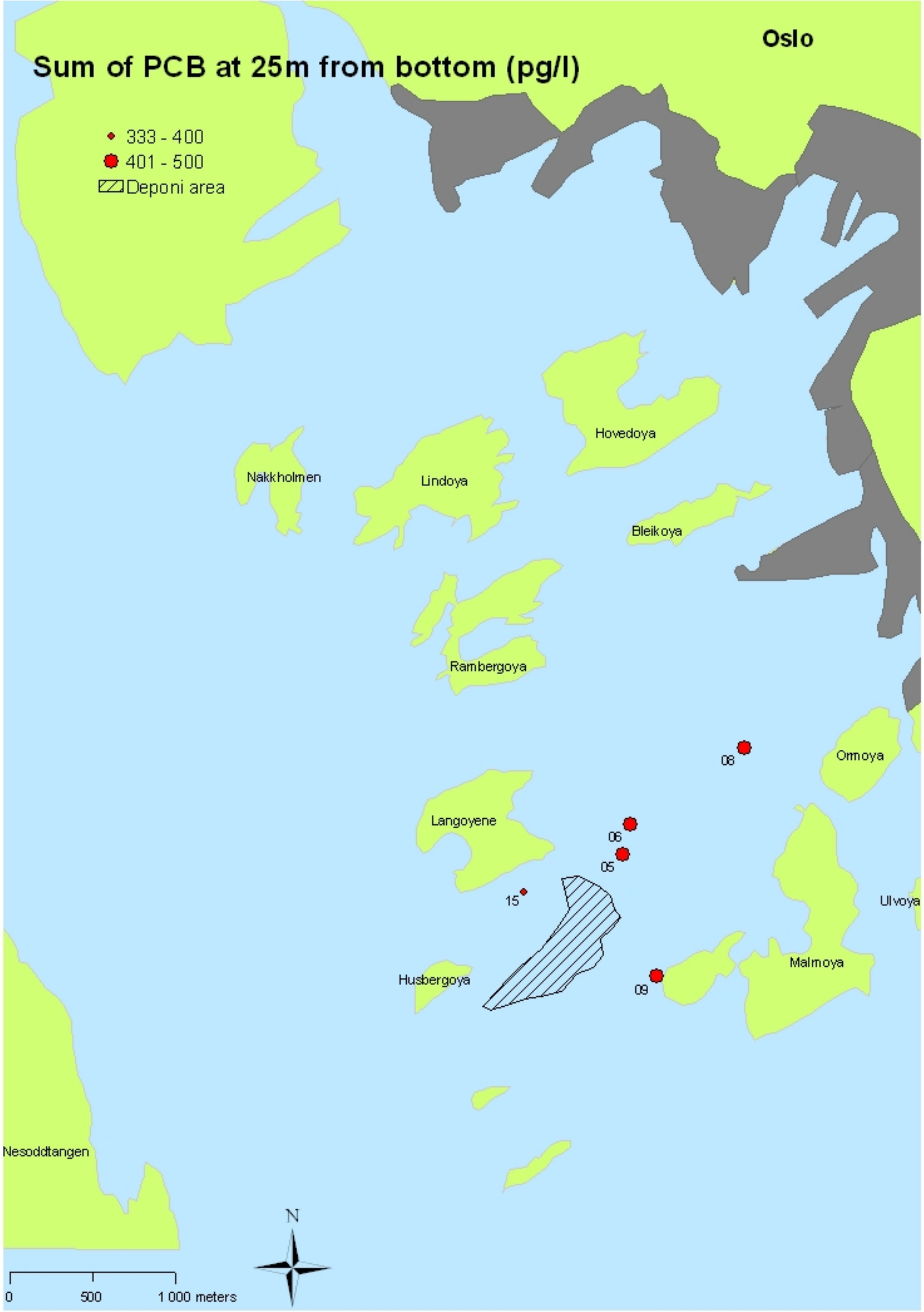

Figure 18. Map showing sum of PCB water concentrations at 25 meter from the bottom in the inner Oslo fjord and especially around the Malmøkalven dumping area from the first sampling period.

