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A chemical and biological study of the impact of a suspected oil seep at the coast of Marraat, Nuussuaq, Greenland

With a summary of other environmental
studies of hydrocarbons in Greenland



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studies of hydrocarbons in Greenland**

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Data sheet

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Abstract: These studies were conducted on the Nuussuaq Peninsula at Marraat, where GEUS discovered oil in porous volcanics in the early 1990ies. This oil was also found in the Marraat-1 core drilled in 1993. At Marraat the presence of oil stained stones scattered along the coast indicates oil bearing strata and the existence of potential oil seeps. The studies reported here had the objective to see, if the suspected seep had a local impact on the chemistry and biological communities in the marine environment at Marraat. The study included sediments, blue mussels and fish that were analyzed for hydrocarbons, a Pollution Induced Community Test (PICT), a sediment toxicity test and a measurement of PAH metabolites in fish gall. The hydrocarbon pattern found in sediment and biota samples indicates input from both immature petrogenic hydrocarbons of possible terrestrial origin and local pollution by fuel oil. But the hydrocarbon levels found were low and do not indicate an input from a natural local oil seep at Marraat. The results of the PICT, the sediment toxicity test and the PAH metabolite study do not either indicate the presence of an oil seep. However, compared to sediments from a larger area of West Greenland the sediments close to Nuussuaq and Disko have higher concentrations of PAH expressed on basis of their content of organic matter. This could be a result of natural seepage of oil in the Nuussuaq/Disko region.

Keywords: Greenland, PAH, sediment, Marraat, environment, hydrocarbons, oil seep.

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Summary

A number of studies have been initiated to develop a “Strategic Environmental Impact Assessment Report” in connection with opening an offshore region at Disko Island, Greenland to hydrocarbon exploration.

One of these studies was conducted on the Nuussuaq Peninsula at Marraat, where GEUS discovered oil in porous volcanics in the early 1990ies. This oil was also found in the Marraat-1 core drilled in 1993.

At Marraat the presence of oil stained stones scattered along the coast indicates oil bearing strata and the existence of potential oil seeps. The study reported here had the objective to see, if the suspected seep had a local impact on the chemistry and biological communities in the marine environment at Marraat.

The study included sediments, blue mussels and fish that were analyzed for hydrocarbons, a Pollution Induced Community Test (PICT), a sediment toxicity test and a measurement of PAH metabolites in fish gall.

The hydrocarbon pattern found in sediment and biota samples indicates input from both immature petrogenic hydrocarbons of possible terrestrial (i.e. land based) origin and local pollution by fuel oil. But the hydrocarbon levels found were low and do not indicate an input from a natural local oil seep at Marraat. The results of the PICT, the sediment toxicity test and the PAH metabolite study do not either indicate the presence of an oil seep. However, the existence of an oil seep emitting low concentrations of oil to the environment cannot be excluded.

However, compared to sediments from a larger area of West Greenland the sediments close to Nuussuaq and Disko have higher concentrations of PAH expressed on basis of their content of organic matter. This could be a result of natural seepage of oil in the Nuusuaq/Disko region.

Dansk resumé

I forbindelse med åbning af offshore olie og kulbrinte eftersøgning ved Diskoøen i Vestgrønland er der startet en række studier, som bidrager til en strategisk miljøvurdering af området.

Et af disse studier blev gennemført på Nuussuaq halvøen ved Marraat, hvor GEUS i begyndelsen af 1990-erne fandt olie i porøse vulkanske bjergarter. Denne olie blev også fundet i borekærnen fra Marraat-1 i 1993.

Tilstedeværelsen af sten med et indhold af olie langs kysten ved Marraat indikerer at der findes en olieholdig horisont og mulighed for olieudslivninger. Studiet, der rapporteres her, havde det formål at undersøge om den forventede olieudslivning har en målelig påvirkning af kemien og biologien i det marine miljø ved Marraat.

Studiet omhandler sedimenter, blåmuslinger, og fisk som blev analyseret for kulbrinter, en test for forureningsinduceret tolerance, (Pollution Induced Community Test (PICT)), en sediment toksikologisk test og en måling af PAH metabolitter i fiskegalle.

PAH-sammensætningen i sediment og biota indikerer både umodne petrogene formodentlig terrestriske kilder, og kilder fra lokal forurening med brændselsolie. Men niveauerne af PAH var lave og indikerede ikke en direkte kilde ved Marraat. Resultaterne af PICT, sediment toksikologi, og af PAH metabolit studierne indikerer heller ikke at der skulle være en lokal naturlig olieudslivning ved Marraat. Det kan dog ikke udelukkes at der eksisterer en svag kilde til udsivning af olie i lave koncentrationer ved Marraat.

Sammenlignes imidlertid sedimenterne fra hele Disko og Nuussuaq området med sedimenter fra det øvrige Vestgrønland ses det at de første har højere indhold af PAH udtrykt på basis af indholdet af organisk stof. Dette kunne være et resultat af naturlig udsivning af olie i Disko/Nuussuaq regionen.

Kalaallisut imaqarniliaq

Kalaallit Nunaata Kitaani Qeqertarsuup eqqaani imaani uuliamik ikummatissiassanillu misissueqqissaarnerit aallarnerneqarnerannut atatillugu misissuinerit qassigiinngitsut aallartinneqarput, misissuinerillu tamatumani avatangiisit periaasissiorfiusumik naliliiffigineqarneranni atorneqassapput.

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Misissuinerimi kinnganikut, uillut, aalisakkallu ikummatissiassakkut akuinik peqarnerisut misissuiffigineqarput, mingutsitsinermut akiuussutissaqartoqarnerisut, immap naqqani kinnganiku toqunartumik misissuiffigineqarpoq kiisalu aalisakkat masiini PAH-p (aamarsuakkunnik sananeqaatillit ikumanikuinit pinngortartut) allanngornerinik sinnikoqarnerisut misissuiffigineqarput.

PAH-p kinnganikumi uumassusilinnilu akui petroleussamit inerilluarisimangitsumit qularnangitsumik nunamit pisuussumit aammalu tamatuma eqqaani ikummatissap ikumanerlukuinit pisuuneranut takussutissaapput. Kisianni PAH annikitsuinnaagami Marraat eqqaanniit toqqaanartumik pisuunissaa ilimanangilaq. Mingutsitsinermut akiuussutissaqalersimasunik misissuinermit paasisat, kinnganikup toqunartoqarneranik, aammalu PAH-p sinnikuinik misissuinerit Marrarni uuliamik aniasoqarneranik takutitaqanngillat. Taamattorli uuliap annikitsunnguulluni Marraat eqqaanni aniarusaarfeqarnera mattunneqavissinnaanngilaq.

Taamaattorli Qeqersuarmi Nuussuarmilu tamarmi kinnganikut Kitaani sumiiffinnut allanut sanilliukkaani takuneqarsinnaavoq PAH uumassusilinneersut tamaaniittoq annerusoq. Qeqertarsuarmi/Nuussuarmi uuliamik nammineerluni seerisoqarusaarneranik tamanna pissuteqarsinnaavoq.

1 Introduction

A number of studies have been initiated to develop a “Strategic Environmental Impact Assessment Report” in connection with opening an offshore region at Disko Island, Greenland to hydrocarbon exploration.

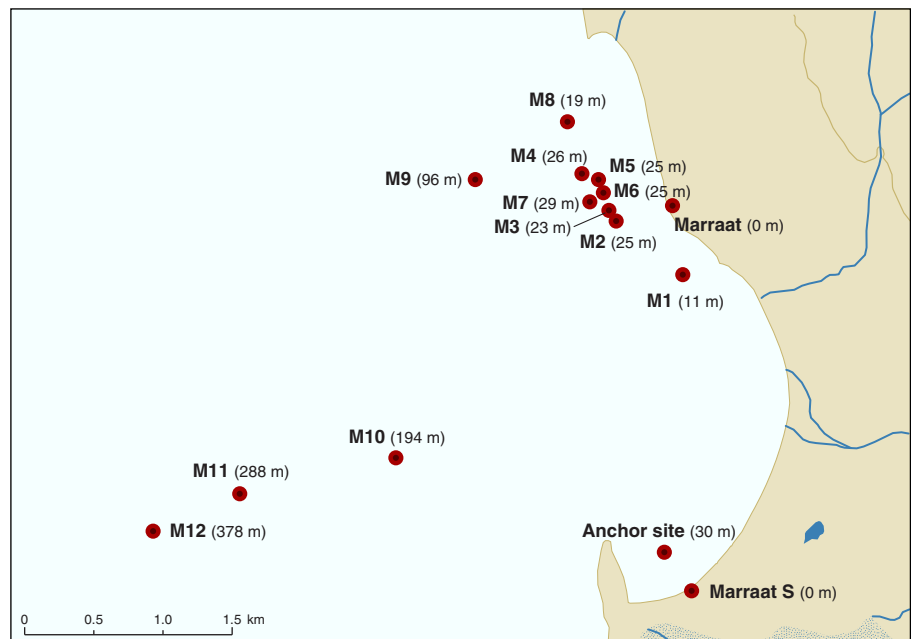
One of these studies was conducted at Marraat on the Nuussuaq Peninsula, one of the most impressive oil seep localities in West Greenland together with Sikillinge towards southeast.

Recent studies (Bojesen-Koefoed et al., 2001) have demonstrated a complex geochemistry of the area with coal bearing strata, and that there seems to be active seepage (mixture of fresh and degraded compounds suggest replenishment).

The presence of oil stained stones scattered along the coast indicates oil bearing strata and the existence of potential oil seeps. The study reported here had the objective to investigate, if the suspected seep had a local impact on the chemistry (section 2) and biological communities (section 3) of the area at Marraat.

Sampling was conducted in 2005 and sites sampled are shown in Figure 1. Data from the study and from other studies of hydrocarbon levels in Greenland (including sediments from offshore areas, from municipal waste dump sites and from sites with no known local pollution sources) have been compiled in Appendix 1. It is a general observation that levels of petroleum compounds in the Greenland environment are very low.

Figure 1. Sampling sites and water depths at and around Marraat, West Greenland.



2 TPH and PAH levels in surface sediment and biota

2.1 Background

This part of the study of the Disko area focuses on background levels of total petroleum hydrocarbons (TPH) and polycyclic aromatic hydrocarbons (PAH) in environmental samples including surface sediment and biota (mussels and fish) from the Marraat area.

During late August 2005 samples of sediment, fish (shorthorn sculpin, *Myoxocephalus scorpius*, and Greenland cod, *Gadus ogac*) and blue mussel (*Mytilus edulis*) were collected in the Marraat area, c.f. Figure 1. 17 sediment samples were collected at different locations (distance from the coast) and at different depths. Table 1 lists the sediment samples that were collected and analysed in this study. The sediments were collected either by hand at the shore at low tide, by a HAPS core sampler, or by a diver.

Table 1. Sediment samples collected at Marraat, West Greenland, August 2005, see also Figure 1.

AM-ID	MIMI-ID	Sample	Position	Depth(m)	Method
33501	5-0460	Anchor site	70°29,72 N - 54°11,67 W	30	diver
33480	5-0466	Marraat S	70°49,33 N - 54°18,78 W	0	by hand
33483	5-0467	M1	70°30,61 N - 54°12,24 W	11	HAPS
33484	5-0468	M2	70°30,92 N - 54°13,23 W	25	HAPS
33485	5-0469	M3	70°30,88 N - 54°13,12 W	23	HAPS
33486	5-0470	M4	70°31,03 N - 54°13,63 W	26	HAPS
33487	5-0471	M5	70°31,02 N - 54°13,43 W	25	HAPS
33488	5-0472	M6	70°30,98 N - 54°13,34 W	25	HAPS
33489	5-0473	M7	70°30,93 N - 54°13,46 W	29	HAPS
33490	5-0474	M8	70°31,20 N - 54°13,93 W	19	HAPS
33491	5-0475	M9	70°30,91 N - 54°14,78 W	96	HAPS
33493	5-0476	Marraat OM	70°51,70 N - 54°20,90 W	0	by hand
33495	5-0477	Marraat-1	70°51,70 N - 54°20,90 W	9.8	diver
33496	5-0478	Marraat-2	70°51,70 N - 54°20,90 W	8.5	diver
33497	5-0479	Marraat-3	70°51,70 N - 54°20,90 W	13.7	diver
33498	5-0480	M10	70°29,81 N - 54°14,88 W	194	HAPS
33499	5-0481	M11	70°29,54 N - 54°16,49 W	288	HAPS
33500	5-0482	M12	70°29,32 N - 54°17,33 W	378	HAPS

Biota samples included 33 shorthorn sculpin (*Myoxocephalus scorpius*) and two Greenland cod (*Gadus ogac*) caught at the Marraat area and one collection of blue mussels (*Mytilus edulis*) from the area. The sculpins and Greenland cod were caught either by angling or in gill net; the catches included both males and females with liver weights ranging from 0.5 to 26 g. The sculpin liver samples were pooled into eight samples and the Greenland cod livers into one sample.

