The Baltic Carrier oil spill
Monitoring and assessment of PAC levels in water, sediment and biota

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Abstract

On March 29th 2001, the Baltic Carrier oil tanker collided with another vessel in the Baltic Sea southeast of the Danish island Falster. The collision resulted in the release of some 2,400 tons of heavy bunker oil, the largest oil spill ever in Danish waters. In the small sound of Grønsund between Falster and other smaller islands about 20 km of coastline, including environmentally sensitive areas such as bird sanctuaries, were heavily polluted by the oil. A monitoring programme was carried out to assess the levels of oil and about 80 different polycyclic aromatic compounds (PACs) in water, sediment and biota samples, and to form the basis for ecotoxicological assessments.

In April, a few days after the oil spill, PAC levels in seawater from the Grønsund area were up to ten times higher than background levels. In June, 2½ months after the spill, total PAC levels in water had decreased significantly; however, the PAC composition revealed that resuspension of oil in those areas directly affected by the oil spill was still taking place. PAC levels in the sediment were very heterogeneous and decreased only gradually. In December, at the end of the monitoring programme, organisms living in locations directly affected by the spill were still observed of having high levels of selected PACs, according to international guidelines; thus the total PAC levels in blue mussels, *Mytilus edulis*, were about five times higher than background levels. Already 1½ months after the oil spill, however, PAC levels in trout (expressed as B(a)P TEQ) from aquafarms in the affected area were of the same order of magnitude as observed in fish from background areas.

1   Introduction - The Baltic Carrier oil spill

On March 29th 2001 the oil tanker Baltic Carrier collided with the bulk carrier Tern in the western Baltic Sea southeast of the Danish island Falster and caused the spill of some 2,400 tons of heavy bunker oil. The harsh weather conditions at the time of the spill made combat operations at open sea impossible. Due to strongs winds and currents the spill drifted towards the narrow sound of Grønsund, where some 1,200 tons stranded and polluted the coastlines of several smaller islands (cf. Figure 1). Another 1,200 tons were cleaned up from near-shore, shallow waters in

the sound. Different types of shorelines were affected by stranded oil. At the island of Møn it was mostly sandy beaches, while at the northeastern part of Falster the shoreline is stony with large boulders, and here steep slopes made access to the beach very difficult and complicated clean-up operations. At the southern part of Bogø, another small island, the stranded oil polluted very sensitive areas with marshland and reed beds that are important wild life habitats. Besides, the polluted area also includes more important bird sanctuaries (like Fanefjord at Møn).
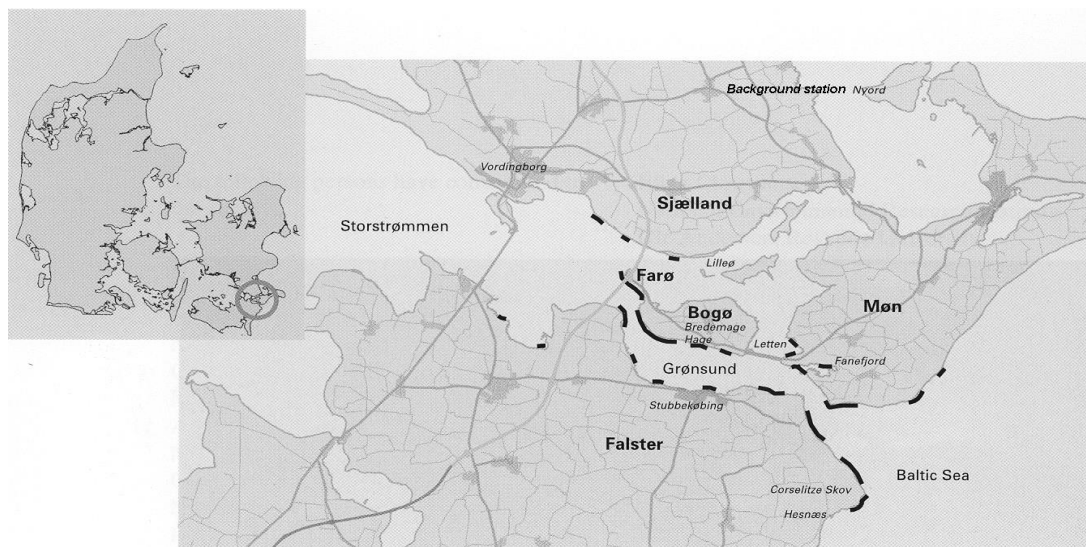

Figure 1. Polluted coastlines along the sound of Grønsund after the Baltic Carrier oil spill in 2001.

2   Composition of the Baltic Carrier oil

The oil spilled from the Baltic Carrier consisted of bunker oil based on heavy distillate residues blended with lighter products of high aromatic content. Bunker oil typically comprises both relatively volatile and water-soluble aromatics, low molecular weight (LMW) polycyclic aromatic compounds (PACs, e.g. alkylbenzenes, naphthalenes, phenanthrenes and dibenzothiophenes) being acutely toxic to marine organisms and higher molecular weight (HMW) PACs which are more persistent in the environment showing long-term adverse effects.

Figure 2a gives a GC-FID chromatogram of the Baltic Carrier oil, and it shows these characteristic features of the bunker oil described above. The chromatogram shows the irregular distribution of n-alkanes from about nC10 to about nC45 centred about nC25 and overlaying a big hump (from nC20 to nC45) of unresolved components (UCM), e.g. HMW aromatics like PACs, typical for heavy fuel oils. At the light end of the chromatogram (left side) distinct clusters of dominating peaks can be seen; these peaks show the pronounced content of the light aromatic fraction blended into the heavy fuel oil. This fraction primarily consists of alkylated naphthalenes and phenanthrenes. In Figure 2b an expanded section of the GC-FID chromatogram is shown, and here the clusters of C1-, C2- and C3-alkylated naphtahlenes (C1-N, C2-N and C3-N, resp.) can easily be identified.

The PAC composition of the Baltic Carrier oil is shown in Figure 3. The PAC fraction made up 1.1% (w/w) of the bunker oil, a rather high fraction compared to other oil types.
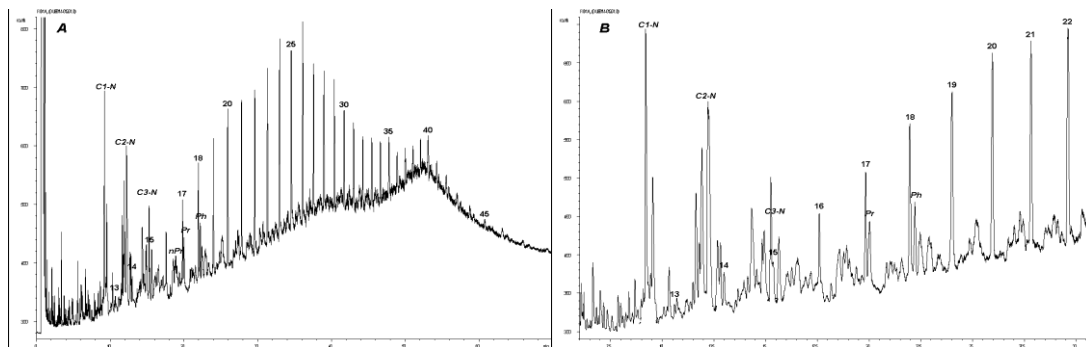
Figure 2. GC-FID chromatograms of the Baltic Carrier bunker oil. A) full scale chromatogram showing n-alkanes from about nC10 to nC40 (numbered peaks); B) expanded section showing the content of LMW aromatics, viz. C1-, C2- and C3-alkylated naphthalenes (C1-N, C2-N and C3-N, resp.).
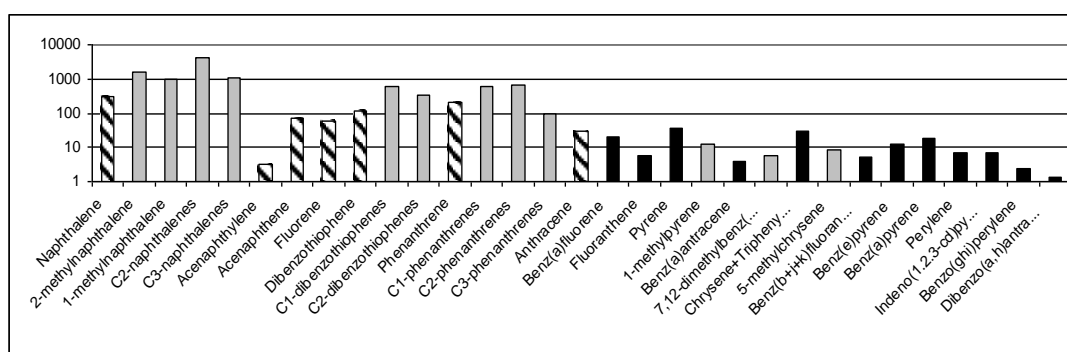

Figure 3. Profile of the PAC composition of the Baltic Carrier bunker oil (µg/kg).