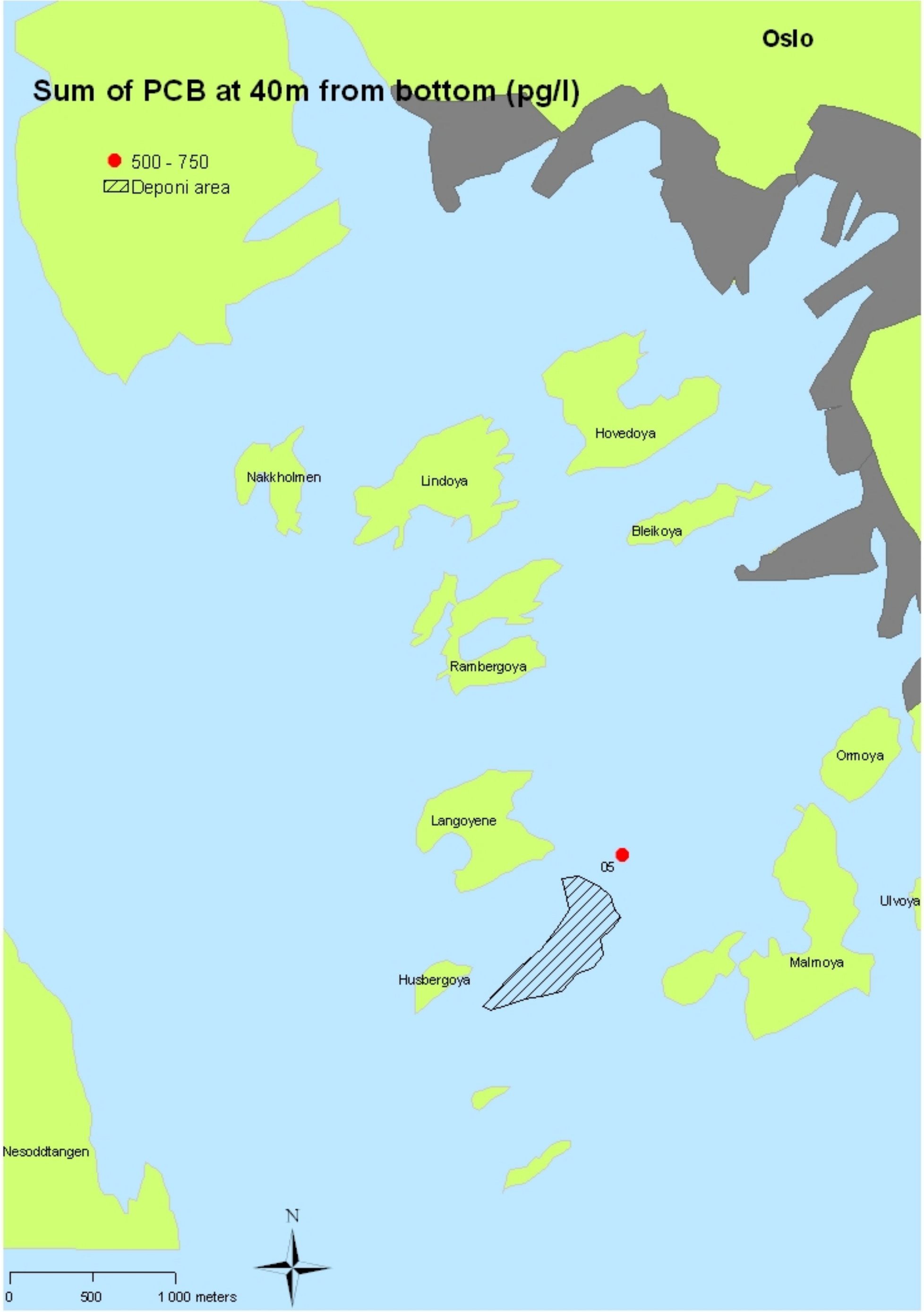

Figure 19. Map showing sum of PCB water concentrations at 40 meter from the bottom in the inner Oslo fjord and especially around the Malmøkalven dumping area from the first sampling period.