Blue mussels were sampled by hand at low tide; they were found only at one location: on the rocks SE of the anchorage (see Figure 1). Their sizes

ranged from 36 to 72 mm shell length, and they were pooled into two samples: 36-49 mm and 60-72 mm, respectively.

2.2 Preparation of biota samples

2.2.1 Fish samples

After thawing at room temperature, all fishes were dissected and their liver and gall bladder removed. Livers were pooled into eight sculpin liver samples and one Greenland cod liver sample; each sample consisted of approximately 10-12 g liver (wet weight). Each sample was homogenized before being analysed. From the gall bladders, the gall juice was recovered and used for analyses of PAH metabolites (reported in section 3 of this report).

2.2.2 Blue mussels

After thawing, the mussels were pooled into two samples according to their size (36-49 mm and 60-72 mm, respectively). The soft parts were then removed, pooled accordingly and homogenized.

2.3 Chemical analyses

Collected sediment and biota samples were extracted and analysed for their content of mineral oil (total petroleum hydrocarbons, TPH, covering the n-alkane range of nC13 to nC38) using GC-FID and more specifically for selected polycyclic aromatic hydrocarbons (PAH), including individual compounds and specific alkylated isomer groups using GC-MS. Prior to the extraction, all samples were spiked with a ^2H - and ^{13}C -labelled recovery spike mix comprising 18 unsubstituted PAHs (2-6-ring PAHs) and one methylated naphthalene.

2.3.1 Extraction and clean-up

The sediments were allowed to equilibrate at room temperature and aliquots of about 40 g were sub-sampled and allowed to dry at room temperature. After drying, approx. 10 g were added a similar amount of pre-conditioned sodium sulphate and mixed thoroughly by grinding in a mortar. The mixture was then charged to a 33 mL ASE stainless steel cell, to which approximately 2 g of HCl activated copper powder for sulphur removal had been pre-charged, eventually spiked with a recovery standard mixture of 19 isotopically labelled PAH after which the cell was closed carefully. The charged cells were then extracted by ASE using dichloromethane-acetone (1:1 v:v) as solvent. Samples were extracted in two cycles at 125°C and 102 atm. (1500 psi). Sediments were extracted in duplicates, and for approximate each 10 samples a laboratory blank was included.

After concentration on a rotary evaporator, the solvent was exchanged to n-hexane, and the extracts eluted through 2 g activated SiO_2 with pentane and dichloromethane, successively, for recovery of the aliphatic and aromatic fractions, respectively. Both fractions were eventually concentrated to 1 mL using rotary evaporation and gentle nitrogen blowing.

Homogenised tissue samples (approximately 2 and 10 g ww for liver and mussel, respectively) were Soxhlet extracted with 500 mL toluene. Water was successively removed using a Dean-Stark condenser. Toluene was removed on a rotary evaporator, and the lipid extracts successively removed by passive diffusion using polyethylene membranes. The lipid-free extracts were eventually eluted through 2 g activated SiO₂ as described above. Again both aliphatic and aromatic fractions were recovered and concentrated to 1 mL.

2.3.2 TPH analysis by GC-FID

Aliphatic and aromatic fractions from the same sample were recombined by mixing 100 µL of each in a GC-vial. The recombined extracts were then analysed by GC-FID using a HP 5890 Ser. GC equipped with a 7365 autosampler and a flame ionisation detector operated at 320°C. 1 µL extract aliquots were injected at 300°C in splitless mode and separated on a 30 m x 0,25 mm ID x 0,25 µm RTX-1 film (Restek) operated from 40-320°C in 40 min. using He as carrier gas. Quantification was based on the external calibration technique (five-point) using mixtures of Brent crude oil as the external standard. The quantification included the n-alkane range of nC₁₃ to nC₃₈.

2.3.3 PAH analysis by GC-MS

The aromatic fractions were spiked with an internal standard mixture of eight ²H-isotopically labelled PAH and analysed by GC-MS in SIM mode using a Thermo DSQ GC-MS instrument equipped with a CTC Pal autosampler. 1 µL extract aliquots were injected at 280°C in splitless mode and separated on a 30 m x 0,25 mm ID x 0,25 µm DB-5 MS film (J&W) operated from 80-280°C in 45 min. using He as carrier gas. Data were acquired in 8 groups including both target, surrogate and internal standard compounds. Quantification was based on the internal calibration technique (six-point) using the aforementioned mixture of ²H-isotopically labelled PAH. Quantified results were corrected for recovery.

2.4 Results and discussion

The results of the chemical analyses (TPH and PAH) of sediment and biota samples are given Table 3-4 and Table 5, respectively. For the sediments, results are presented for each sample, while as mentioned above, the biota samples have been pooled into nine fish liver samples and two blue mussel samples.

2.4.1 TPH levels in sediments

TPH levels (nC₁₃ to nC₃₈) in sediments range from < 50 to 580 mg/kg dry weight and with a geometric mean of 82.9 mg/kg dw. Apart from a few samples having levels at a few hundred mg/kg levels are relatively low and only give weak indication of oil seeps or other local petrogenic sources. GC-FID analysis did not record typical petroleum compounds like n-alkanes, but only unresolved humps. These humps may include various complex hydrocarbons from natural biogenic input or from severely degraded oil.

Subsequent GC-MS fingerprinting analyses of selected sediment extracts (M-1, M-9 and M-10) have revealed only minor levels of petroleum hydrocarbons. The n-alkanes (nC₂₃ to nC₃₁) showed a high odd-even predominance, which generally indicate immature petrogenic input of terrestrial (i.e. land based) origin. The hopane pattern (recorded at m/z 191) also showed the presence of compounds probably related to immature petrogenic hydrocarbons. Also the very low levels of regular C₂₇-C₂₉ steranes and elevated levels of C₃₀ steranes (recorded at m/z 217 and 218) could indicate terrigenous input. Highest signals were recorded from methylated PAH naphthalenes, phenanthrenes, dibenzothiophenes and pyrenes. Comparing the hopane pattern with that of extracts from oil-stained stones collected at the beach at Marraat, did not enable the identification of mussel or liver extracts as hydrocarbons originating from the "Marraat" oil.

The TPH recorded in the sediment samples indicates that the sources are local pollution from fuel oil, e.g. marine diesel, whereas data does not indicate contribution from local oil seeps.

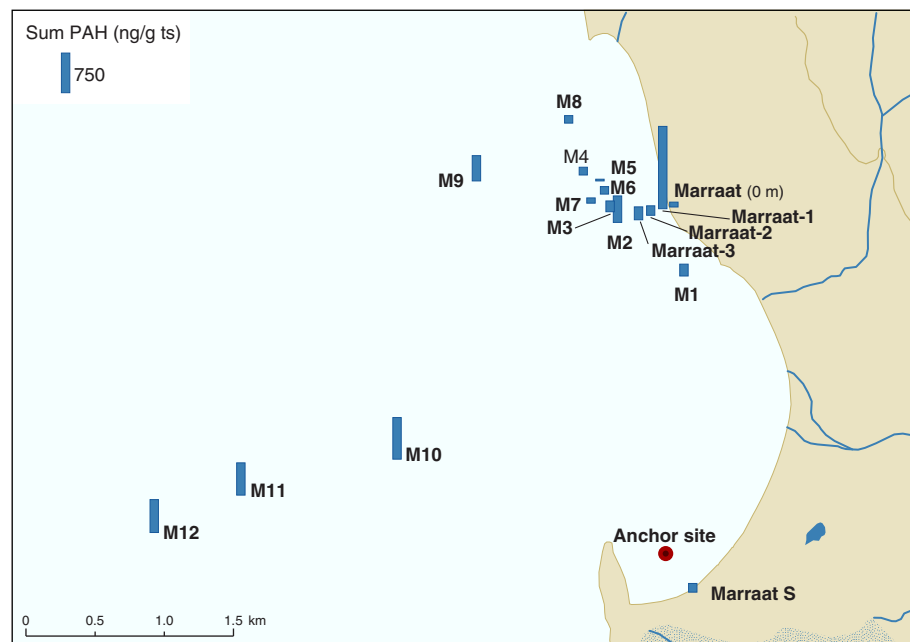
Other studies of TPH in sediment samples from the Arctic area generally show similar, but also rather varying results (Dahle et al., 2006). In the Barents Sea, open sea sediments have a content of up to 80 mg/kg dw, while harbour sediments have somewhat higher contents, 120 - 700 mg/kg dw. In the White Sea, TPH levels were generally low with values ranging from 0.5 to 2.5 mg/kg dw in the Dvina and Kadalaksha bays and 0.5 to 1.0 mg/kg dw in the Onega Gulf; more recent studies of sediment from the same area, however, have shown somewhat higher levels, 4.2 - 33.2 mg/kg dw. In the Kara Sea, TPH levels were low and observed to range between 0.5 to 7 mg/kg dw with lowest levels of the shallow water sediments and highest of sediments from the central area; in the Laptev Sea, levels were distinctly higher ranging between 10 and 180 mg/kg dw.

2.4.2 PAH levels in sediments

The PAH analyses included 19 unsubstituted PAHs (2-6 ring systems), three methylated PAH and eight groups of alkylated PAH (naphthalenes, phenanthrenes and dibenzothiophenes). PAH levels in sediments from the Marraat area range from just below 100 µg/kg to above 1500 µg/kg on a dry weight (dw) basis as illustrated in Figure 2. The lowest values were observed for the shallow sediments just outside the coast of Marraat. One sample (Marraat 1), however, sampled at 10 m depth, showed the largest value of all: 1558 µg/kg dw. Other shallow (down to 25 m depth) samples from up to 500 m from the coast ranged from about 100 µg/kg to about 500 µg/kg dw (c.f. Table 3).

The PAH data have also been calculated on basis of the organic content (estimated as loss on ignition) in the sediment samples (c.f. Table 4). PAHs are primarily associated with (i.e. bound to) particles rich in organic matter in sediment, and a much better correlation is obtained for the PAHs with the organic content than with the dry matter content (c.f. Paragraph 2.4.3.).

Figure 2. PAH concentrations in sediments at Marraat, 2005.



Other samples from greater depths (200-400 m) and more than 1000 m from the coast showed 3 to 4 times higher levels than samples closer to the coast. This may be attributed to the fact that the sedimentation rate is higher and with higher binding capacity for PAH at greater depths than at near-shore shallow depths, where primarily coarse particles with less binding capacity will sediment.

The levels of PAH recorded in this study have been compared to other recent studies from the Arctic, e.g. levels in sediments from Norwegian and Russian areas (Dahle et al., 2006). This shows that the levels observed in Greenland are comparable to values observed elsewhere (Table 2), but also that some areas with pronounced oil spills have very high levels. In comparison, levels from Danish bottom sediments generally seem to be significantly higher than levels in the Arctic.

Table 2. PAH levels (geometrical means) in Arctic sediment from Greenland, Norway and Russia and bottom sediment from Denmark (ng/g DW).

Arctic area	Location	Σ PAH (ng/g dw)	Number of samples
Greenland	Qaanaaq (Thule) ¹	238	10
	Marraat (Disko Bay) ²	241	17
Russia ³	Pechora Sea	46	53
	White Sea	56	11
	Kara Sea – shelf	92	18
	Barents Sea – S-E	146	34
	Barents Sea – S-W	270	45
	Ob-Yenisei estuaries	301	9
	Barents Sea – N-E	389	15
	Barents Sea – N-W	1587	65
	Kola-Pechenga Bays	2365	12
Norway ³	Svalbard, inshore	7396	20
Denmark (2003) ⁴	Wadden Sea	1569	14
	Aarhus Bugt	3457	6
	Kattegat	1051	7
	Øresund (reference)	228	4
	Øresund (hot spot)	3214	4
	Baltic Sea	1878	5

¹Riget et al. (2003).