3   The monitoring programme

Immediately after the spill, Storstrøm County (responsible authority) together with the National Environmental Research Institute (NERI) and Roskilde University (RUC) set up a preliminiray programme for the collection of water and sediment samples from the areas in Grønsund polluted by the oil spill. A few weeks later a more extensive monitoring programme was established that included the collection of water, sediment and biota samples in June and December 2001 (Pécseli et al., 2002).

3.1   Collection of samples

Samples for chemical analysis were collected three times in the first year following the spill. In early April, shortly after the accident, the first sampling programme was initiated. In mid-June the second part of the sampling took place, and in December a third series of samples were collected. A few biota samples, flounder and shrimps, were additionally sampled and analysed in May 2002.

The sampling in April comprised 12 stations located in the areas most affected by the oil spill (cf. Figure 1). From all stations, a water sample and two sediment samples were collected (cf. Figure 4 and 7, resp.). The second sampling took place in the period of June 11th – June 15th. This programme comprised 22 seawater and sediment stations (cf. Figure 4 and 7, resp.) and 10 stations for collection of biota (cf. Figure 12). The third sampling round took place from 11th to 18th December, 2001. Sediment and biota were collected at 15 stations (cf. Figure 7 and 12, resp.);

no seawater samples were collected. Finally, in early May 2002, flounders were caught at two stations, and shrimps at one station in the sound of Grønsund.

3.2 Sampling and analysis methods

Sediment samples were collected using kajak tubes with a diameter of 5 cm to 8 cm. In a few cases, deep-water sediment samples were collected using a HAPS sampler. The upper two centimetres from 3 to 7 cores were pooled to one sample of approx. 200 g. Sediment samples were frosen and stored in Rilsan® bags until analysed.

Water samples were collected in 1-litre bottles and analysed right after sampling.

Mussels (*Mytilus edulis*) were collected by hand and depurated in water from the station for 24 hrs. after which they were sorted and dissected. Subsequently, the soft tissue (incl. the adductor muscle) was frozen and stored in Rilsan® bags until analysed.

Bristle worms *(Polychaets)* were dug up by hand and sifted out using a sieve. Subsequently, they were depurated in water from the station for 24 hrs., frozen and stored in Rilsan® bags until analysed.

Fish and shrimps were caught in fish traps, frozen and stored in Rilsan® bags.

The chemical analyses weres performed according to the standard analytical methods used at NERI, as described elsewhere (Pécseli et al., 2002).

4 The oil spill – spreading and degradation of the spilled oil

Physical and chemical processes determine the ecological impact of any oil spill. These processes control the amount and alter the toxic potential of oil that enters and remains in different ecosystems. Subsequently, there was an expressed need to describe the likely expectations for any long-term contamination remaining in the Grønsund area after the initial physical clean-up and remediation.

Aromatic components of oil, particularly PACs, are generally assumed to be the more toxic fraction of marine oil spills. Therefore, much attention was paid to this group of compounds in the monitoring programme established after the Baltic Carrier oil spill. PAC levels were measured in various compartments of the environment in the polluted areas of Grønsund. This gave a general view of the long-term toxicological potential in time and space as a consequence of the spill. PAC baseline levels were estimated from the national Danish monitoring program (NOVA) and by comparison to PAC levels measured at the background station Nyord, situated outside the area affected by the spill. Measurements of various petroleum biomarkers and other components of the oil were performed to assess the fate of the spilled oil.

4.1 Weathering of the spilled oil

In a study by Christensen (2002), the early fate of petrogenic compounds from the Baltic Carrier oil spill was analysed. Small stones (size approx. 30-50 cm^3) were sampled from a polluted stony beach of Falster. Samples were collected 8, 32 and 138 days after the accident. Stones sampled at day 32 were furthermore exposed to hydrocarbon-degrading microorganisms for 21 days in a small preliminary laboratory experiment. Each sample was analysed for compositional changes of more than 150 compounds focusing on naphthalenes, phenanthrenes and dibenzothiophenes.

Changes in composition of the various components of the oil could be described by explorative multivariate data analyses in combination with standard univariate statistics. During the first period after the spill compositional changes were caused by physical processes, mainly evaporation and dissolution. Between day 32 and day 138, biodegradation became an increasingly important process.

Introduction of hydrocarbon-degrading bacteria in the laboratory experiment increased the degradation of both aliphatic compounds and PACs. On the basis of these experiments it therefore seemed likely that remediation of polluted areas by oil-degrading microorganisms would speed up the removal of unrecovered oil.

4.2 Polycyclic aromatic compounds in seawater

Figure 4 shows the sum of PACs measured in seawater from the Grønsund area after the oil spill. As shown in the figure, the concentrations of PACs in seawater decreased considerably in the period from April to June. The average decrease in PAC concentration was 96 % during this 2-month period.

Comparative data of PACs in water samples are few. In Table 1, PAC concentrations from Grønsund are compared to levels measured elsewhere in Danish coastal waters as well as to levels measured in the Baltic Sea. All data presented are based on analyses of unfiltered surface water.

Tabel 1. PAC levels measured in seawater at monitoring stations in 2001(ng/L).

Location	$\Sigma PAC(15)^a$	$\Sigma PAC(total)^b$	$\Sigma PAC(NOVA)^c$	$(B(a)P^d$
Grønsund, April 2001	53.5 – 1,450	641 – 12,833	595 – 12,659	n.d. – 9.86
Grønsund, June 2002	19.2 – 41.3	28.9 – 124	28.9 – 116	n.d. – 2.06
Background st., June 2001	2.58 – 25.6	5.04 – 77.8	18.2 – 39.0	0.04 – 0.70
Danish coastal waters[e]	33.0 – 76.7	n.d.	71.8 – 186	n.d. – 3.0
Baltic Sea[f]	3.85 – 14.1	n.d.	n.d.	0.01 – 0.12

[a]sum of 15 parent PACs according to Law et al. (1997); [b]sum of all 86 PACs measured in this study; [c]sum of PACs routinely measured in the National Danish Water Monitoring Programme; [d]B(a)P, benzo(a)pyrene; [e]average values (Pritzl, unpublished results); [f]Witt (1995); n.d., not determined.

In April, 11 days after the oil accident, total PAC levels measured in the whole Grønsund area were more than 10 times higher than levels normally detected in Danish coastal waters, and more than 10 times higher than PAC levels measured at the background station, Nyord, in June. In June, 2½ month after the spill, the values measured at all stations in the Grønsund area were close to background levels, even at Bredemade Hage and Fanefjord outer station, the sites most affected by the spill. In the areas directly affected by the oil spill the level of benzo(a)pyrene was, however, still above baseline levels in June, 2001.