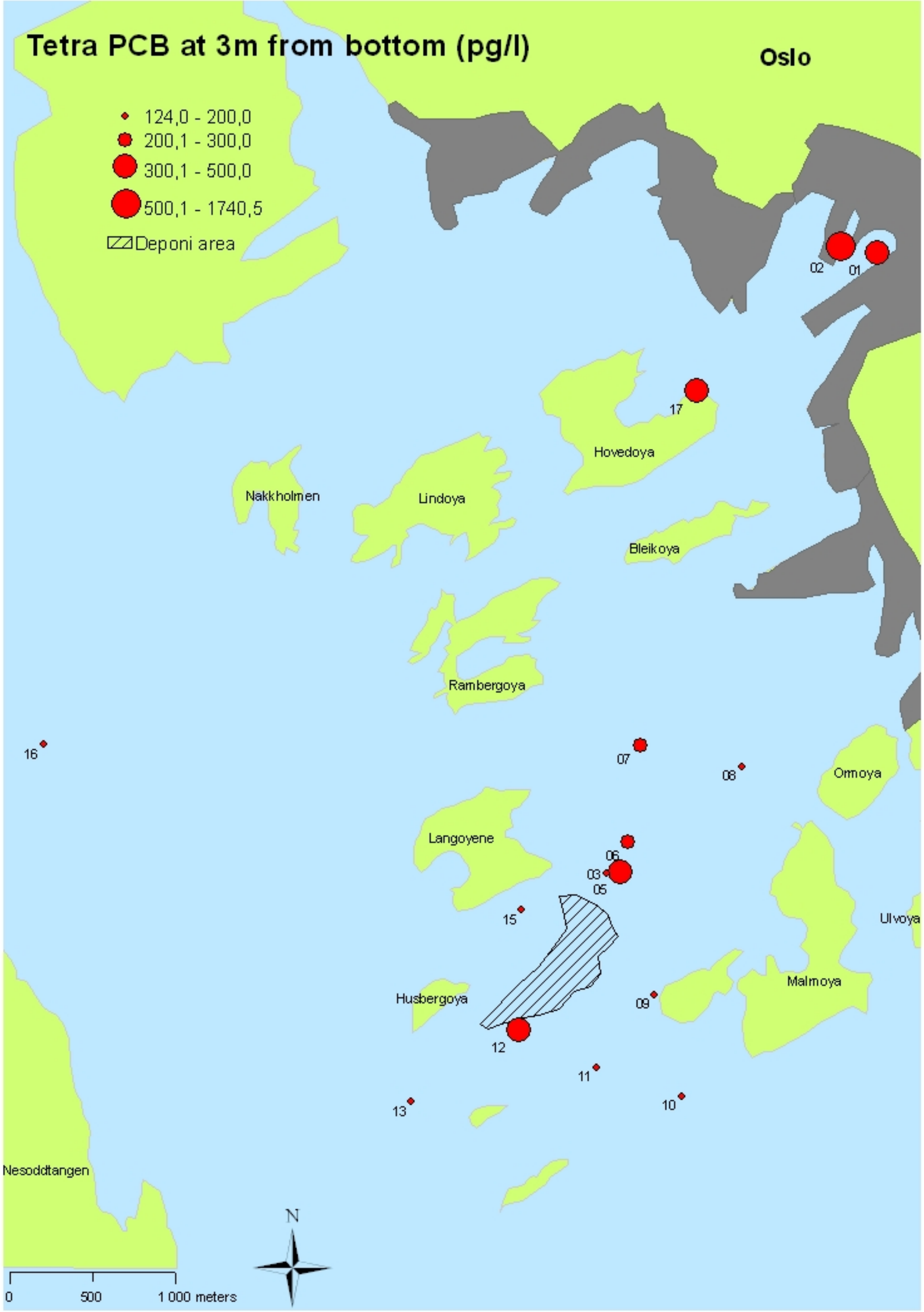

Figure 20. Map showing tetra-CB water concentrations at 3 meter from the bottom in the inner Oslo fjord and especially around the Malmøkalven dumping area from the first sampling period.