²This report.

³Dahle et al. (2006), ⁴NERI, unpublished results (NOVA sediment compiled, 2003).

2.4.3 PAH in sediments explained by ignition loss and grain size

The sediments from Marraat have been collected over a period of 3 days and inside a very small area at Marraat. They will be used to investigate the basic relations between grain size, loss on ignition (LOI) and concentration of PAH. On all Marraat sediments the following has been measured (tables 3, 4, 11, and 12):

- Sum PAH, $\mu\text{g}/\text{kg} = \text{ng}/\text{g}$ measured by NERI.
- Grain size distribution, here only the fraction less than 63μ is used ($\%<63\mu$) measured by GEUS.
- Loss on ignition measured as % by NERI. This is assumed to be a good measure of the content of organic matter.

In Figure 3 the LOI is plotted against the grain size distribution (% less than 63μ).

As can be seen there is a strong linear correlation between LOI and grain size. (One point is of unknown reasons an outlier). This correlation means that it is not possible effectively to distinguish between the influence by grain size and the influence from loss on ignition on PAH levels.

Figure 3.The loss on ignition for the Maaraat sediments plotted against the grain size.

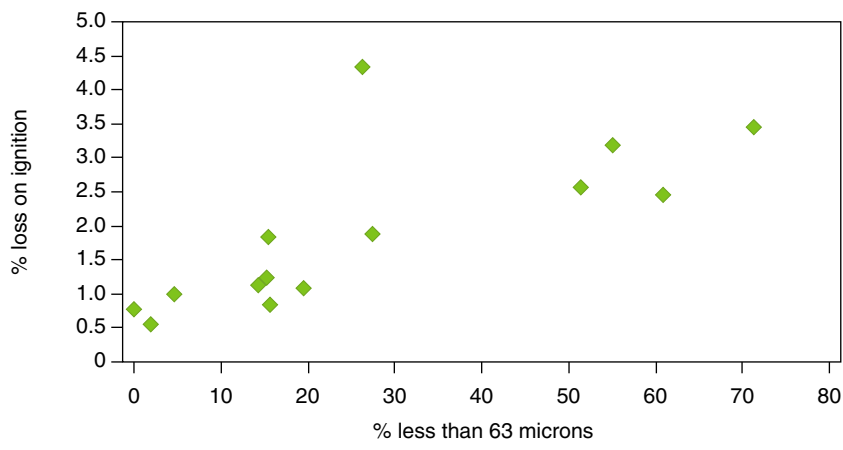
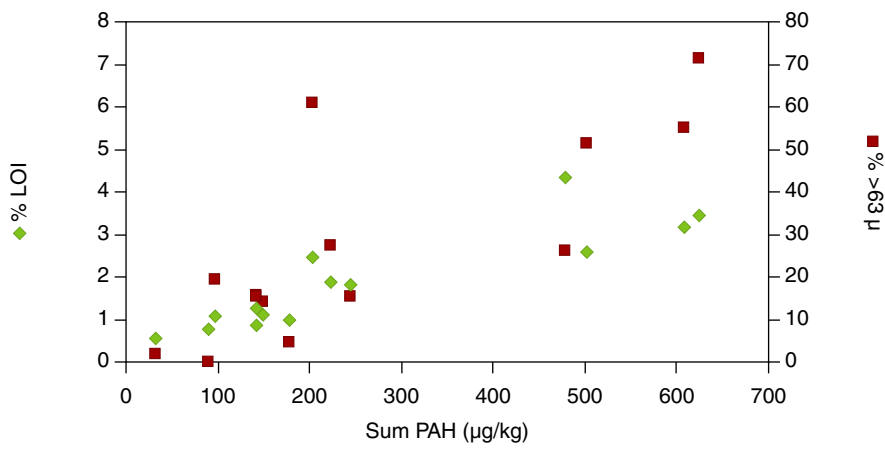


Figure 4. The loss on ignition and the grain size plotted against the concentration of PAH for the Marraat sediments.



In figure 4 is both the LOI and the grain size plotted against the PAH concentration in the sediments. It looks as if the LOI gives the best explanation of the PAH as also a statistical treatment shows.

Statistical treatment of the data in figure 4

If the PAH concentration is treated as a linear function of both the grain size and the ignition loss after the formula:

$$\text{PAH ng/g} = m_2 \times (\% \text{LOI}) + m_1 \times (\% < 63 \mu) + b$$

one finds the following regression parameters:

	m2	m1	B	R ²
All data from Marraat	116,7	2,46	-20	82,5
Outlier removed	278,4	-3,5	-123	88,4

It is seen that there is a good degree of explanation (high R²), and better if the outlier is removed. A negative value for b means that if the ignition loss is low and the sediment is coarse, the model predicts a negative concentration of PAH. This is of course not possible. As the model furthermore shows that the significance of m2 is much larger than that of m1, it is reasonable to simplify the model to:

$$\text{PAH ng/g} = m \times (\% \text{ LOI})$$

That means proportionality between PAH and the loss on ignition.

The simplified regression parameters are:

	M	R ²
All data from Marraat	144,6	0,93
Outlier removed	157,8	0,94

Conclusion about the Marraat sediments

Based on the Marraat sediments alone one can conclude that the loss on ignition and the grain size are strongly correlated, but the loss on ignition gives the best explanation of the PAH concentrations measured in the sediments. There is proportionality between LOI and the sum concentration of PAH with a R² as high as 0.93 to 0.94. It seems as if all the variation in the concentration of PAH is explained by the LOI and very little variation is left to be explained by the proximity of the sediment to the Marraat oil seep.

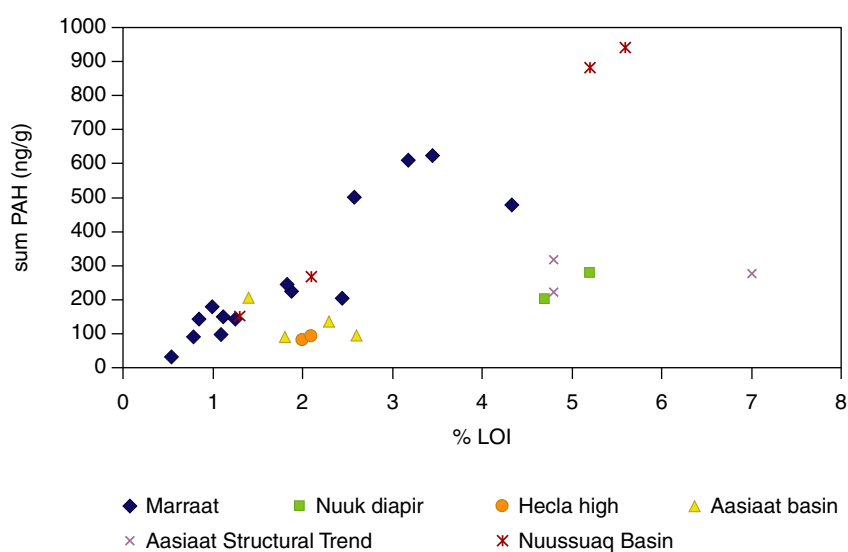
Thus it appears that the Marraat oils seep either does not affect the sediments or that it affects them all equally much.

Comparison with other sediments data from West Greenland

With this knowledge all the newest sediment data from West Greenland can be treated in the same way and compared.

In figure 5 sum PAH is plotted against loss on ignition (LOI, assumed to be the content of organic matter) for the Marraat sediments and sediments collected in other parts of West Greenland, with different signatures for the different geological settings.

Figure 5. Plot of the concentration of PAH against the loss on ignition for Greenland west coast sediments.



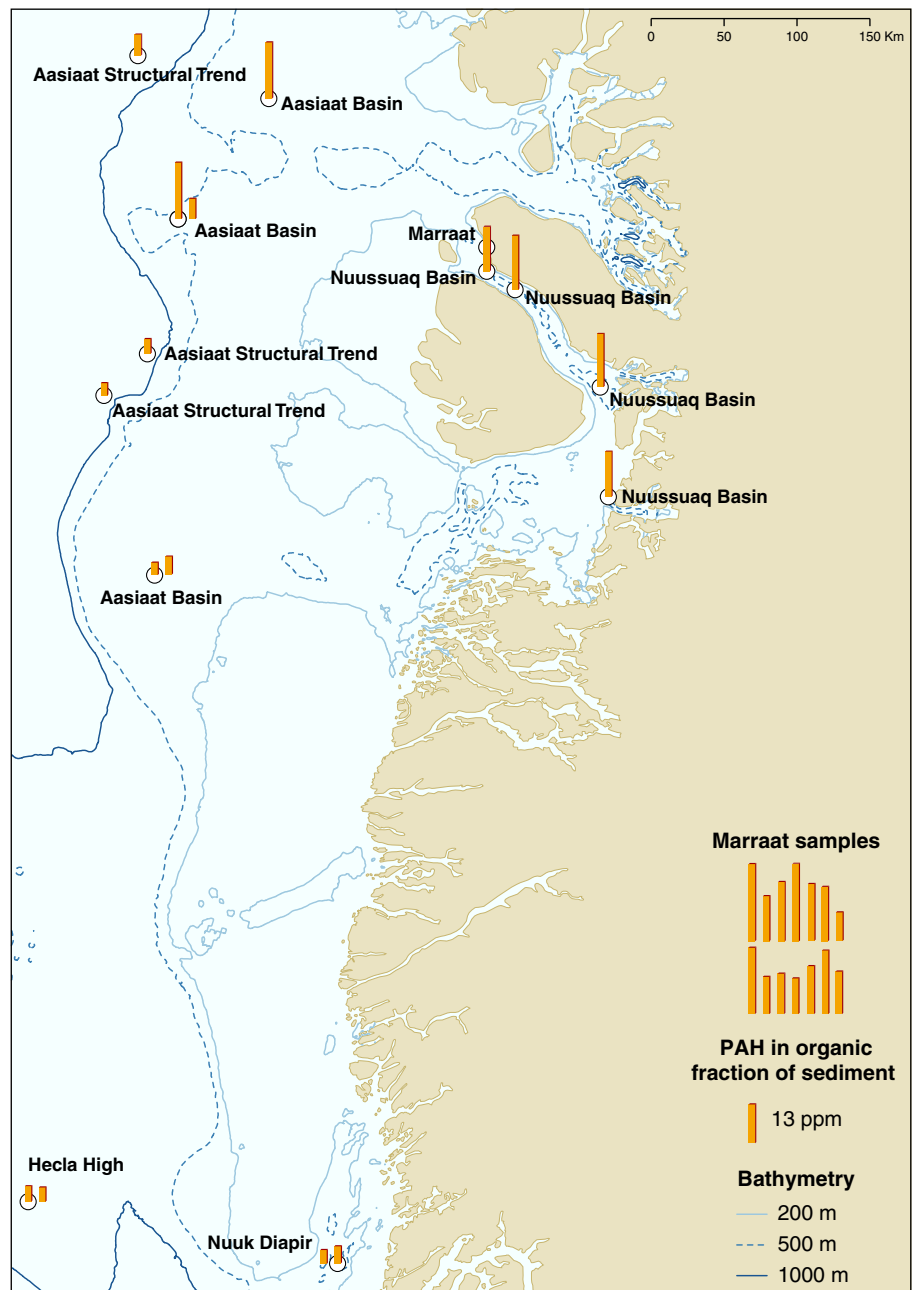
It is seen that the Marraat sediments and the Nuussuaq Basin sediments all fall on the same line, and all the other sediments (with one exception) have 2 to 4 times lower concentrations of sum PAH for a given LOI. The Nuussuaq Basin sediments are all sampled in Vaigat Sound or in the Disko Bay.

The elevated PAH concentrations may be caused by the oil containing rocks on Nuussuaq and Disko Island or may be a result of all the Marraat and Nuussuaq basin sediments being sampled in semi enclosed waters (Vaigat Sound or Disko Bay) while the other sediments are sampled in the open waters of the Davis Strait. However, if the PAH concentrations are expressed on basis of the loss on ignition there is a clear picture showing that the sediments from areas close to Nuussuaq and Disko are higher than the sediments from elsewhere on the Greenland west coast, see figure 6.

Conclusion

Taking the loss on ignition into account, the Marraat and the Nuussuaq basin sediments are high in PAH, but it appears that the Marraat sediments are not directly influenced by the proximity of the known oil see page area of Marraat.