The PAC levels measured in the sound of Grønsund and at the background station Nyord in June were higher than PAC levels measured in the water column in adjacent waters of the Baltic sea (cf. Table 1). This might be expected, though, as the samples analysed in this study were from shallow-water stations close to land, whereas the levels reported by Witt (1995) were measured in deeper waters, and they showed a decreasing gradient in the PAC concentrations away from land.
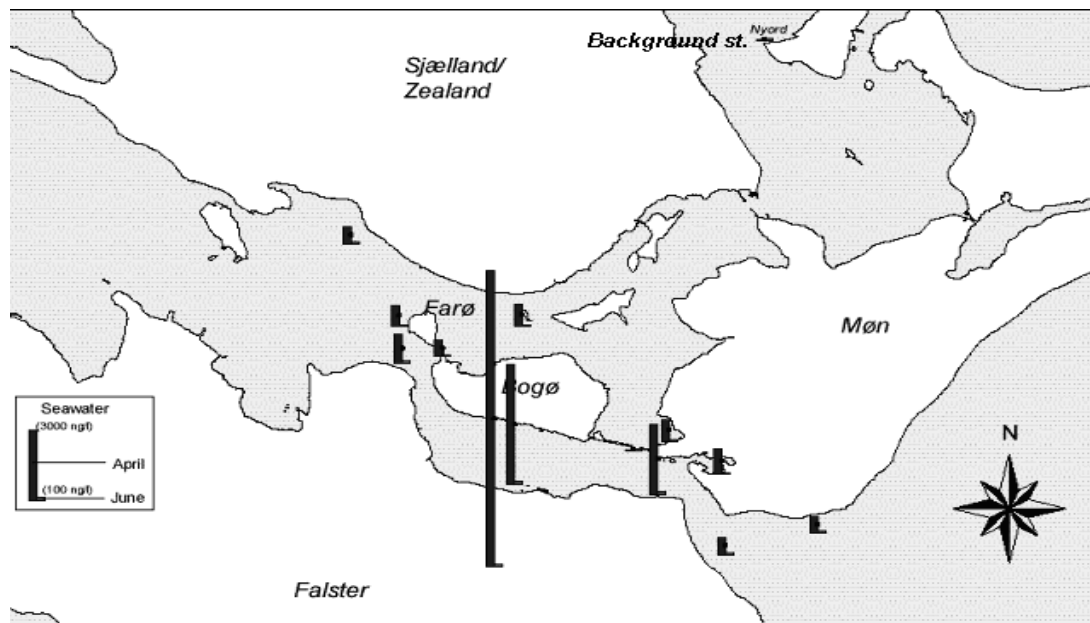
Figure 4. Concentration of ΣPAC_{total} (ng/L) in seawater from the Grønsund area in April and June, 2001; black dots show the locations of sampling stations.

In a recent study of the North Cape oil spill, where 2,700 tons of fuel oil were spilled to the sea in coastal areas of Rhode Island, USA, 54 water samples were collected in a period from 4 to 132 days (Reddy and Quinn, 1999); here the mean concentration of PACs in the water phase were $21,9 \cdot 10^3$ ng/L during this period with a maximum of $115 \cdot 10^3$ ng/L (sum of 2-4 ringed PACs and alkylated derivatives). These concentrations are much higher than those measured after the Baltic Carrier accident. The fast decrease observed in PAC concentrations in seawater from Grønsund corresponds to measurements after the Braer oil spill, where an exponential decrease of hydrocarbons in the water phase was observed: from more than 10,000 ng/L immediately after the spill, values had decreased to between 10 and 20 ng/L three month later (The Environmental Impact of the Wreck of the Braer, 1994).

Macroalgae have formerly been used for the monitoring of heavy metals as a sort of "natural passive samplers" (e.g. Villares et al., 2001; Sawidis et al., 2001), but analyses of organic contaminants in macroalgae are rather scarce. In a preliminary study the PAC composition was measured in a few samples of the macroalgae, *Fucus vesiculosus* (bladder wrack), collected in December 2001 from the background station at Nyord, from two stations at Bredemade Hage and from Kirkegrund close to Vordingborg. These values show that the levels measured at Bredemade Hage, the most affected area, have increased compared to the background station. These findings agree well with the PAC levels measured in water samples from June which indicated the return to baseline levels in most areas except from Bredemade Hage. PAC levels in bladder wrack from Grønsund are within the same range as levels reported in the literature.

As expected, according to the physico-chemical properties of the various PACs, the PAC composition in the water samples are characterised by a high proportion of the LMW and alkylated compounds compared to the PAC composition in sediments. Not only the concentration level, but also the composition of PACs in the water phase changed from April to June. In this study, differences in PAC compo-

sition ratios have been evaluated by principal component analysis (PCA) using the normalised concentrations of the individual PAC profiles (normalised to ΣPAC) of the water samples as descriptive variables (cf. Figure 5). Data were mean-centered and autoscaled prior to analysis.
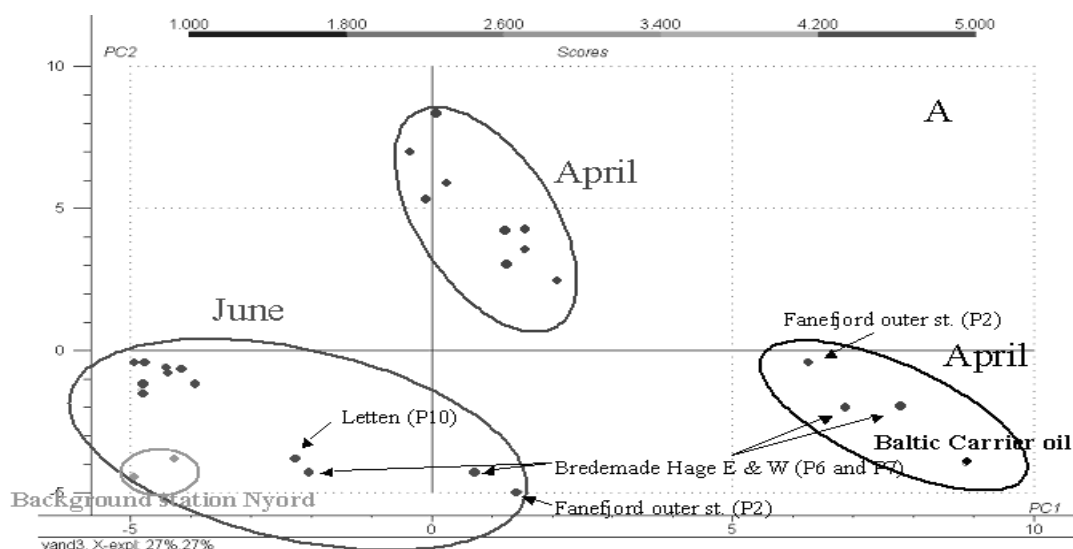

Figure 5. Score plot (PC1 vs. PC2) of the PAC distributions in seawater from Grøn-sund showing the grouping of individual samples from April and June, 2001.

Figure 5 displays the relationships between the 59 original variables (individual PAC profile data) and the 26 water samples together with the Baltic Carrier oil in a hyperspace spanned by the first and second principal component (PC1 vs. PC2). These two PCs explain 27% and 27%, resp., of the variation of the original 59 dimensional dataset. A separation between the water samples is clearly observed in the score plot along both PC1 and PC2, dividing the water samples into several groups. One group is formed by Bredemade Hage and Fanefjord outer station – the stations directly affected by the oil spill in April – while the rest of the water samples collected in April form a second group. The water samples from June form a third group in the score plot with most of the samples clustering at low PC1 values; samples from Fanefjord outer station, Bredemade Hage and Letten have low levels in PC2 and medium levels in PC1.