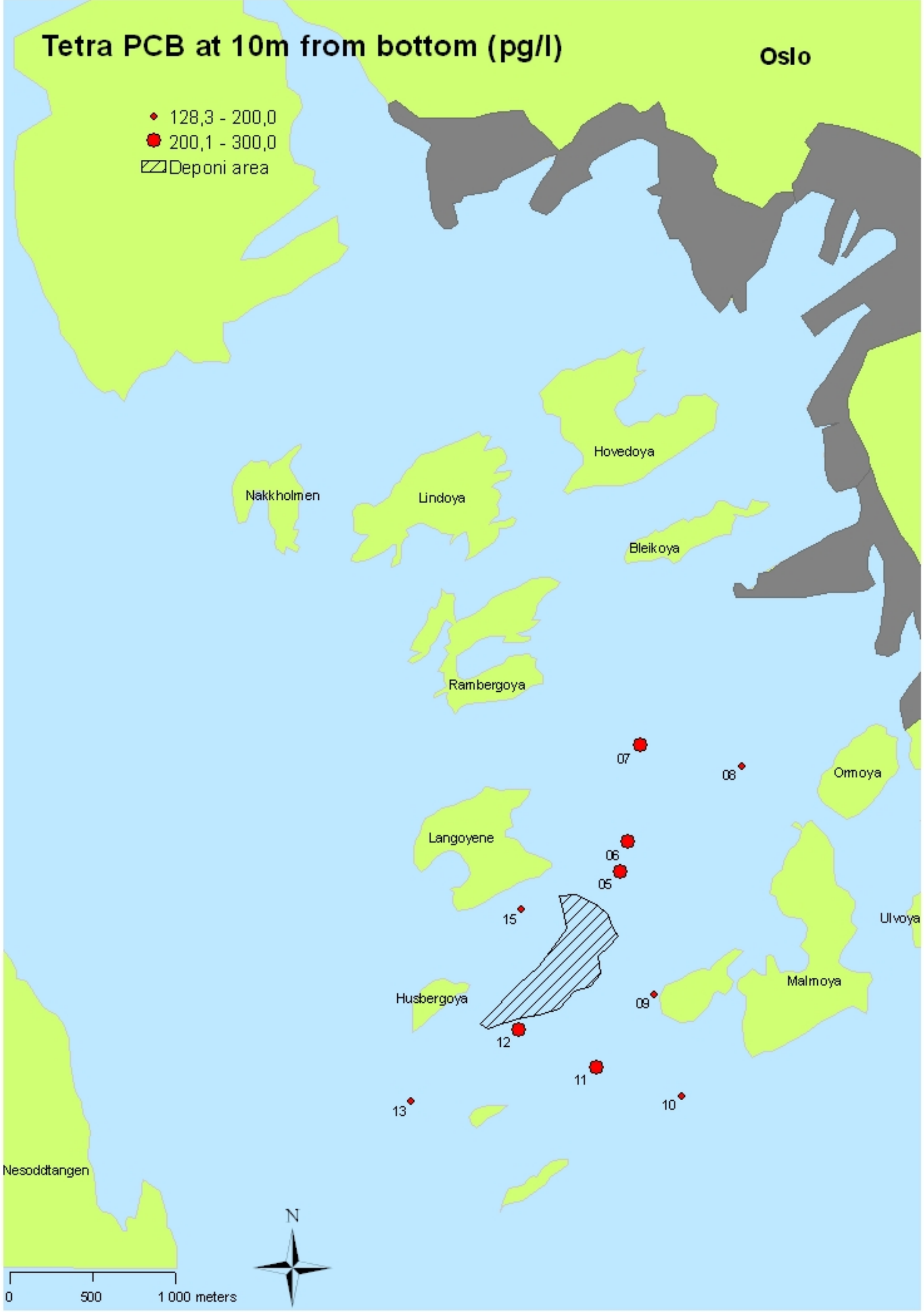

Figure 21. Map showing tetra-CB water concentrations at 10 meter from the bottom in the inner Oslo fjord and especially around the Malmøkalven dumping area from the first sampling period.