Figure 6. Map of West Greenland showing the different locations where both PAH and LOI has been measured. The bars show the concentration of PAH expressed on basis of LOI, as ppm PAH in organic matter. The figure shows that the PAH in organic matter is clearly higher in the areas close to Nuussuaq and Disko and at two locations rather close to Nuussuaq/Disko.



2.4.4 PAH composition in sediments

The relative PAH composition of sediment extracts is shown in the following figures (7A-D). The relative PAH content (relative to the total sum) in offshore sediments has been plotted together in groups of stations with similar characteristics (distance from the coast). The alkylated PAH (naphthalenes, phenanthrenes and dibenzothiophenes) are relatively dominant in most sediments; this generally is an indication that they are of petrogenic origin.

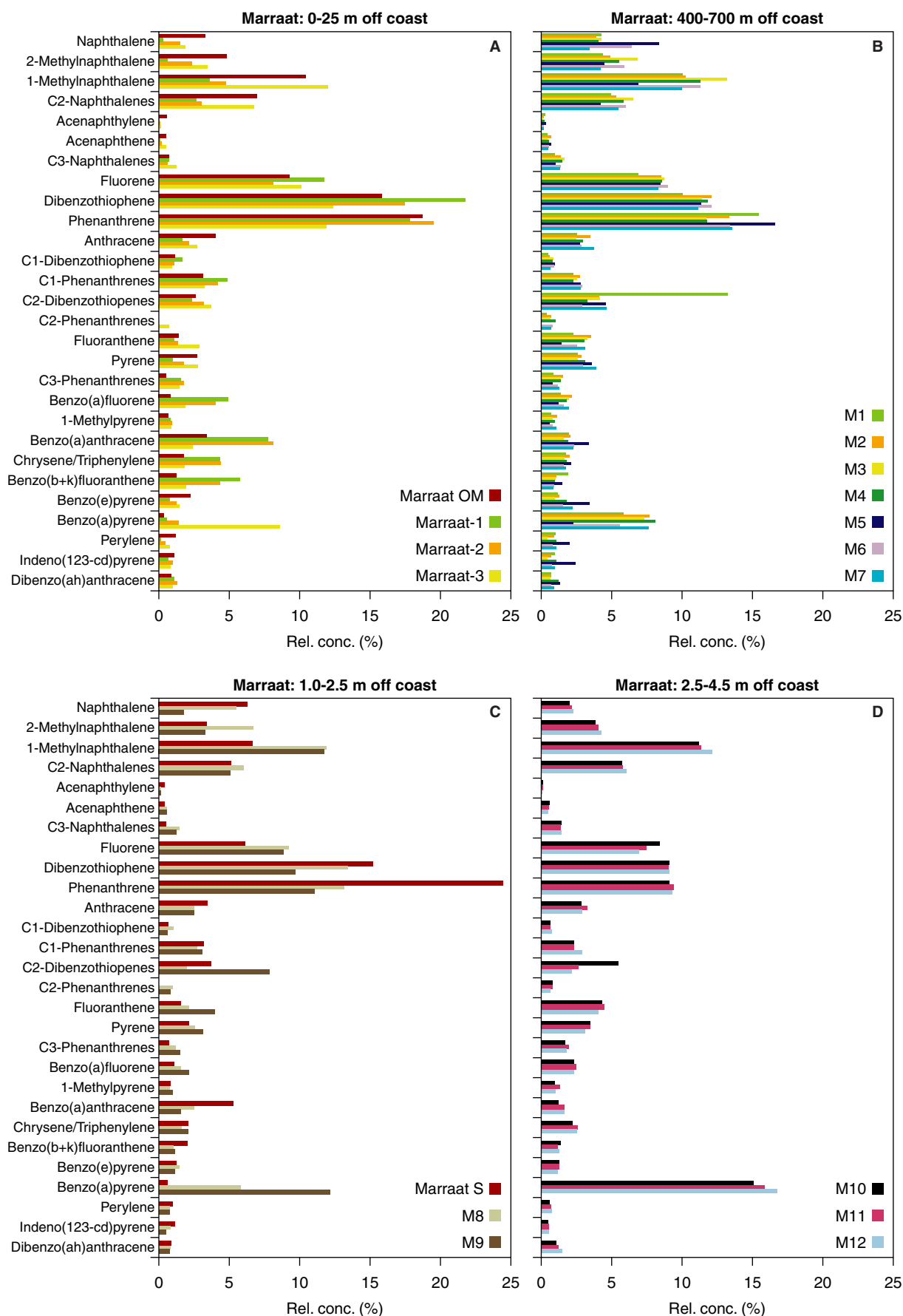


Figure 7A-D. Relative PAH concentrations in offshore sediment samples from the Marraat area, 2005.

The sediments from larger depths are characterized by a relatively high perylene content. This often indicates a high level of recent organic/biogenic material as a source.

2.4.5 PAH sources in sediments

To investigate whether the observed sediment levels of PAH could be due to oil seepage from source rocks present in the Marraat area or primarily diffuse anthropogenic input to the area a preliminary source allocation of the PAH was investigated.

Various ratios between individual PAH have been used frequently to distinguish between petrogenic (i.e. petroleum derived) and pyrogenic (i.e. combustion derived) sources (Oros and Ross, 2005). Such ratios include MP/P, BaA/C, Fl/Py and IPy/BPe. None of these ratios, however, gave clear indication of the possible sources in this area. Most ratios gave values that could indicate a mixture of petrogenic and pyrogenic sources, and even for those samples having the higher levels, there were no clear indications of a definite petrogenic source. These observations seem to be consistent with the results of the GC-MS fingerprinting of selected sediments. Here we did not record significant levels of any typical mature petrogenic biomarkers.

2.4.6 TPH levels in biota

TPH levels (nC13 to nC38) in biota samples range from 0.13 mg/g ww in mussels to 0.54 mg/g in sculpin liver. For three samples, values were just below the detection limit. In blue mussel an average of 0.15 mg/g ww was found (range: 0.13-0.17 mg/g ww); in sculpin liver it was 0.40 mg/g ww (range: 0.27-0.54 mg/g ww), and in Greenland cod liver 0.38 mg/g ww. Values for individual pooled samples are given in Table 5.

As for the sediment samples, none of the biota samples analysed by GC-FID chromatograms showed clear signs of regular petroleum compounds (e.g. n-alkanes). However, GC-MS fingerprinting of the mussel and liver extracts showed low concentrations of aliphatic hydrocarbons (e.g. n-alkanes), and as for the sediment samples, a distinct odd-even predominance (nC19 to nC31) was observed. Lighter alkylated PAH (naphthalenes, phenanthrenes and dibenzothiophenes) and petroleum biomarkers (hopanes) showed the regular pattern of light fuel oil. Again, by comparing the hopane pattern with that of extracts from oil-stained stones collected at the beach at Marraat, did not enable the identification of mussel or liver extracts as hydrocarbons originating from the "Marraat" oil. Therefore, the observed hydrocarbons in the biota samples probably indicate input from both immature petrogenic hydrocarbons of possible terrestrial origin and local pollution by fuel oil.

2.4.7 PAH levels in biota

The PAH analyses of biota included the same compounds as in sediment. The following levels were observed: blue mussels, 0.12 µg/g ww (range: 0.10-0.14 µg/g ww); shorthorn sculpin (liver), 0.39 µg/g ww (range: 0.29-0.49 µg/g ww); Greenland cod (liver), 0.39 µg/g ww. Values for individual samples are given in Table 5.

For some of the samples, the recovery of naphthalene and methyl-naphthalene (based on spiked isotopically marked standards) was quite low (< 30%). As this may lead to a considerable overestimation of the content of especially the alkylated naphthalenes, these values have therefore not been reported for those samples having recoveries < 30%.

Compared to previous results, the levels for blue mussels observed here are similar to those reported by Riget et al. (2003) for species sampled at the Qaqortoq area in South Greenland; those values ranged from 0.04 to 0.21 µg/g ww. Also for shorthorn sculpin liver samples, the values observed here are similar to those reported by Riget et al. (2003), where levels ranged from 0.36 to 0.49 µg/g ww.

Similar results were obtained when comparing the PAH levels in the biota samples analysed here with those of another study from the Qaanaaq/Thule Airbase area (Glahder et al., 2002). Results from the Danish monitoring and assessment programme for the aquatic environment (NOVA 1998-2003)-2004) show that average values for PAH in mussels range from 0.1 to 0.2 µg/g ww.

As for the sediments samples, source indicative isomer ratios of individual PAH have been calculated for the biota samples. Again these ratios do not seem to indicate input of distinct petrogenic hydrocarbons to the area. Most ratios indicate mostly mixed petrogenic-pyrogenic input as from fuel oil spills.

2.5 Conclusions and Perspectives

Sediments close to Nuussuaq and Disko have higher concentrations of PAH expressed on basis of the organic matter than sediments on deep water along the Greenland west coast. But this study does not indicate directly the existence of a local and active seepage in the Marraat area. Observed levels of both TPH and PAH are comparable to other Greenland and Arctic areas where no seepage is present and lower than would be expected had an active seepage been present. Furthermore, comparison of petroleum biomarker patterns (e.g. hopanes) in analysed samples with that of a known oil-bearing strata from the same area does not indicate a petrogenic source from a local and active seepage. In stead, simple calculated PAH isomer ratios indicate a mixed petrogenic/pyrogenic source like fuel oil spills.

Table 3. TPH levels (mg/kg dry weight) and PAH levels (µg/kg dry weight) in sediment samples from the Marraat area, West Greenland, 2005. (n.d.: not detected; n.m.: not measured).