From the clustering of variables in the loading plot (Figure 6) it appears that the samples collected in April at the locations with visible oil pollution, Bredemade Hage and Fanefjord outer station, are characterised by a relatively higher percentage of dibenzothiophene (Dbt) and C1-alkylated dibenzothiophenes (MDbt) together with C2- and C3-alkylated naphthalenes (DMN, EN and TMN) compared to the other stations. This indicates an on-going dissolution of the compounds of lowest molecular weight at Bredemade Hage and outer Fanefjord in April. The rest of the water samples from April are distinguished by relatively high fractions of many dimethylated dibenzothiophenes and phenantrenes (DMDbt and DMP), indicating that most of the lowest molecular weight PACs have evaporated at stations not directly polluted by the oil spill.
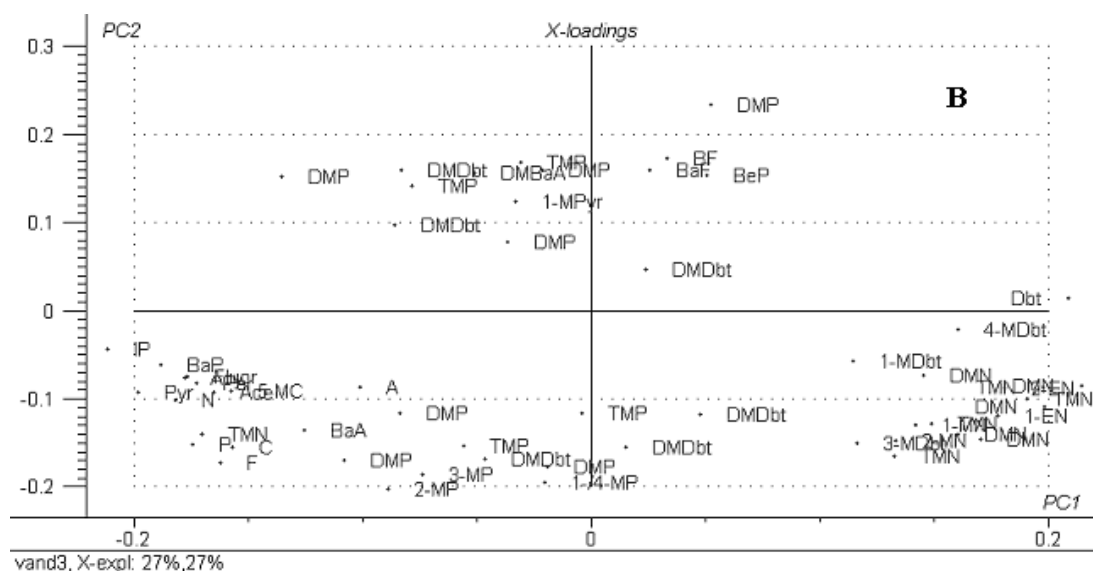
Figure 6. Loading plot (PC1 vs. PC2) of the PAC distributions in seawater samples from Grønsund, April and June, 2001, showing the grouping of individual PACs.

From April to June, weathering processes have changed the PAC composition in the water phase even more. The background station Nyord and most of the samples collected in June are characterised by a relatively high percentage of unsubstituted compounds, e.g. Naphthalene (N), Phenanthrene (P), Chrysene (C), Fluorene (F), Pyrene (P), Benzo(a)pyrene (BaP) and Indeno(1,2,3-cd)pyrene (IP). The samples from June are characterised by low levels in PC2 and intermediate levels in PC1; Letten, Bredemade Hage and Fanefjord outer stations have relative high levels of some mono-, di- and trimethylated phenanthrene derivatives (MP, DMP and TMP) and some dimethylated dibenzothiophenes (DMDbt), indicating dissolution of weathered oil at these stations.

Thus, the most water-soluble PACs of the oil were apparently dispersed in the water phase throughout the entire Grønsund area right after the oil spill. After 2½ months, when total PAC levels had decreased to near baseline levels at all stations, the fraction of alkylated aromatic compounds had decreased, the fraction being more prone to weathering. In June the PAC composition at most stations was therefore comparable to the PAC composition in the water phase from the background station, Nyord, characterised by a relatively higher fraction of unsubstituted parent compounds. At Bredemade Hage and Fanefjord outer station, the alkylated compounds constituted a relatively larger fraction of the PAC level compared to the other stations in June. This indicates the on-going dissolution of the oil at these stations.

4.3 Polycyclic aromatic compounds in sediments

The PAC concentrations in sediment samples at various stations in the Grønsund area are shown in Figure 7. The PAC levels in sediments are decreasing at a much slower rate than PAC levels in the water phase. This is not surprising, as PACs dissolved in the water phase is much more prone to evaporation, photooxidation and biodegradation, just as part of it will eventually be adsorbed to the sediment. Halflives of PAC in seawater are reported in the range of hours to days, while the halflives in sediments are measured in months to years (e.g. WHO, 1998).
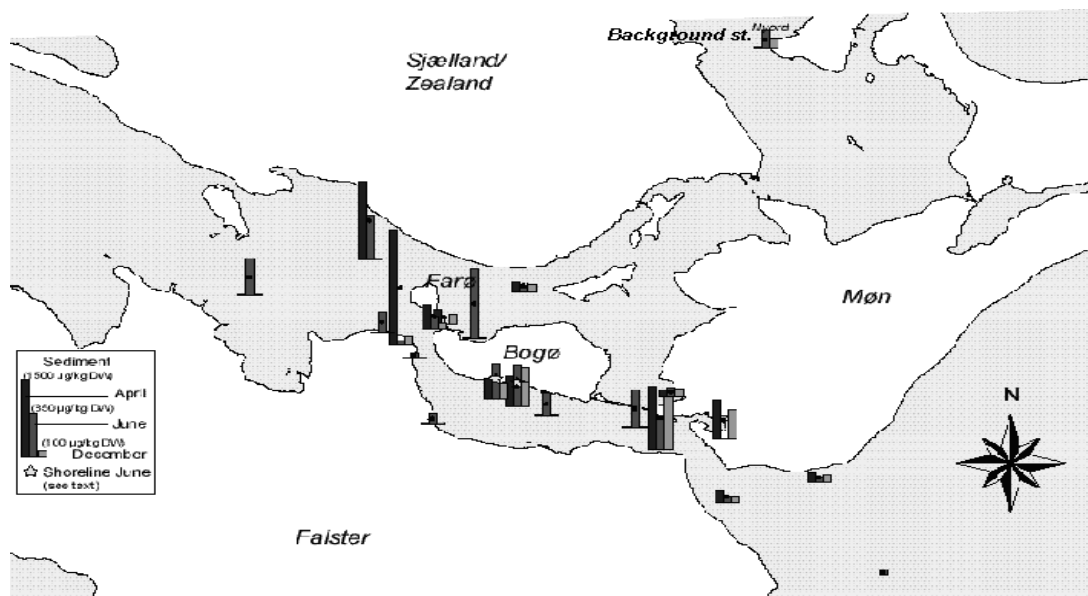
Figure 7. Concentration of ΣPAC_{total} (μg/kg dw) in sediments from the Grønsund area in April, June and December 2001; stars denote samples collected in the tidal zone at Bredemade Hage where concentrations were 4,051 and 6,470 μg/kg dw; black dots show the locations of sampling stations.

Tabel 2. PAC levels in sediments at monitoring stations in 2001 (μg/kg dw).

Location	$\Sigma PAC(15)$[a]	$\Sigma PAC(total)$[b]	$\Sigma PAC(NOVA)$[c]	$(B(a)P$[d]
Grønsund, April 2001	48.0 – 2160	89.8 – 4119	85.6 – 4018	3.0 – 87.3
Grønsund, June 2001	33.1 – 698	45.8 – 1304	45.7 – 1282	0.57 – 61.7
------ tidal zone, June 2001	(745 – 1572)	(4051 – 6470)	(3893 – 6083)	n.d.
Grønsund, December 2001	46.2 – 612	81.1 – 1018	79.3 – 935	1.8 – 46.6
Danish coastal areas[e]	42.7 – 4537	n.d.	60.7 – 6231	1.65 – 464
Baltic Sea[f] (1999)	3.96 – 22100	n.d.	n.d.	0.23 – 1440
Baltic Sea[g] (1995)	9.53 – 1871	n.d.	n.d.	0.36 – 210

[a]sum of 15 parent PACs according to Law et al. (1997); [b]sum of all 86 PACs measured in this study; [c]sum of PACs routinely measured in the National Danish Water Monitoring Programme; [d]B(a)P, benzo(a)pyrene; [e]Henriksen et al. (2001); [f]Baumard et al. (1999); [g]Witt (1995); dw, dry weight; n.d., not determined.