Figure 22. Map showing tetra-CB 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 23. Map showing tetra-CB 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.

The maps in figures 20, 21, 22 and 23 show the sum of tetra-CBs at the different sampling depths. At 3 and 10 meter from the bottom is visible distribution of PCB to the north and to the south.

PCA "finger printing"

In order to see the relationship between the different sampling sites PCA statistical method has been used. By combining the results of the 79 different PCB congeners the similarities between the sampling sites can be tested. In figure 24 and 25 are the comparison of sites from the first sampling period presented. The numbering 0501 is indicating that it is site 05 and on 3 meter from the bottom. The numbers ending with 02, 03, 04 indicates 10 m, 25 m and 40 m from the bottom, respectively. Sampling site 2 is excluded since it is an extreme site and the information from that point showed the same as site 1 but much stronger. By avoiding the site 2 data the differences between the other sites are more visible.

In figure 24 it can be seen that site 1 is closely related to sites 0501, 0502, 0504, 0701, 0702, 0602 and 1102, which means that the PCB pollution finger print from these sites resembles the finger print from Bjørvika site 1. Site 16, the background site at Näsudden is on opposite side of the plot, indicating that the PCB finger print is most different for this site. The above mentioned sites resembling site 1 is thus similar to site 1 but the finger print is diluted by the background finger print to lower or larger extent. The typical compounds causing the similarities are mainly the lower chlorinated PCBs.

Site 1301 and 1302, and also to lesser extent 1201 is different in finger print suggesting that an additional PCB source is adding to their finger print. It is, as mentioned before, an influence of hexa- and hepta-CBs that differentiate these sites.