MIMI-no.	5-0460	5-0466	5-0467	5-0468	5-0469	5-0470	5-0471	5-0472	5-0473	5-0474	5-0475	5-0476	5-0477	5-0478	5-0479	5-0480	5-0481	5-0482
Sample	Anchor site	Marraat S	M1	M2	M3	M4	M5	M6	M7	M8	M9	Marraat OM	Mar- raat1	Mar- raat2	Mar- raat3	M10	M11	M12
Pos.	70°29,72 N 54°11,67W	70°29,60 N 54°11,23 W	70°30,61N 54°12,24W	70°30,92N 54°13,23W	70°30,88N 54°13,12W	70°31,03N 54°13,63W	70°31,02N 54°13,43W	70°30,98N 54°13,34W	70°30,93N 54°13,46W	70°31,20N 54°13,93W	70°30,91N 54°14,78W	70°30,99N 54°11,23W	See Fig. 1	See Fig. 1	See Fig. 1	70°29,81N 54°14,88W	70°29,54N 54°16,49W	70°29,32N 54°17,33W
TPH (nC13-nC38)	n.m.	< 60	276	107	179	67,6	57,1	60,7	80,1	85,4	580	< 60	60,5	< 60	68,9	327	158	< 60
Naphthalen	2,325	10.27	9.578	7.951	21.38	6.051	2.756	9.144	3.343	7.760	8.351	2.975	4.612	2.643	4.556	15.88	13.05	14.16
2-Methylnaphthalene	3,500	3.687	6.491	6.343	22.03	5.256	0.999	5.416	2.517	6.099	9.454	2.878	5.218	2.650	5.087	18.69	15.51	16.52
1-Methylnaphthalene	1,813	1.881	3.325	3.699	12.47	2.990	0.481	2.978	1.638	3.417	6.305	1.464	3.902	1.515	3.305	11.84	9.256	9.975
C2-Naphthalenes	18,20	10.86	22.58	20.94	66.26	16.82	2.274	16.06	9.815	16.80	56.28	9.462	55.79	8.521	29.33	88.12	69.28	75.93
C3-Naphthalenes	10,21	8.348	11.17	10.87	32.96	8.702	1.394	8.555	5.398	8.461	24.41	6.290	41.31	5.375	16.57	45.26	35.36	37.71
Acenaphthylene	n.d.	0.627	0.690	0.360	0.547	0.363	0.114	0.249	0.201	0.172	0.602	0.485	0.445	0.169	0.359	0.864	0.676	0.546
Acenaphthene	n.d.	0.608	0.956	1.438	2.292	0.791	0.226	0.755	0.487	0.769	2.602	0.469	0.976	0.301	1.223	4.635	3.450	3.340
Fluorene	3,238	0.805	2.165	2.803	8.386	2.217	0.330	1.957	1.305	2.060	5.959	0.642	11.04	1.078	2.983	11.27	8.586	8.856
Phenanthrene	6,500	9.994	15.48	17.42	43.77	12.73	2.775	12.77	8.160	12.99	42.48	8.403	183.0	14.51	24.72	66.08	45.67	43.27
C1-Phenanthrenes	33,18	24.84	22.54	24.73	57.37	17.54	3.738	17.15	10.93	18.95	46.48	14.34	339.2	31.33	30.29	71.41	55.07	57.04
C2-Phenanthrenes	4,150	39.94	34.66	27.27	58.94	17.52	5.460	19.07	13.27	18.62	53.01	17.00	277.4	34.98	29.06	71.47	57.25	57.87
C3-Phenanthrenes	4,063	5.635	5.694	7.170	12.50	4.406	0.907	4.027	3.696	3.504	12.01	3.660	25.99	3.838	6.650	22.70	19.97	18.06
Dibenzothiophene	1,900	1.075	1.069	1.215	4.330	1.211	0.323	1.327	0.665	1.479	2.988	1.005	25.68	1.962	2.205	4.871	4.061	4.653
C1-Dibenzothiophenes	26,48	5.179	5.160	5.583	12.88	3.381	0.922	4.135	2.771	3.823	14.84	2.818	76.03	7.457	7.878	18.18	14.07	18.05
C2-Dibenzothiophenes	5,463	6.076	29.77	8.462	20.88	4.858	1.503	4.124	4.528	2.816	37.50	2.343	36.66	5.692	9.123	42.81	16.32	13.36
Anthracene	16,88	n.d.	0.922	1.458	3.413	1.510	n.d.	1.143	0.703	1.354	3.863	n.d.	n.d.	n.d.	1.707	6.605	4.835	4.353
Fluoranthene	3,275	2.522	5.085	7.231	16.37	4.540	0.480	3.609	3.060	3.008	19.01	1.274	16.40	2.380	6.973	33.97	27.19	25.27
Pyrene	6,288	3.465	5.888	5.885	13.11	4.645	1.179	4.214	3.847	3.621	15.09	2.447	15.19	3.112	6.801	27.33	21.32	19.28
1-Methylpyrene	8,775	1.210	1.902	3.121	7.083	2.054	0.266	1.696	1.276	1.676	7.169	0.466	24.35	3.122	3.478	13.54	11.82	11.16
Benzo(a)fluorene	n.d.	1.766	3.074	4.404	10.01	2.708	0.410	2.269	1.905	2.135	10.25	0.764	76.12	7.225	4.616	18.33	15.20	14.54
Benzo(a)anthracene	8,988	1.301	1.601	2.305	4.125	1.464	0.198	1.175	1.052	1.084	4.804	0.617	12.42	1.632	2.145	7.985	7.918	6.553
Chrysene/Triphenylene	3,150	8.612	4.377	4.229	8.154	2.862	1.112	3.285	2.227	3.580	7.281	3.078	120.5	14.57	5.787	9.868	10.00	10.13
Benzo(b+k)fluoranthene	2,325	3.406	3.956	4.092	8.336	2.720	0.700	2.256	1.697	2.248	9.939	1.615	67.18	7.876	4.471	17.57	15.75	15.93
Benzo(e)pyrene	2,388	3.321	4.302	2.193	5.215	1.425	0.498	1.340	0.869	1.473	5.288	1.124	89.75	7.766	4.688	10.95	7.303	7.953
Benzo(a)pyrene	2,450	1.994	2.632	2.663	4.932	2.698	1.137	2.217	2.187	2.047	5.354	2.014	11.71	2.255	3.533	9.986	7.731	7.224
Perylene	2,325	1.018	13.08	15.68	36.91	12.03	0.750	7.967	7.503	8.217	58.08	0.292	8.740	2.537	21.01	118.6	96.67	104.8
Indeno(123-cd)pyrene	2,563	1.639	2.355	1.919	2.331	1.627	0.664	1.150	1.052	1.054	3.687	1.088	2.141	0.845	1.837	4.798	4.449	4.730
Dibenzo(ah)anthracene	2,850	1.862	2.178	1.425	2.174	1.576	0.805	1.043	0.958	1.203	2.361	0.969	9.954	1.743	1.955	3.651	3.360	3.485
Benzo(ghi)perylene	n.d.	1.448	1.632	1.493	3.267	1.838	0.436	0.982	0.886	1.138	3.734	0.786	16.56	2.292	2.412	8.522	7.488	9.129
PAH sum	183	163	224	204	502	149	32.8	142	98.0	142	479	90.8	1558	179	245	786	609	624

Table 4. TPH levels (mg/kg ignition loss) and PAH levels (µg/kg ignition loss) in sediment samples from the Marraat area, West Greenland, 2005. (n.d.: not detected; n.m.: not measured).

MIMI-no.	5-0467	5-0468	5-0469	5-0470	5-0471	5-0472	5-0473	5-0474	5-0475	5-0476	5-0477	5-0478	5-0479	5-0480	5-0481	5-0482
Sample	M1	M2	M3	M4	M5	M6	M7	M8	M9	Marraat OM	Mar- raat1	Mar- raat2	Mar- raat3	M10	M11	M12
Pos.	70°30,61N 54°12,24W	70°30,92N 54°13,23W	70°30,88N 54°13,12W	70°31,03N 54°13,63W	70°31,02N 54°13,43W	70°30,98N 54°13,34W	70°30,93N 54°13,46W	70°31,20N 54°13,93W	70°30,91N 54°14,78W	70°30,99N 54°11,23W	See Fig. 1	See Fig. 1	See Fig. 1	70°29,81N 54°14,88W	70°29,54N 54°16,49W	70°29,32N 54°17,33W
% <63µ	27.52	60.90	51.33	14.27	1.94	15.65	19.50	15.36	26.19	0.04		4.67	15.44		55.13	71.27
Ignition loss (%)	1.88	2.45	2.57	1.12	0.54	0.85	1.09	1.25	4.33	0.78	n.m.	0.99	1.83	n.m.	3.18	3.45
TPH (nC13-nC38)	14681	4367	6965	6036	10574	7141	7349	6832	13395	< 7692		< 6061	3765		4969	< 1739
Naphthalen	510	325	832	540	508	1074	307	623	193	380		266	248		411	411
Methylnaphthalenes	523	410	1342	737	273	986	381	763	364	555		419	457		780	769
C2-Naphthalenes	1203	856	2577	1502	419	1886	901	1348	1301	1209		857	1599		2181	2204
C3-Naphthalenes	595	444	1282	777	257	1005	495	679	564	804		541	903		1113	1095
Acenaphthylene	37	15	21	32	21	29	18	14	14	62		17	20		21	16
Acenaphthene	51	59	89	71	42	89	45	62	60	60		30	67		109	97
Fluorene	115	115	326	198	61	230	120	165	138	82		108	163		270	257
Phenanthrene	825	712	1702	1137	512	1499	749	1042	982	1074		1460	1347		1438	1256
C1-Phenanthrenes	1201	1010	2231	1567	689	2014	1004	1520	1075	1833		3150	1651		1733	1655
C2-Phenanthrenes	1847	1114	2292	1564	1007	2240	1218	1494	1226	2172		3518	1584		1802	1679
C3-Phenanthrenes	303	293	486	393	167	473	339	281	278	468		386	362		629	524
Dibenzothiophene	57	50	168	108	60	156	61	119	69	128		197	120		128	135
C1-Dibenzothiophenes	275	228	501	302	170	486	254	307	343	360		750	429		443	524
C2-Dibenzothiopenes	1586	346	812	434	277	484	416	226	867	299		572	497		514	388
Anthracene	49	60	133	135	N.D.	134	65	109	89	N.D.		N.D.	93		152	126
Fluoranthene	271	295	637	405	89	424	281	241	439	163		239	380		856	733
Pyrene	314	240	510	415	217	495	353	290	349	313		313	371		671	560
Benzo(a)fluorene	164	180	389	242	76	266	175	171	237	98		727	252		478	422
Benzo(a)anthracene	85	94	160	131	37	138	97	87	111	79		164	117		249	190
Chrysene/Triphenylene	233	173	317	256	205	386	204	287	168	393		1465	315		315	294
Benzo(b+k)fluoranthene	211	167	324	243	129	265	156	180	230	206		792	244		496	462
Benzo(e)pyrene	229	90	203	127	92	157	80	118	122	144		781	256		230	231
Benzo(a)pyrene	140	109	192	241	210	260	201	164	124	257		227	193		243	210
Perylene	697	641	1435	1074	138	936	689	659	1343	37		255	1145		3043	3043
Indeno(123-cd)pyrene	125	78	91	145	122	135	97	85	85	139		85	100		140	137
Dibenzo(ah)anthracene	116	58	85	141	148	123	88	96	55	124		175	107		106	101
Benzo(ghi)perylene	87	61	127	164	80	115	81	91	86	100		230	131		236	265
PAH sum	11851	8222	19262	13082	6005	16485	8873	11222	10913	11540		17724	13153		18786	17783

Table 5. TPH levels (mg/g wet weight) and PAH levels (µg/g wet weight) in biota samples from the Marraat area, West Greenland, 2005. n.a.: not available; M = male species, F = female species.

MIMI-no.	5-0734	5-0735	5-0698	5-0699	5-0700	5-0701	5-0702	5-0703	5-0704	5-0705	5-0706
Sample	Blue mussels	Blue mussels	Liver (Sh. sculpin)	Liver (Sh. sculpin)	Liver (S. sculpin)	Liver (Sh. sculpin)	Liver (Sh. sculpin)	Liver (Sh. sculpin)	Liver (Sh. sculpin)	Liver (Sh. sculpin)	Liver (Uvak)
Size/pool	Length: 3.6-4.9 mm	Lenght: 6.0-7.2 mm	2 M + 2 F (10.97 g)	1 M (25.99 g)	8 M + 2 F (9.543 g)	5 M + 2 F (9.675 g)	2 F (10.45 g)	3 F (12.02 g)	3 F (13.23 g)	3 F (10.16 g)	1 M + 1 F (4.165 g)
TPH (nC13-nC38)	0.17	0.13	0.43	< 0.37	< 0.37	0.38	0.46	< 0.37	0.54	0.51	0.38
Naphthalen	n.a.	n.a.	0,021	0,016	n.a.	0,027	0,021	0,021	n.a.	0,017	n.a.
2-Methylnaphthalene	n.a.	n.a.	0,009	0,008	n.a.	0,013	0,011	0,009	n.a.	n.a.	n.a.
1-Methylnaphthalene	n.a.	n.a.	0,006	0,006	n.a.	0,007	0,008	0,006	n.a.	n.a.	n.a.
C2-Naphthalenes	n.a.	n.a.	0,032	0,029	n.a.	0,036	0,040	0,029	n.a.	n.a.	n.a.
C3-Naphthalenes	n.a.	n.a.	0,079	0,079	n.a.	0,087	0,101	0,069	n.a.	n.a.	n.a.
Acenaphthylene	n.a.	0,000	0,001	0,001	0,001	0,001	0,001	0,001	0,001	0,001	0,000
Acenaphthene	0,010	0,005	0,017	0,017	0,025	0,019	0,021	0,015	0,017	0,021	0,019
Fluorene	0,012	0,008	0,039	0,054	0,035	0,028	0,025	0,025	0,022	0,029	0,075
Phenanthrene	0,016	0,014	0,054	0,043	0,053	0,057	0,044	0,041	0,044	0,048	0,049
C1-Phenanthrenes	0,010	0,009	0,030	0,025	0,031	0,035	0,028	0,025	0,028	0,030	0,026
C2-Phenanthrenes	0,008	0,007	0,024	0,021	0,025	0,030	0,023	0,021	0,026	0,025	0,031
C3-Phenanthrenes	0,001	0,001	0,006	0,003	0,003	0,010	0,002	0,005	0,002	0,005	0,032
Dibenzothiophene	0,002	0,002	0,005	0,004	0,005	0,006	0,005	0,004	0,004	0,004	0,005
C1-Dibenzothiophenes	0,006	0,006	0,018	0,015	0,019	0,022	0,018	0,014	0,018	0,016	0,018
C2-Dibenzothiopenes	0,008	0,010	0,033	0,030	0,030	0,030	0,029	0,028	0,032	0,029	0,066
Anthracene	0,000	0,000	0,001	0,001	0,001	0,001	0,001	0,001	0,000	0,001	0,001
Fluoranthene	0,007	0,013	0,037	0,025	0,035	0,028	0,027	0,030	0,024	0,022	0,022
Pyrene	0,005	0,007	0,024	0,016	0,023	0,021	0,021	0,021	0,022	0,017	0,018
1-Methylpyrene	0,000	0,000	0,001	0,000	0,001	0,000	0,000	0,000	0,001	0,000	0,000
Benzo(a)fluorene	0,001	0,001	0,002	0,001	0,002	0,002	0,001	0,002	0,002	0,002	0,001
Benzo(a)anthracene	0,001	0,001	0,002	0,002	0,004	0,002	0,002	0,002	0,003	0,002	0,003
Chrysene/Triphenylene	0,002	0,002	0,004	0,003	0,008	0,004	0,003	0,004	0,006	0,004	0,005
Benzo(b+k)fluoranthene	0,001	0,001	0,003	0,004	0,004	0,004	0,004	0,004	0,004	0,005	0,004
Benzo(e)pyrene	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000
Benzo(a)pyrene	0,001	0,001	0,001	0,001	0,002	0,002	0,001	0,001	0,002	0,002	0,001
Perylene	0,001	0,001	0,002	0,003	0,003	0,003	0,003	0,003	0,003	0,002	0,003
Indeno(123-cd)pyrene	0,000	0,000	0,002	0,002	0,002	0,002	0,002	0,002	0,002	0,002	0,002
Dibenzo(ah)anthracene	0,000	0,000	0,000	0,001	0,000	0,000	0,001	0,000	0,001	0,001	0,001
Benzo(ghi)perylene	0,000	0,000	0,001	0,001	0,001	0,001	0,001	0,001	0,001	0,001	0,001
PAH sum	0,09	0,09	0,46	0,41	0,31	0,48	0,45	0,38	0,26	0,28	0,38