In Table 2 the PAC levels measured in the Grønsund area are listed together with values measured elsewhere in Danish coastal waters as part of the national Danish monitoring programme (NOVA) and data from the open literature. The data from the Baltic Sea are gradients ranging from highly urbanised areas near large harbours like Kiel and Warnemünde to open water background stations. In the same way data from the Danish NOVA programme cover values from low level background areas to levels in highly urbanised areas. Comparison with literature values of PAC concentrations can be a challenge as the number of PAC compounds measured varies substantially from study to study; therefore various sums are calculated in Table 2 to enable the comparisons of levels.

PAC concentrations have not formerly been measured in the Grønsund area, and background levels of PAC derived from other sources than the Baltic Carrier oil spill were estimated by measuring the PAC levels in sediments from the background

station Nyord. Total PAC levels at Nyord were 322 ±267 µg/kg dw in June and 162 ±54,9 µg/kg dw in December, respectively; the high variation between replicates illustrates the natural heterogeneity that must also be taken in to account in the interpretation of the results.

GC-FID screening

GC-MS fingerprints

TPH chromatogram   **Hopanes, m/z 191**   **14α-steranes, m/z 217**
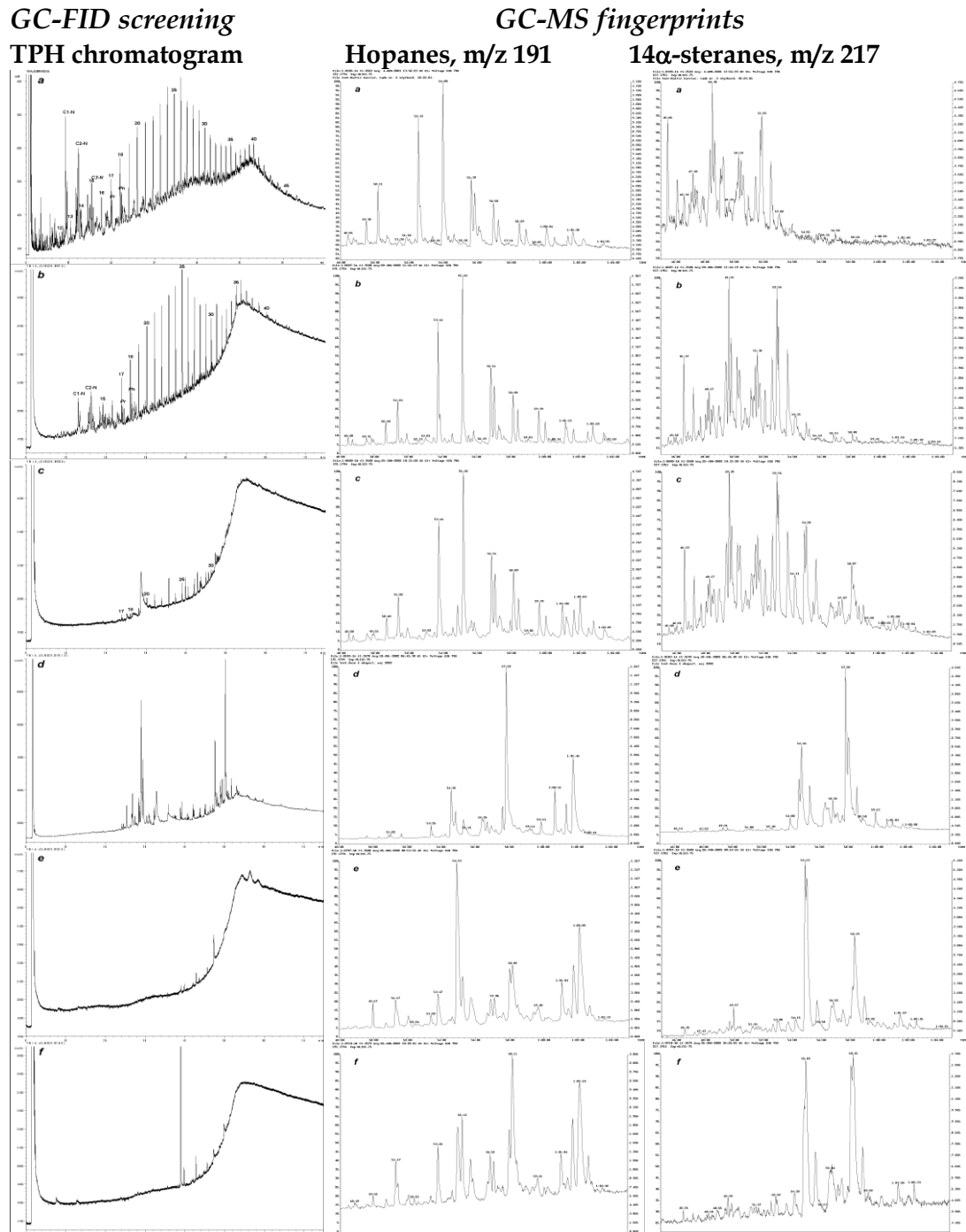

Figure 8. GC-FID and GC-MS chromatograms of the Baltic Carrier oil and sediment extracts from the Grønsund area. a) Baltic Carrier oil, b) Bredemage Hage shoreline, c)Bredemage Hage, P6, d) Farø N, e) Vordingborg and f) between Lilleø and Bogø.

As it appears from Table 2, total PAC levels measured in sediments from Grønsund were within the range reported elsewhere in Danish waters and the adjacent Baltic Sea. Many stations in the area even had PAC levels in the range found at the background station Nyord – this goes for the stations on the northern coast of Falster, the two stations east of Grønsund (P8 and P9), at Lilleø (P11) north of Bogø, and Letten (P10). At the rest of the stations, PAC levels were higher than those observed at the background station. To interpret these results, however, it is necessary to distinguish the PAC pollution from the Baltic Carrier oil from other sources of PAC contamination in the area.

In an attempt to distinguish between hydrocarbon inputs from the Baltic Carrier oil spill and other possible sources in the Grønsund area, petroleum biomarker fingerprints were recorded for selected sediment samples. For spill identification and source correlation the hopane and sterane biomarkers normally possess strong diagnostic features being generic petroleum hydrocarbons (Peters and Moldowan, 1993).

In Figure 8a-f the GC-MS fingerprints of triterpanes (hopanes) and steranes together with GC-FID chromatograms of a series of sediments samples (extracts) from the Grønsund area and the Baltic Carrier bunker oil are presented.

Only the two samples from Bredemade Hage, shoreline (Figure 8b) and station P6 (Figure 8c), respectively, show obvious resemblance with the Baltic Carrier oil (Figure 8a) when comparing both the GC-FID chromatograms and the two biomarker GC-MS fingerprints. From the GC-FID chromatogram it appears that the P6 sample is considerably influenced by weathering and degradation, the n-alkanes having almost completely disappeared, but that these processes have only marginally affected the biomarker fingerprints. The three other samples from stations located at Farø N (Figure 8d), at Vordingborg (Figure 8e), and north of Bogø (Figure 8f) (cf. Figure 7) hardly show any signs of petroleum hydrocarbons in the GC-FID chromatograms. Similarly, the biomarker fingerprints do not display the typical patterns normally associated with petroleum products, and these sediment samples do not seem polluted by petroleum hydrocarbons. Instead, the patterns displayed in the biomarker fingerprints may be associated with much more recent biogenic sources.
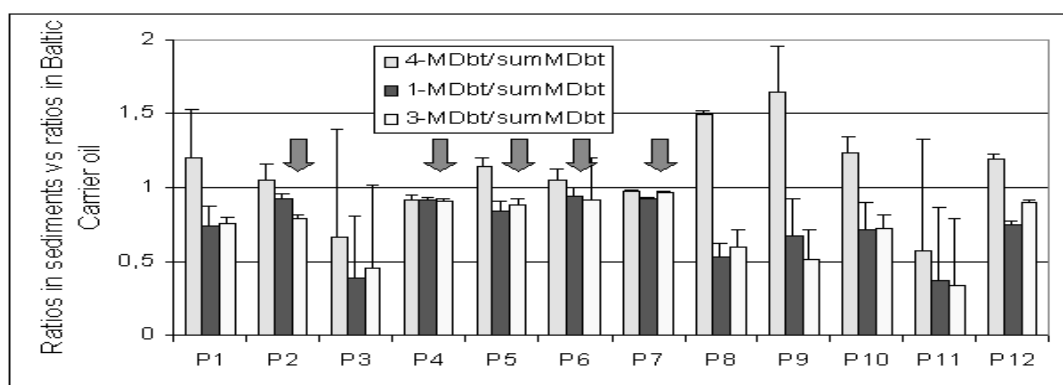
Figure 9. Calculated diagnostic ratios for sediment samples (April 2001) relative to those of the Baltic Carrier oil. Arrows indicate those sampling stations (cf. Figure 7) that have ratios close to 1 and that are most probably polluted by the oil spill. P1: Fanefjord, inner st.; P2: Fanefjord, outer st.; P3: Farø SE; P4: Farø SW; P5: Farø N; P6, Bredemade Hage E; P7: Bredemade Hage W; P8: Madsens Løb; P9: Middelgrund; P10: Letten; P11: Lilleø; P12: Vordingborg.