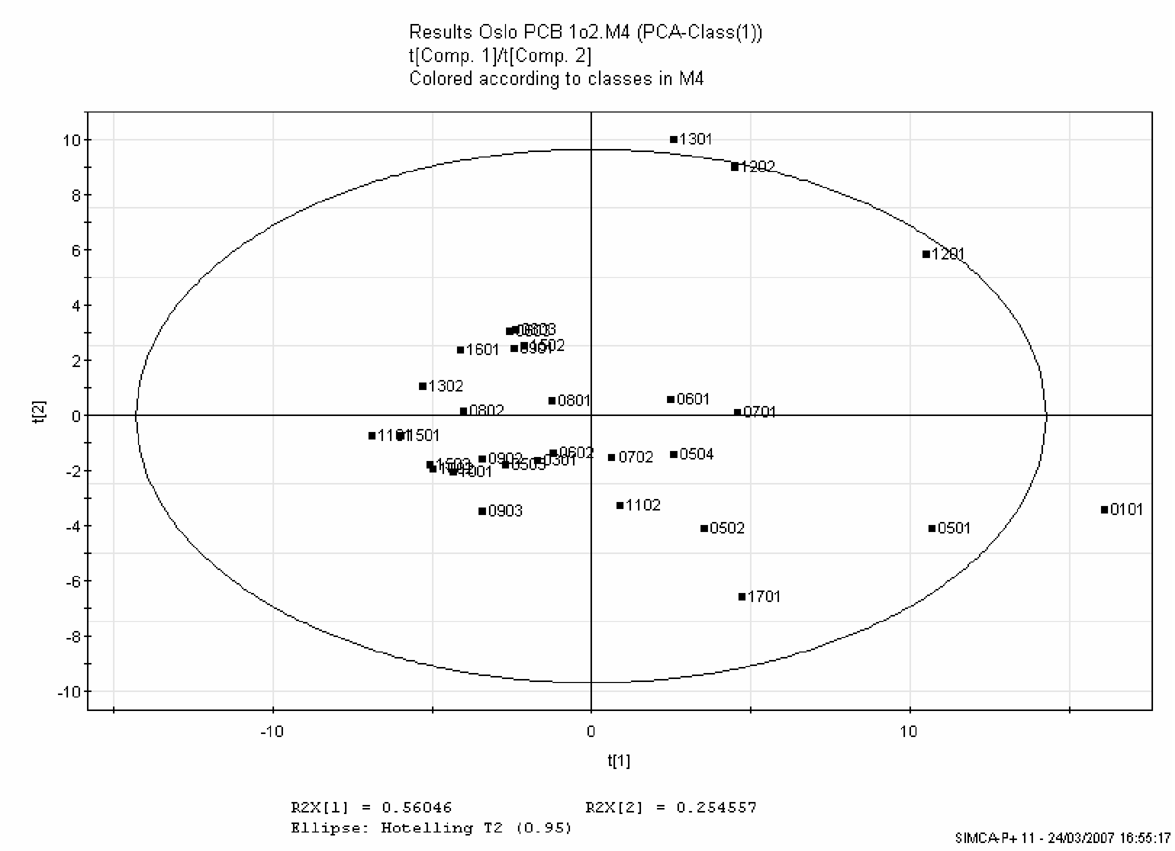

Figure 24. t1/t2 Scatter plot of all PCB data from the first sampling period.