3 Effects of oil seeps on sediment communities

3.1 Background

Marine sediments are habitats for a large range of organisms ranging from macro fauna to bacteria. The abiotic characteristics of the sediment habitat with respect to grain size, organic matter input, and physical disturbance sets the limitation for the type of habitat that can be developed, and thereby what organisms that will constitute the communities, as well as the productivity and sustainability of the community. Hazardous substances is an other group of abiotic factors that can set limitations on a habitat, both due to direct toxic effects on certain organism groups and through indirect effects due to food web interactions.

Natural oil seeps provide an excellent opportunity to study long term impact of oil contamination in structuring the benthic community. This study is a first attempt to investigate if changes due to selection processes induced by oil contamination could be traced in the bacterial community. Furthermore, the toxicity, or sustainability of the sediment as habitat, was investigated. The results can be used in assessing potential impacts from exploration and exploitation of hydrocarbons.

3.1.1 Pollution Induced Community Tolerance (PICT)

The theory behind PICT is that a community that has been under pressure from a pollutant loses its less tolerant species due to toxic impact. The remaining community consists of species with higher tolerance, which is able to function also under the pollutant pressure (Blanck et al. 1988).

Applying this theory to the natural oil seep, the most tolerant community should exist close to the seep, while a sediment community further away should be less tolerant. However, if the impact of oil affects a larger area, then the whole biological community will be affected and tolerance will not be present. To test for resilience three fresh sediment samples were collected at different distances from the presumed seep, (oil stained stones): 1) at the beach of the presumed seep, 2) at Marraat Syd (0.5 m water depth, c. 2 km from the seep area) and 3) at the anchor site (30 m water depth, c. 2.5 km from the seep area). The sediments were kept cool from sampling to arrival in Denmark where the experiments were performed. To each of the sediments a concentration gradient of a crude oil was added to obtain oil concentrations of 0, 10, 100 and 1000 µg/kg ww. Oxygen consumption was chosen as end-point, which represents an overall measure of bacterial activity. Eight grams of sediment in 50 ml oxygenated water, from each place, and for each oil concentration, were incubated at 4°C until a sufficient difference in oxygen concentration compared to the start concentration was achieved. Each treatment contained four replicates. At the end of the incubation the oxygen concentration was measured using an oxygen fibre optrode.

3.1.2 Sustainability test

The sustainability, or sediment toxicity test, was done in order to assess whether the oil seep affects the abiotic characteristics of the sediments in such a way that organisms are limited in their growth and/or survival. This test was performed on sediments that were frozen at sampling, and using the marine mud shrimp *Corophium volutator*, collected at a pristine site on the Orkney Island. This mud shrimp is commonly used in marine sediment toxicity tests (OSPAR 1995).

Whole sediments bioassays are used in several countries (NL, UK, USA etc.) to evaluate the toxicity of dredged materials for example harbour sediments.

Sediment bioassays are used as a supplement to the chemical analyses of toxic substances, as the bioassays are expected to reflect the bioavailability of the toxic substances and the possible presence of various unidentified toxic substances.

In the Netherlands the following toxicity classification is used in assessment of dredged materials;

Species	parameter	non-toxic	Toxic	highly toxic
<i>C. volutator</i>	% mortality	< 20	>20 - < 50	≥ 50

In the UK a lower assessment level is accepted as sediments are classified as toxic at 40 % mortality of *Corophium volutator*.

Three sediments were chosen to represent a high, medium, and low PAH concentration. Sediment sampled at Marraat-1 contained the most PAH (~ 1558 µg/kg ww), sediment from M10 a medium concentration (~786 µg/kg ww) and Marraat Syd was chosen as the low concentration, or reference area (~163µg/kg ww) (Table 3). To these three sediments (n=3) twenty *C. volutator* were added and left for ten days, at 20°C under gentle aeration, as recommended in the standard tests. After the ten days mortality was determined as well as the RNA-DNA ration of surviving organisms. The RNA-DNA ratio was a used as an indication of growth potential. An organism that has a healthy growth will have a higher RNA content than a growth limited organism, whereas the DNA content stays the same for both. A higher ratio will thereby indicate if growth limitations are present during the experiment, presumably a more sensitive end-point than mortality. The sediment from the reference area was furthermore divided up in two batches, one to which excess organic matter was added, one to which a crude oil was added (100 mg/kg ww). These two extra treatments represent two controls for growth/survival in order to evaluate growth without substrate limitation, and growth under oil stress.

3.1.3 PAH metabolites in fish gall

One more indicator for exposure of PAHs was investigated, the presence of PAH metabolites in fish gall. PAHs are metabolised by fish and can thereby be difficult to trace. The breakdown products or metabolites are more persistent and concentrated in the gall bladder, thereby making the presence of such metabolites an indicator for PAH exposure (OSPAR 1997). The metabolites can be analysed using costly chromatographic

techniques, but in this project a fluorescent screening technique was used, where the concentration of metabolites are normalised to 1-hydroxy pyrene equivalents (Ariese et al 2005). It should be noted that due to conjugation of metabolites in gall, the pure standard is measured at 343 nm, whereas in the samples the metabolites are measured at 341 nm.

3.2 Results

3.2.1 Pollution Induced Community Tolerance (PICT)

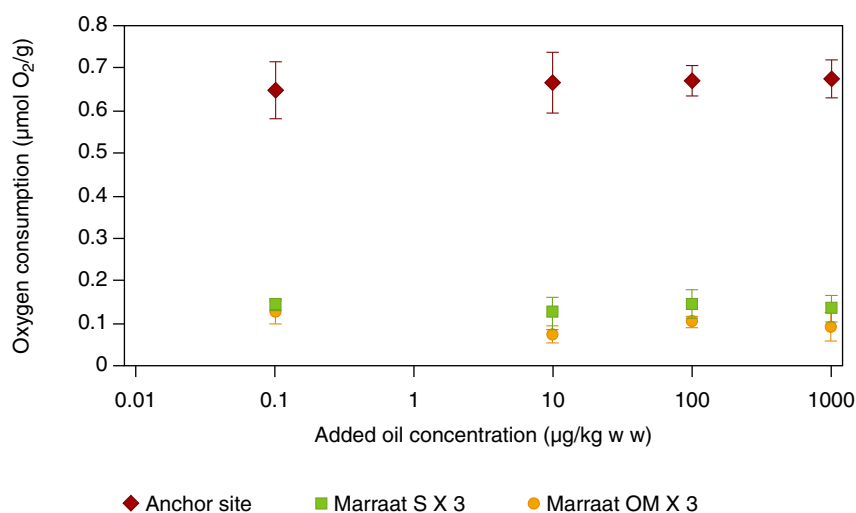
The three fresh sediments contained approximately the same amount of PAHs (Table 6), with only slightly higher concentrations at Marraat it self. The analysis of oil content in the sediments gave no clear indication of oil contamination, and at the presumed source other unidentified substances apart from normal oil components were present. Due to the small amount of sample available no further analysis could be made to identify these compounds.

Table 6. PAH concentrations, and Loss on Ignition (LOI) as a proxy for organic content for the fresh sediments used in the PICT study.

Sediment	PAH ($\mu\text{g}/\text{dw}$)	LOI (% of dry weight)
Marraat OM	90.8	1.2
Marraat S	163	1.9
Marraat, Anchor site	183	1.8

The biological activity of the sediments, measured as oxygen consumption in the controls, was more than an order of magnitude larger at the anchor site (Figure 8). Overall the oxygen consumption was low compared to other sediments previously tested in Greenland (Petersen 2007).

Figure 8. Oxygen consumption in the fresh sediments at different concentrations of oil addition. Note that the consumption for Marraat S. Marraat OM are three times lower than indicated in the graph.



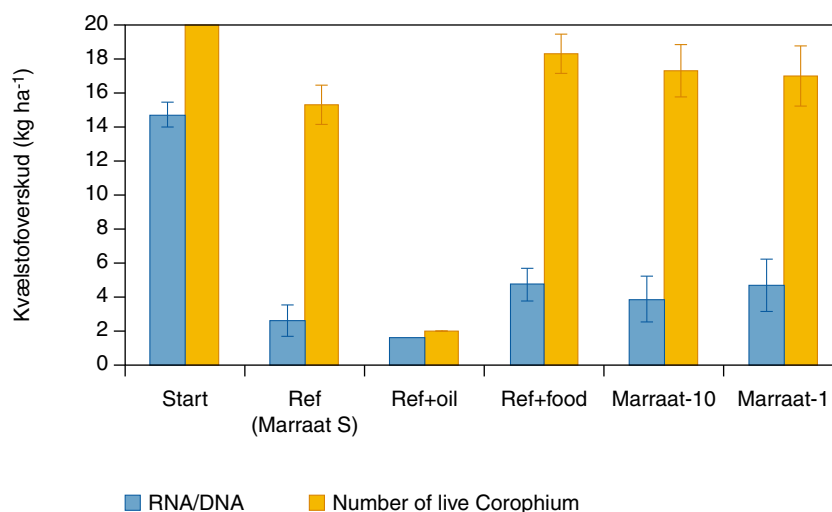
The additions of oil only caused an effect on the sediment at the source, where a reduction with increasing oil contamination was noted. These experiments could not verify that there had been a selection towards a more tolerant bacterial community at any of the sites. This is most likely due to the low and similar PAH contamination at the three sites, in other words, that there is no room for selection. These results therefore suggest that the sediments used here can be characterised as having low biologi-

cal activity due to poor sustainability of the sediment in terms of organic matter, and possible physical disturbance at the site. The only response occurred in the sediment close to the source, where there was an indication of a further stress factor as oil was added.

3.2.2 Sustainability test

The sustainability test showed that none of the sediments from the Marraat area were suitable for maintaining a healthy *C. volutator* population. Of the twenty *C. volutator* added to each of the sediments at the start of the experiment, between 15 and 18 survived in each replicate (Figure 9). The lowest survival was noted for the oil amended sample where only two *C. volutator* of the 60 added in all three replicates survived. The reference site (Marraat S) had the second lowest survival, but when fresh available food was added, the survival increased and became higher than for the other two Marraat sediments.

Figure 9. Growth potential (blue bars) and survival (yellow bars) for *C. volutator* in the 10 day experiment.



The RNA/DNA ratio shows that the growth of *C. volutator* declined dramatically in all the sediments, again reaching the lowest levels for the oil amended and reference sediments. The addition of food provided better growth potential in the reference sediment. The original intention was to use an Arctic benthic mud shrimp for this test. Such organisms were collected but were unfortunately disposed of by the ship crew. Instead *C. volutator* was used, as it is commonly used in such assays. However, *C. volutator* is not an Arctic species and we cannot exclude that the lack of response could be caused by not using a species known to be present in the sediment that where sampled in this study. We have now initiated a PhD-project that will investigate the arctic mud shrimp in more detail, and among other things, develop a methodology for sediment assays and also for tolerance test.