The diversity in PAC source could also be derived from diagnostic ratios calculated for sediment samples collected in April (cf. Figure 9). The diagnostic ratios applied here can be used to distinguish between various sources of PAC pollution as well as different oil types (Wang et al., 1999). Sediments from sampling stations polluted by the Baltic Carrier oil show diagnostic ratios close to the ratios found in the Baltic Carrier oil, that is values close to 1; arrows mark these stations in Figure 9. Bredemade Hage, the outer station in Fanefjord, the southwestern Farø and possibly Farø north showed signs of petrogenic pollution based on these ratios.

Incomplete combustion of organic material is an important source of PACs in urbanised areas. Petrogenic sources of PAC pollution may, however, be distinguished from pyrogenic sources by higher fractions of substituted and sulphur containing compounds. In Figure 10 the PAC composition of the sediment samples were examined by principal component analysis, PCA, using the log-transformed concentrations of the 59 PAC measured in the sediment samples as descriptive variables. Data were mean-centered before analysis.
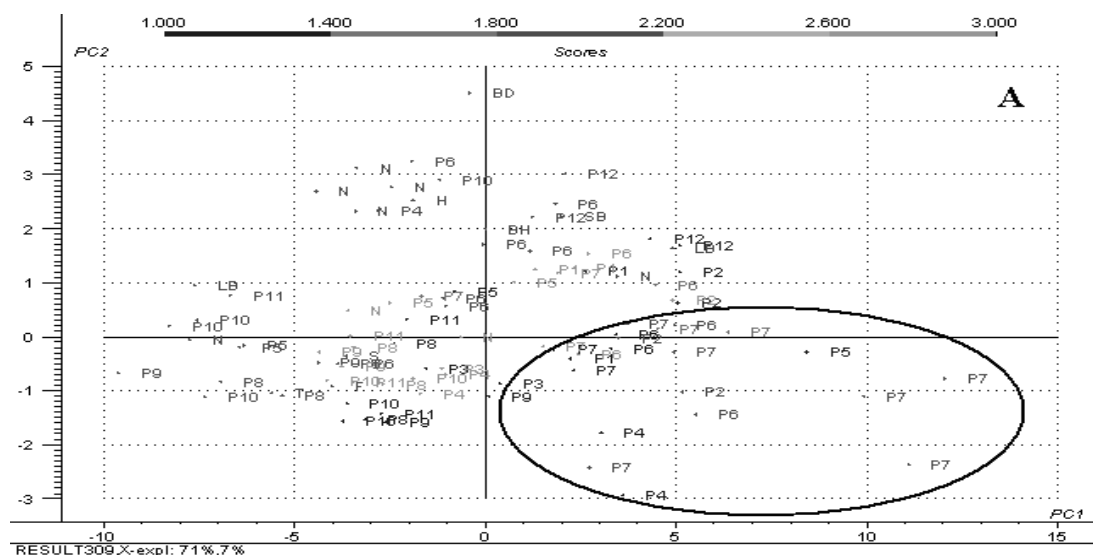
Figure 10. Score plot (PC1 vs. PC2) of the PAC distributions in sediments from the Grønsund area showing individual samples from April, June and December, 2001.

The first, principal component (PC1) accounts for 71% of the variation in the log-transformed PAC variables and describes mainly differences in concentration levels between the samples. All variables have positive loadings in PC1 (cf. Figure 11); this implies that all PAC variables have a positive covariation, such that high total PAC concentrations are more or less reflected in high concentrations of all PAC variables. The second principal component (PC2) accounts for 7% of the variation in data, and describes to a larger extent than PC1 differences in PAC composition among the samples. The compounds encircled in the loading plot (Figure 11) are compounds characteristic of oil pollution: alkylated PAHs and derivatives of dibenzothiophene. Samples in the score plot (Figure 10) characterised by high scores in PC1 and low scores in PC2 have high absolute levels of these compounds; these samples can in other words be regarded as the samples most affected by oil. These samples, encircled in the score plot are primarily samples from Bredemade Hage (P6 and P7), Fanefjord outer station (P2) and Southwestern Farø (P4).

Figure 11. Loading plot (PC1 vs. PC2) of the PAC distributions in sediments from the Grønsund area, April, June and December, 2001, showing individual PACs.

Indications of elevated PAC levels in sediments as a consequence of the oil spill were observed at Bredemade Hage (P6 and P7), at the outer part of Fanefjord (P2) and south west of Farø (P4), while elevated PAC levels elsewhere in the area could be assigned to more pyrogenic sources. The PAC levels in the oil-polluted sediments did not show a steady decline at all stations during the three series of sampling. At the southwestern Farø, total levels declined, but this was not the case at the other oil-polluted stations, maybe due to the resuspension of oil deposits.

In conclusion, PAC levels in sediments are slowly decreasing in the oil-polluted areas of Grønsund. The PAC levels are, furthermore, very heterogeneous and in some areas difficult to distinguish from PAC pollution from other sources, such as pyrogenic input and boat traffic. Re-exposure of oil deposits is apparently still going on, and this could explain the slight increase in PAC concentrations from June to December in some areas. There may also still be unrecovered oil present in the area; thus, when the Bogø Dam was repaired in July 2002 unrecovered oil from Baltic Carrier spill was found under the entire southern side of the construction.

4.4 Polycyclic aromatic compounds in biota
During the months after the oil spill, concentrations of PACs were measured in biota from Grønsund to evaluate the degree of oil exposure and potential toxic effects to the organisms in the area.

Measurements of PAC in biota serve two purposes: It integrates the levels of contamination in a broader abiotic environment and gives information of the bio-availability of contaminants measured in water and sediments. A multi-species approach is often reasonable as different organisms are exposed to different compartments of the abiotic environment. Therefore, various organisms were analysed at Bredemade Hage, one of the locations most heavily affected by the oil spill.

4.4.1 Blue mussels (*Mytilus edulis*)
In Figure 12 the levels of sum PAC measured in blue mussel, *Mytilus edulis*, in June and December 2001 are shown. The median value of concentrations of

ΣPAC in mussel tissue was 304 and 207 µg/kg ww in June and December, respectively.