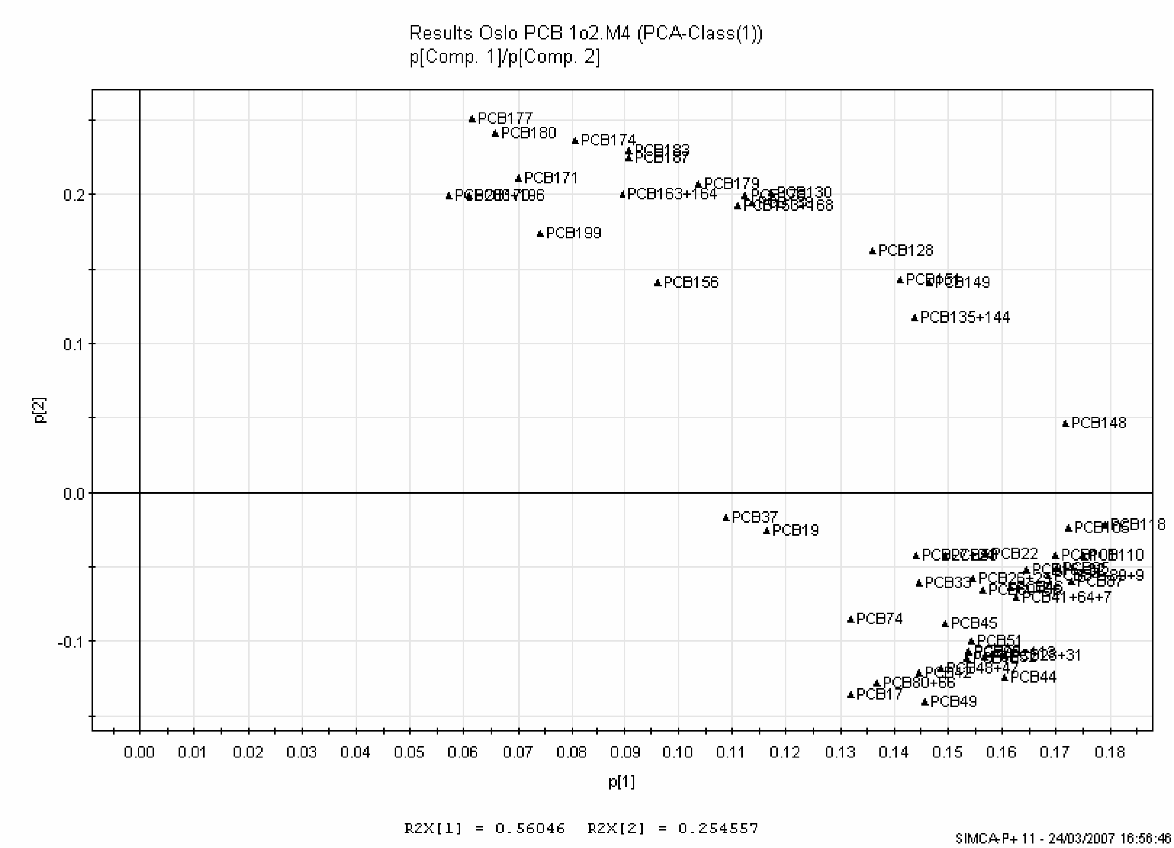

Figure 25. p1/p2 Scatter plot of all PCB data from the first sampling period.

The results from sampling two, which is presented in figure 26 and 27 suggest the similar conclusions. In this case also 0301 and 0401 resembles the source pattern from Bjørvika.

As a side effect we can also see that the pollution finger print at site 17 also resembles the Bjørvika pattern, which suggests that a direct spreading from the excavation place can influence the site 17.

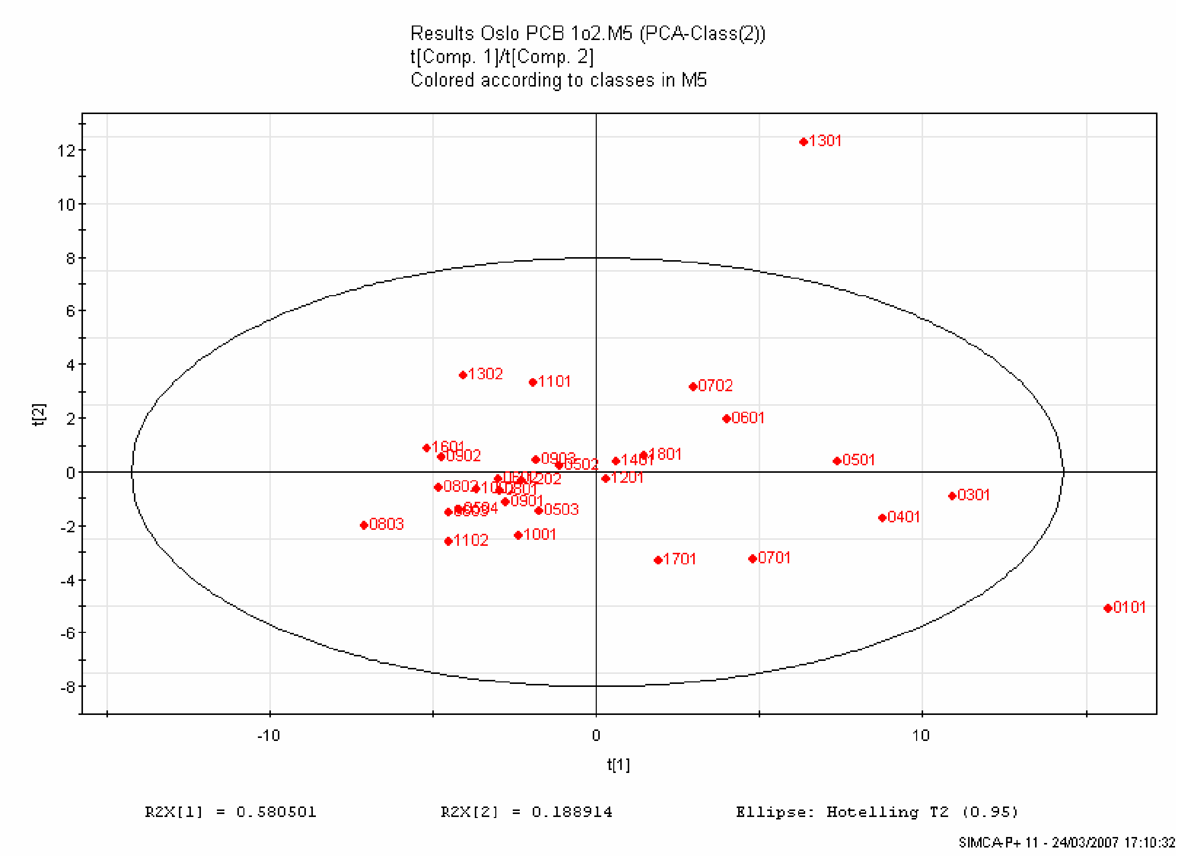

Figure 26. t1/t2 Scatter plot of all PCB data from the second sampling period.