3.2.3 PAH metabolites in fish gall

Gall bladders were sampled from 20 fish and the content of PAH-metabolites was determined as 1-OH-Pyrene equivalents.

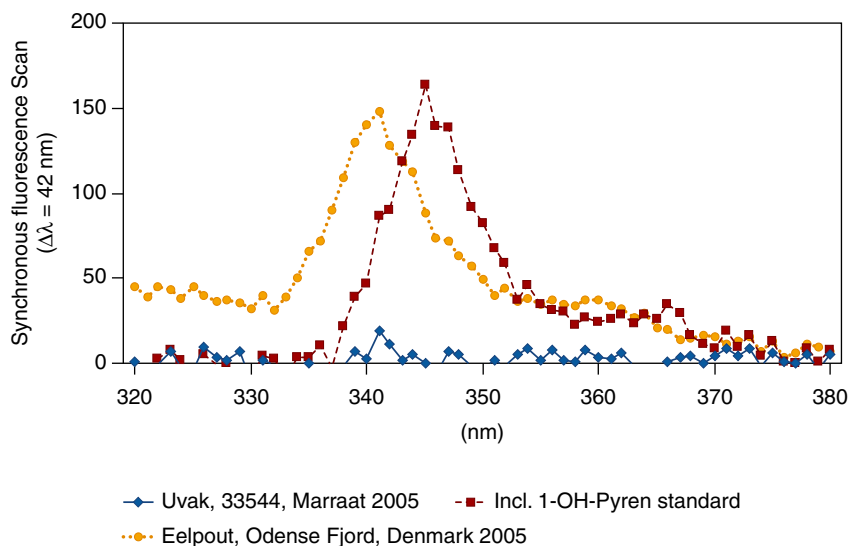
Metabolites could only be detected in one sample, but at a level around the detection limit, and therefore with large uncertainties in the meas-

urement (Table 7). As an example of PAH-metabolites in fish from a known contaminated area a gall sample from Odense fjord is shown in Figure 10. The concentrations of PAHs from around the Marraat area are generally not high enough to be detected in fish, although indications of PAH degradation in fish was evident in one sample from Greenland cod.

Table 7. PAH metabolites in fish gall.

							PAH metabolites (1-OH-pyrene equivalents (µg/ml))	Liver somatic index
	Sex	Station	weight (g)	length (cm)	liver weight (g)	Somatic weight		
Sculpin	F	Anchor site	73.1	18.0	3.5	54.0		15.2
Sculpin	F	Anchor site	83.1	18.5	4.1	58.8		14.2
Sculpin	F	Anchor site	33.1	13.0	0.6	24.4	n.a.	38.9
Sculpin	F	Anchor site	71.9	17.0	3.0	53.1	<0.1	17.7
Sculpin	F	Anchor site	76.6	17.0	3.3	58.8		17.6
Sculpin	F	Anchor site	112.1	20.5	5.7	83.8	<0.2	14.8
Sculpin	F	Anchor site	90.4	19.0	3.2	66.4		20.5
Sculpin	F	Anchor site	101.0	19.0	4.5	70.0	<0.2	15.7
Sculpin	F	Anchor site	60.7	17.0	2.5	49.7	<0.1	20.2
Sculpin	F	Anchor site	68.0	16.0	2.6	51.0	<0.2	19.6
Sculpin	F	Anchor site	96.6	18.5	5.0	71.3	<0.2	14.4
Sculpin	F	Anchor site	98.2	19.5	5.7	73.9	<0.2	13.0
Sculpin	F	Anchor site	95.2	19.0	4.4	75.5	<0.2	17.1
Sculpin	F	Anchor site	120.3	20.5	6.0	93.1	<0.1	15.4
Sculpin	M	Anchor site	23.7	13.0	0.6	19.7		34.7
Sculpin	M	Anchor site	20.0	11.5	0.4	16.2		44.4
Sculpin	M	Anchor site	43.1	15.5	0.7	33.9		51.7
Sculpin	M	Anchor site	55.1	17.0	1.2	44.2	<0.1	38.1
Sculpin	M	Anchor site	51.8	16.5	1.3	43.7	<0.1	34.8
Sculpin	M	Anchor site	21.2	12.0	0.5	17.5		37.8
Sculpin		Anchor site	116.0	20.0	5.2	87.3	<0.2	17.0
Sculpin	F	Marraat 0m	33.2	14.5	0.7	26.5		39.8
Sculpin	F	Marraat 0m	61.6	16.5	2.7	47.8	<0.1	17.5
Sculpin	M	Marraat 0m	24.5	12.5	0.7	19.3		29.6
Sculpin	M	Marraat 0m	25.1	13.0	0.9	20.5		24.0
Sculpin	M	Marraat 0m	20.2	12.0	0.6	16.7		28.7
Sculpin	M	Marraat 0m	27.4	13.0	0.5	22.0		40.3
Sculpin	M	Marraat 0m	35.1	13.5	0.5	29.1		57.9
Sculpin	M	Marraat 0m	47.6	14.5	1.1	36.9	<0.2	34.0
Sculpin	M	Marraat 0m	75.3	17.0	1.1	51.2	<0.2	47.0
Sculpin	M	Marraat 0m	48.5	16.0	0.8	37.8		45.1
Sculpin	M	Marraat 0m	103.8	20.0	2.7	80.1	<0.1	29.4
Sculpin	M	Marraat 0m	429.5	30.0	26.0	330.0	<0.2	12.7
Greenland cod	F	Marraat 0m	114.1	21.5	2.8	96.2	<0.2	34.9

Figure 10. Comparison of Synchronous Fluorescence Scan of 1-hydroxy-pyrene in fish bile from Greenland (blue line), standard (red line) and eelpout from Odense fjord, Denmark (yellow line).



3.3 Discussion

Although the biological test and the measurements of PAH-metabolites in fish gall had a low experimental variability, it could not be concluded that there is an existence of an oil seep in the vicinity of Marraat, or a gradient of PAH concentrations. The reference sediments used in the PICT-test showed an overall low biological activity suggesting a lack of biological available organic material. Therefore the effect of the oil additions could not be detected. Furthermore, the sustainability test using *C. volutator* showed that the organisms radically reduced their growth potential when exposed to the three different Marraat sediments, which supports the suggestion of low availability of organic matter. Although reasonably high concentrations of PAHs were detected in the sediments, they do not tell us for how long they have been accumulating for. If the sediment accumulation rate is low, the top centimetre can represent up to ten years accumulation. If that is the case then the daily exposure of the organisms is very low and the PAHs present in the sediment will be less bioavailable due to binding of more inert organic and inorganic matter with time. This is further supported by the low or not detectable PAH-metabolites in fish gall. However, using fish as a bio-indicator for PAH contamination does assume that the fish is stationary and feeds on locally produced organic matter and not matter that could be transported to the site from surrounding areas.

It cannot however be excluded that a long term impact of an oil seep can cause these effects, but other factors such low organic production in the water mass, and physical impacts such as wave action and strong bottom currents, may have similar effects.

3.4 Conclusion and Perspectives

It was not possible to detect any effect from a potential oil seep using tolerance or sustainability tests, nor using PAH-metabolites measured in fish bile, a result which is in accordance with the PAH measurements performed in the area. However, it cannot be excluded that such a seep is

present, but modifications to the approach used in this study has to be made, in accordance with the knowledge produced of the area from this project.

For example, the low content of organic matter in the sediments indicates that there is little sedimentation in the area, and that the sea-floor is dominated by transport conditions, resulting in that PAHs are not accumulated in the sediments. Therefore, in order to confirm presence of an oil seep that might emit low concentrations of oil to the environment, an integrated sampling over time in the water phase would be necessary. This can be done using passive samplers for water.

To detect effects of such oil seeps, transplantation experiments with organisms from a reference site can be performed, including for example macro algae and mussels.

Lastly, a reference site for sediment studies with the same physical characteristics as Marraat, with respect to temperature, currents, salinity and wave action could be investigated to evaluate if the low biological activity and sustainability of the sediment found in this study can be referred to long-term low exposure in the whole of Disko bay from oil seeps, or if it is a result of the physical factors present.

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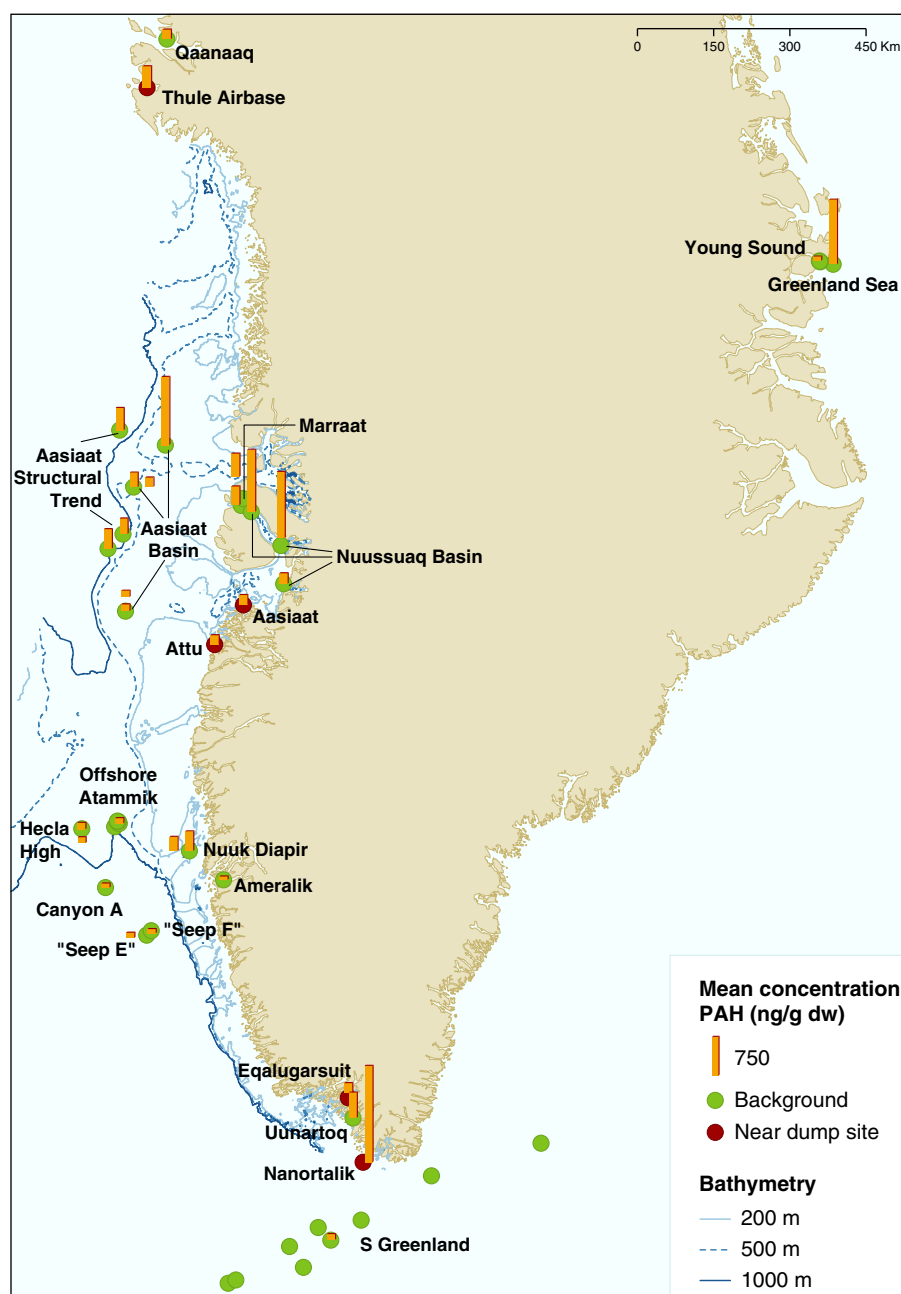
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Appendix I. Summary of studies of hydrocarbons in the Greenland environment

This appendix presents all recent studies of hydrocarbons in the Greenland environment. The map shows where studies have been carried out and summarizes the results.