Total PAC levels in blue mussels from Grønsund were generally higher than levels measured in Danish waters and adjacent waters of the Baltic Sea, both in June and December 2001. Especially, the highly carcinogenic compound benzo(a)pyrene (B(a)P) was found in rather high concentrations (cf. Table 4). At eight locations mussels were collected in both June and December. At Fanefjord outer station, at the Bogø Dam, at Middelgrund and at the two stations closest to the shore at Farø the total PAC levels in mussels decreased 12-49%. At the stations close to the Farø Bridge, Storstrøm Bridge and at Letten there was, though, an increase in total PAC level of 5-40% during the 6-month period from June to December (cf. Figure 12).
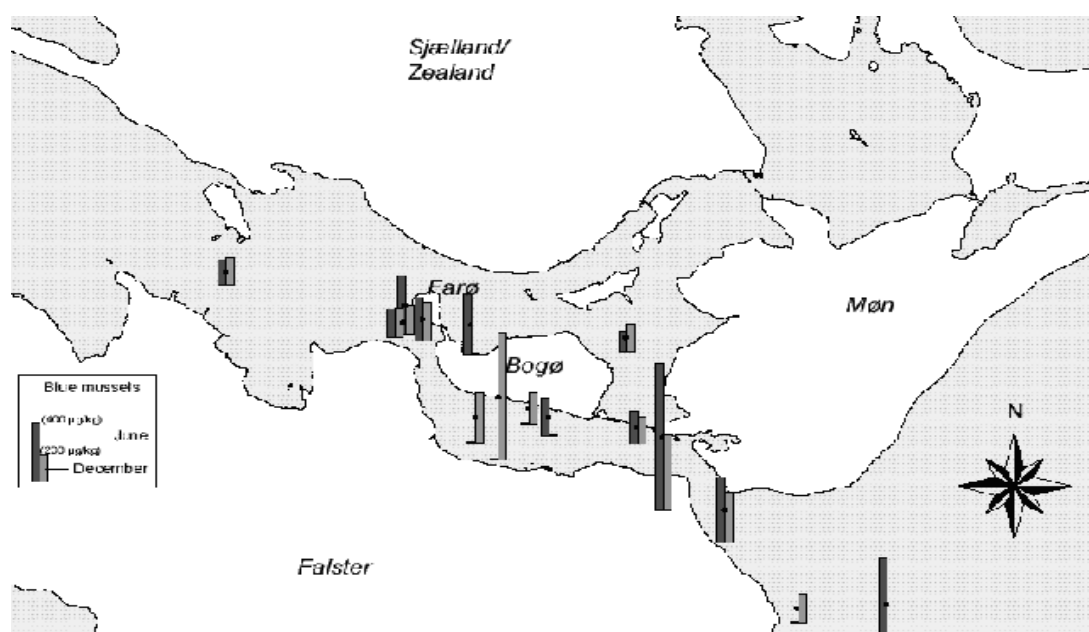

Figure 12. Concentration of ΣPAC$_{total}$ (µg/kg ww) in blue mussels, *Mytilus edulis*, from the Grønsund area in June and December, 2001; black dots show the locations of sampling stations.

Tabel 3. PAC levels measured in blue mussels at monitoring stations (µg/kg ww).

Location	ΣPAC(11)[a]	ΣPAC(total)[b]	ΣPAC(NOVA)[c]	(B(a)P[d]
Grønsund, June 2001	34.3 – 131	132 – 1031	124 – 795	3.67 – 22.9
Grønsund, December 2001	55.2 – 299	185 – 894	154 – 698	2.42 – 18.1
Danish waters[e]	25.3 – 100	n.d.	54.0 – 285	0.25 – 5.60
Baltic Sea[f] (1999)	12.1 – 50.0	n.d.	n.d.	0.35 – 1.24
Skagerak/Kattegat[g] (1996)	6.40 – 10.4	n.d.	n.d.	0.4 – 0.6

[a]sum of 11 parent PACs according to Förlin et al. (1996); [b]sum of all 86 PACs measured in this study; [c]sum of PACs routinely measured in the National Danish Water Monitoring Programme; [d]B(a)P, benzo(a)pyrene; [e]Henriksen et al. (2001); [f]Baumard et al. (1999); [g]Förlin et al. (1996); ww, wet weight; n.d., not determined.

A general challenge in explaining organic contaminants concentrations in biota is to take the natural variation into account; that is the variation in PAC levels reflecting variations according to age, sex and reproductive status of sampled spe-

cies. In the national Danish monitoring programme, NOVA, Blue mussels (*Mytilus edulis*) are collected from October to November as this is the time of year the body-burden of various contaminants is subject to least natural variation. In summer the mussels are spawning and the total bodymass of the animals therefore varying considerably over a short time span. In earlier studies an increase in PAC levels from summer to winter has been reported (Webster et al., 1997). This means that some of the variation seen from June to December might be blurred by a natural increase in bodyburden of contaminants during the season. This could be the explanation for the increase in PAC level at close to the Farø Bridge, the Storstrøm Bridge and at Letten.

Local differences in PAC levels and composition were visualised by PCA of the log-transformed 59 PAC variables for all mussel samples collected in June and December 2001 (cf. Figure 13).
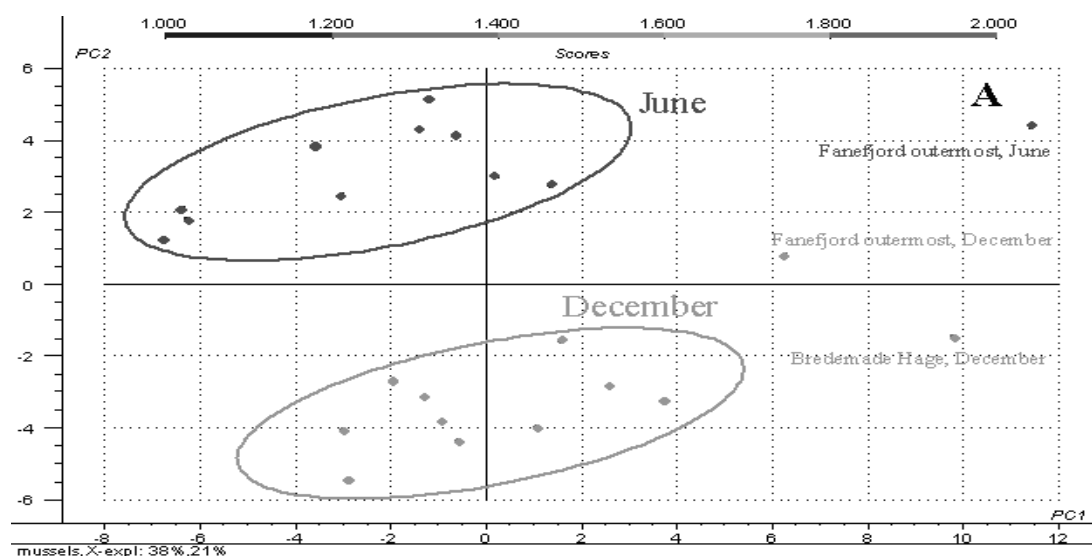

Figure 13. Score plot (PC1 vs. PC2) of the PAC distributions in blue mussels from the Grønsund area showing grouping of samples from June and December, 2001.

Figure 13 illustrates the scores of the different mussel samples according to PC1 and PC2. The first principal component (PC1) accounts for 38% of the variation in the log-transformed PACs, while the second principal component (PC2) accounts for 21% of the variation in data. The score plot for the PCA analysis reveals a grouping of mussels according to sampling time. Mussels sampled in December 2001 are characterised by slightly higher levels in PC1 and lower levels in PC2 than mussels collected in June 2001. A few stations differ from the other stations, i.e. Fanefjord outer station from June and December and Bedemade Hage from December, by having higher scores in PC1. Samples with high scores in PC1 in the score plot are characterised by high levels of variables with high loadings in PC1. Thus, it can be seen from the loading plot in Figure 14 that especially the alkylated PACs have high loadings in PC1. Mussels from Fanefjord outer station and Bredemade Hage have high levels of these compounds. This corresponds with the prevalence of petrogenic sources at these two stations.