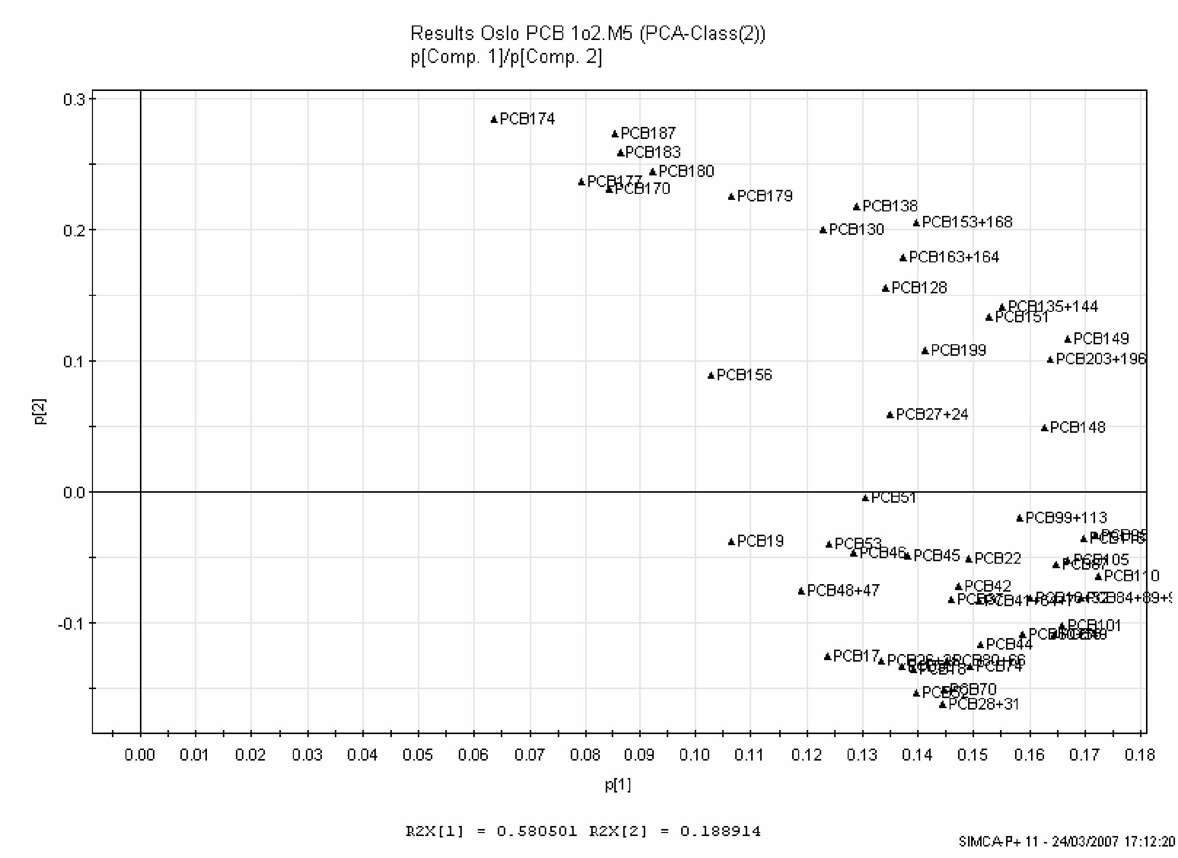

Figure 27. p1/p2 Scatter plot of all PCB data from the second sampling period.

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