Mussel samples collected in June and December are divided into two groups along PC2, indicating a difference in composition. The separation of the variables in

PC2 is not distinct (Figure 13), while, however, there is a tendency of higher loadings (Figure 14) of light and relatively water-soluble compounds like naphthalene (N), acenaphthene (Ace), acenaphthylene (Acy) and several alkylated compounds. Mussels collected in June show higher absolute concentrations of theses compounds. The more heavy unsubstituted parent compounds like e.g. fluoranthene (Fluor), pyrene (Pyr) and benzo(a)antracene (BaA) have relatively low loadings in PC1 and negative loadings in PC2. The majority of mussel samples from December with negative loadings in PC2 is thus seen to have higher absolute levels of these unsubstituated PACs than mussels sampled in June.
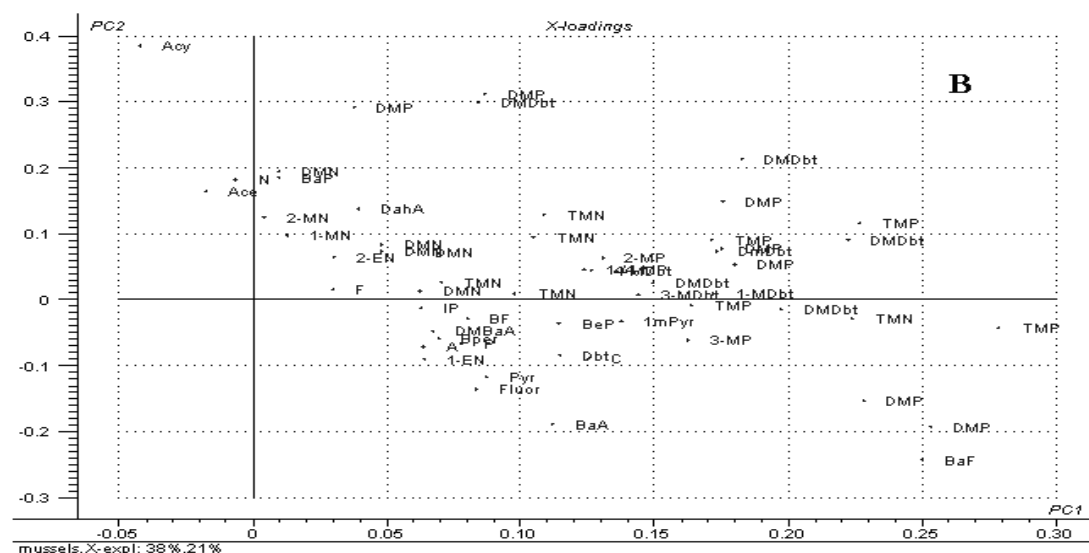

Figure 14. Loading plot (PC1 vs. PC2) of the PAC distributions in blue mussels from the Grønsund area, June and December, 2001, showing individual PACs.

Blue mussels sampled in June show higher absolute levels of many of the light and water-soluble PACs compared to mussels sampled in December, which on the other hand show higher absolute levels of unsubstituted parent compounds. This picture agrees well with the PAC composition seen in water samples after the oil spill, when the alkylated PACs were found in water samples from the whole Grønsund area in April. 2½ months later the unsubstituted PACs made up a relatively higher fraction of the PACs in most of the water samples due to weathering processes primarily removing the light and alkylated PACs from the water. The changes in PAC composition found in mussels is delayed compared to the composition in the water phase. The epifaunal blue mussels collect PACs from the water phase and show a limited capability of metabolising PACs (Porte and Albaiges, 1994, Livingstone, 1992; Broman et al., 1990). However, the light and alkylated compounds can to some extent be excreted prior to metabolism, while the PACs with more than 4 rings are observed to bioaccumulate (Baumard et al., 1998).

Mussels collected at Fanefjord outer station in June and December and at Bredemade Hage in December show high absolute levels of e.g. many alkylated dibenzothiophenes, that are characteristic of recent petrogenic pollution. This reveals on-going oil exposure of the mussels at these locations.

4.3.2 Other biota

Total PAC concentration in shrimps caught in Grønsund 11 days after the oil spill in April 2001 could be compared to levels measured approximately one year later, in May 2002. Total PAC levels in the shrimps decreased 93% during this period of 13 months. This difference was especially due to initially higher concentrations of the light and alkylated PAC compounds, the relatively water-soluble fraction of the PACs found in the Baltic Carrier oil. The crustaceans are primarily exposed to PACs in the water phase, and the decrease in PAC burden of these species therefore agrees well with the decrease of PACs in seawater in Grønsund. Furthermore, crustaceans have a higher capability than e.g. mussels to metabolise PACs (Stegeman and Lech, 1991). The faster decrease of PAC concentrations in crustaceans compared to mussels was also seen after e.g. the Braer and Sea Empres oil spills.

Total PAC levels in fish from Grønsund from both 2001 and 2002 are higher than earlier reported in the same species from Danish waters. The difference in PAC composition in flounder from Grønsund caught immediately after the oil spill and one year later is not as pronounced as for the crustaceans. Total PAC levels in flounder were about twice as high in spring 2001 as compared to 2002. This difference was due to differences in light and alkylated compounds, especially alkylated phenanthrenes. The fish caught in 2002 showed higher levels of the heavy PACs, however. Compared to invertebrates, fish have a high potential of metabolising PACs. The slow decrease in PAC level in fish from Grønsund therefore indicates a continued exposure. PAC concentrations in the liver indicate recent exposure, while concentrations in muscle tissues show PACs accumulated by the organism (Hellou, 1996). The high level of PACs in liver compared to muscle tissues therefore also indicates recent exposure. This agrees well with the slow decline in sediment concentrations in the area. The flounder is a bottom-dwelling fish, and exposure directly from the sediment and feeding on organisms living in the sediment has earlier been shown as an important way of exposure to contaminants.

The PAC levels in trouts from aquacultures in the sound of Grønsund were measured 1½ months after the oil spill, and based on B(a)P tox-equivalents (TEQ) values were of the same order of magnitude as data from comparable areas not affected by oil spills. Besides, benzo(a)pyrene was not detected in trouts from these aquafarms.

After the Braer oil spill, maximum PAC levels recorded in salmon flesh were approximately 14,000 µg/kg ww. Already one week after the spill, levels began to decrease. Six months after the spill, PAC levels in salmon were approaching background levels at all affected sites. Tainting was, however, observed in fish with PAC concentrations near baseline levels – with large differences between single individuals. For wild fish, the PAC level was also decreasing exponentially after the oil spill, approaching background levels after 1½ and 3 months after the oil spill for flatfish and roundfish, respectively (The Ecological Steering Group on the oil spill in Shetland, 1994).

4.5   Conclusion

The levels of PACs in all compartments of the environment in the Grønsund area are within the range of concentrations measured elsewhere in Danish waters. Levels are elevated, though, when compared to the background station Nyord, and

elevated when bearing in mind that Grønsund was an area without any pronounced sources of PAC pollution prior to the oil spill. The elevated PAC levels in the water phase fell to near background levels during the first 2½ months after the oil spill, while the decrease in PAC levels in sediments and mussels proceeds more slowly. Laboratory studies and diagnostic ratios calculated for field samples indicate that the oil is being removed both by evaporation and dissolution, but to some extent also by biodegradation.

5   Summary

Spilled oil may disappear and/or change in toxicological potency as a result of various processes like evaporation and biodegradation. Analysis of the composition of spilled Baltic Carrier oil at a test locality show disappearing of the oil as a result of physical and chemical processes as well as biodegradation. In April 2001, PAC levels in seawater from the Grønsund were of the range 641 to 12,833 ng/L with a median value of 1,115 ng/L. Even after 2½ months, PAC concentrations in seawater had decreased to 28.9-124 ng/L, which is close to baseline levels. In general the sediments were very heterogenous in PAC content. The largest petrogenic input was found at the southern coast of Møn, Bogø and Farø. PAC levels measured in sediments from April, 11 days after the oil spill, were in the range 89.8-4,119 μg/kg dw. In June the overall level was 45.8-1,304 μg/kg dw, and in December total concentrations of 81.1-1,018 μg/kg dw were measured in sediments from the Grønsund area.

The PAC level in blue mussels, *Mytilus edulis,* only decreased slowly. In June concentrations of 132-1,031 μg/kg ww were measured, while levels in December were 185-894 μg/kg wet weight. These values are up to 5 times above levels measured elsewhere in Danish waters. The overall decrease in PAC bodyburden from June to December was due to excretion of light (2-3 ringed) and substituted compounds. Mussels sampled in December, on the other hand, had higher levels of many parent compounds of higher molecular weight (4-6 ringed). PAC levels in shrimps from Grønsund decreased by a factor of 10 during the first year after the Baltic Carrier accident; again, this decrease was mainly due to a reduction in light (2-3 ringed) and substituted compounds.

6   Acknowledgement

7   References

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