Figure 11. Map of Greenland showing the different locations from where sediments have been sampled and analysed, either from background (reference) sites or from near dump sites. The bars indicate the levels of sum of PAH in the analysed samples. (not normalized for organic content or sediment grain size).



Appendix 2. Sea sediments from Southwest, South and East Greenland

In 2004, a project was initiated to assess the background levels of PAH in sea sediments from areas where there had been indications of potential natural petroleum seeps and from some background areas. Thus, samples were collected in six different areas at Southwest Greenland and two areas at East Greenland. Average values of total PAH for the different areas are given in Table 8 below.

Table 8. Concentrations (geometric means) of PAH ($\mu\text{g/kg dw}$) in sea surface sediments from West and East Greenland, 2004 (Hansen, 2005). Southwest Greenland were sampled by M/V Charles Darwin and M/V Dana. East Greenland were sampled by NERI personnel from motor boat.

Location	Southwest Greenland						East Greenland	
	Eirik/S Greenland (n=8)	Atammik (n=11)	Seep F (n=3)	Seep E (n=3)	Canyon A (n=3)	Lysefjord Ameralik (n=3)	Young Sound (n=1)	Green-land Sea (n=3)
Position	57°30' - 60°10' N - 39°07' - 48°60' W	64°32' - 64°38' N - 55°42' - 55°51' W	63°00' N - 53°29' W	62°54' N - 53°38' W	63°30' N - 55°33' W	65°05' N - 51°15' W	74°15' N - 20°07' W	74°07' - 74°15' N - 19°23' - 20°07' W
Depth (m)	768-3496	972-992	1447	1662	1547	742	<80	<80
Naphthalene	13.71	22.02	7.07	14.47	2.04	15.34	3.49	47.85
2-Methylnaphthalene	3.10	2.00	2.62	3.82	1.82	1.02	2.45	33.92
1-Methylnaphthalene	2.08	1.17	1.49	2.10	1.14	0.63	1.54	28.49
C3-Naphthalenes	6.43	4.19	5.09	7.15	4.85	2.37	6.94	109.43
C2-Naphthalenes	3.17	2.48	2.74	3.47	2.97	0.88	4.04	104.16
Acenaphthylene	0.26	0.27	0.13	0.15	0.13	0.22	0.37	2.35
Acenaphthene	0.21	0.21	0.21	0.26	0.16	0.24	0.52	3.66
Fluorene	0.67	0.63	0.50	0.62	0.51	0.38	0.92	8.19
Dibenzothiophene	0.48	0.38	0.33	0.41	0.38	0.19	0.56	5.83
C1-Dibenzothiophenes	1.10	0.97	0.61	0.80	0.71	0.50	0.91	13.72
C2-dibenzothiophenes	2.22	2.04	0.68	0.84	0.84	0.73	0.94	10.20
Phenanthrene	4.08	2.65	2.73	3.51	3.11	1.38	2.24	33.75
C1-Phenathrenes	5.49	3.71	3.53	4.66	4.27	2.04	3.82	61.22
C2-Phenanthrenes	6.68	5.47	3.78	5.08	4.59	2.52	6.02	71.91
C3-Phenanthrenes	1.07	0.89	0.37	0.52	0.42	0.57	1.13	13.79
Anthracene	0.17	0.14	0.17	0.18	0.16	0.19	0.41	3.41
Fluoranthene	2.29	2.03	1.81	1.95	1.93	1.56	1.39	17.41
Pyrene	4.34	3.96	3.09	3.79	3.28	3.60	3.92	20.99
Benzo(a)fluorene	0.79	0.64	0.50	0.64	0.62	0.23	1.05	15.13
1-Methylpyrene	0.33	0.29	0.18	0.21	0.21	0.09	0.63	9.32
Benzo(a)anthracene	0.83	0.63	0.64	0.75	0.72	0.61	1.20	12.42
Chrysene/Triphenylene	2.97	1.88	1.76	2.31	2.06	1.00	1.25	17.69
Benzo(b+k)fluoranthenes	5.76	4.10	4.86	5.47	5.74	1.96	2.16	29.55
Benzo(e)pyrene	1.85	1.37	1.44	1.68	1.75	0.55	1.10	21.66
Benzo(a)pyrene	1.92	1.73	1.13	1.32	1.22	1.19	1.83	10.49
Perylene	2.38	4.08	3.51	4.18	4.50	4.86	4.09	169.14
Indeno(123-cd)pyrene	2.83	2.36	3.08	3.13	3.82	1.32	1.32	11.83
Benzo(ghi)perylene	1.80	1.66	1.78	1.87	2.28	1.04	1.46	26.91
Dibenzo(ah)anthracene	0.86	0.62	0.71	0.82	0.86	0.59	0.95	6.24
Σ PAH	80	75	57	76	57	48	59	921

Only samples from Greenland Sea and one sample from Lysefjord (453 µg/kg dw. not included in the average) showed levels considerably higher than background levels. When comparing ratios between petrogenic and pyrogenic PAHs, no significant petrogenic sources were revealed, and no natural petroleum seeps were indicated.

Disko Bay area

At Marraat in the Disko Bay area a study of TPH and PAH levels at possible natural seeps was initiated in 2005. Several sediment and biota samples (blue mussels, sculpins and Greenland cod) were collected at the coast of the Nuussuaq Peninsula near Marraat, West Greenland. These samples were analysed in order to establish the level of TPH and PAH. The Geological Survey of Denmark and Greenland have previously studied this area and discovered oil porous volcanic rocks. Pebbles and rock debris from the coast are also oil stained and thus indicate natural seeps (Bojesen-Kofoed et al., 1999). In 1993 oil was also observed in the Marraat-1 drilling.

THP levels in sediments

TPH and PAH levels in 17 sediment samples at and off the coast of Marraat are presented in Table 9 (see also Table 3).

TPH levels (nC13 to nC38) in sediments range from < 50 to 580 mg/kg dry weight and with a geometric mean of 82.9 mg/kg dw. Apart from a few samples having levels at a few hundred mg/kg, levels are relatively low and only give weak indication of oil seeps or other local petrogenic sources. GC-FID analysis did not record typical petroleum compounds like n-alkanes, but only unresolved humps. These humps may include various complex hydrocarbons from natural biogenic input or from severely degraded oil.

Subsequent GC-MS fingerprinting analyses of selected sediment extracts (M-1, M-9 and M-10) have revealed only minor levels of petroleum hydrocarbons. The n-alkanes (nC23 to nC31) showed a high odd-even predominance, which generally indicate immature petrogenic input of terrestrial origin. The hopane biomarker pattern also showed the presence of compounds probably related to immature petrogenic hydrocarbons. Also the very low levels of regular C27-C29 steranes and elevated levels of C30 steranes could indicate terrigenous input. Highest signals were recorded from methylated PAH naphthalenes, phenanthrenes, dibenzothiophenes and pyrenes. Comparing the hopane pattern with that of extracts from oil-stained stones collected at the beach at Marraat, did not enable the identification of mussel or liver extracts as hydrocarbons originating from the "Marraat" oil. This seems to indicate that the TPH recorded in the sediment samples also are a result of local pollution from light fuel oil, e.g. marine diesel.

Table 9. Average (geomean) concentrations and range of TPH (nC10-nC39) and PAH (sum of 29 compounds) in sediment samples from the Disko area (Marraat), West Greenland, 2005. TPH values are in mg/kg dw, while PAH values are in µg/kg dw (Hansen, 2006).

Location	Marraat – W. Greenland Onshore – 25 m off coast		Marraat – W. Greenland 400 - 700 m off coast		Marraat – W. Greenland 1 – 2.5 km off coast		Marraat – W. Greenland 2.5 – 4.5 km off coast	
Position	70°31' N – 54°13' W		70°31' N – 54°13' W		70°31' N – 54°13' W		70°29' N – 54°16' W	
Depth	0 – 14 m (n=4)		11 – 29 m (n=7)		19-96 m (n=3)		194-378 m (n=3)	
	Geomean	Range	Geomean	Range	Geomean	Range	Geomean	Range
TPH (mg/kg dw)	40,2	25-68,9	99,9	57,1-276	107	25-580	109	25-327
PAH (µg/kg dw):								
Naphthalen	3,58	2,64-4,61	7,01	2,76-21,4	8,73	7,76-10,3	14,3	13,0-15,9
C1-Naphthalenes	6,10	4,16-9,12	7,59	1,48-34,5	9,42	5,57-15,8	27,2	24,8-30,5
C2-Naphthalenes	19,1	8,52-55,8	15,2	2,27-66,3	21,7	10,9-56,3	77,4	69,3-88,1
C3-Naphthalenes	12,3	5,38-41,3	8,08	1,39-33,0	12,0	8,35-24,4	39,2	35,4-45,3
Acenaphthylene	0,34	0,17-0,49	0,31	0,11-0,7	0,40	0,17-0,63	0,68	0,55-0,86
Acenaphthene	0,64	0,30-1,22	0,80	0,23-2,3	1,07	0,61-2,60	3,77	3,34-4,64
Fluorene	2,19	0,64-11,0	1,92	0,33-8,4	2,15	0,80-5,96	9,50	8,59-11,3
Phenanthrene	27,3	8,40-183	12,3	2,77-43,8	17,7	9,99-42,5	50,7	43,3-66,1
C1-Phenanthrenes	46,4	14,3-339	16,9	3,74-57,4	28,0	18,9-46,5	60,8	55,1-71,4
C2-Phenanthrenes	46,8	17,0-277	20,1	5,46-58,9	34,0	18,6-53,0	61,9	57,2-71,5
C3-Phenanthrenes	7,02	3,66-26,0	4,37	0,91-12,5	6,19	3,50-12,0	20,2	18,1-22,7
Dibenzothiophene	3,25	1,00-25,7	1,10	0,32-4,3	1,68	1,08-3,0	4,52	4,06-4,87
C1-Dibenzothiophene	10,6	2,82-76,0	3,88	0,92-12,9	6,65	3,82-14,8	16,6	14,1-18,2
C2-Dibenzothiophenes	8,17	2,34-36,7	6,86	1,50-29,8	8,63	2,82-37,5	21,1	13,4-42,8
Anthracene	1,71	1,71-1,71	1,33	0,70-3,4	2,29	1,35-3,86	5,18	4,35-6,60
Fluoranthene	4,32	1,27-16,4	3,93	0,48-16,4	5,24	2,52-19,0	28,6	25,3-34,0
Pyrene	5,30	2,45-15,2	4,55	1,18-13,1	5,74	3,46-15,1	22,4	19,3-27,3
1-Methylpyrene	3,33	0,47-24,3	1,75	0,27-7,1	2,44	1,21-7,17	12,1	11,2-13,5
Benzo(a)fluorene	6,64	0,76-76,1	2,52	0,41-10,0	3,38	1,77-10,3	15,9	14,5-18,3
Benzo(a)anthracene	2,28	0,62-12,4	1,27	0,20-4,1	1,89	1,08-4,80	7,45	6,55-7,99
Chrysene/Triphenylene	13,3	3,08-121	3,21	1,11-8,2	6,08	3,58-8,61	10,0	9,87-10,1
Benzo(b+k)fluoranthene	7,86	1,61-67,2	2,68	0,70-8,3	4,24	2,25-9,94	16,4	15,7-17,6
Benzo(e)pyrene	7,78	1,12-89,8	1,70	0,50-5,2	2,96	1,47-5,29	8,60	7,30-11,0
Benzo(a)pyrene	3,70	2,01-11,7	2,44	1,14-4,9	2,80	1,99-5,35	8,23	7,22-10,0
Perylene	3,42	0,29-21,0	8,80	0,75-36,9	7,86	1,02-58,1	106	96,7-119
Indeno(123-cd)pyrene	1,38	0,84-2,14	1,45	0,66-2,4	1,85	1,05-3,69	4,66	4,45-4,80
Dibenzo(ah)anthracene	2,39	0,97-9,95	1,36	0,81-2,2	1,74	1,20-2,36	3,50	3,36-3,65
Benzo(ghi)perylene	2,91	0,79-16,6	1,28	0,44-3,3	1,83	1,14-3,73	8,35	7,49-9,13
ΣPAH	281	91-1558	148	33-502	223	142-479	668	609-786

PAH levels in sediments

The PAH analyses included 19 unsubstituted PAHs (2-6 ring systems), 3 methylated PAH and 8 groups of alkylated PAH (naphthalenes, phenanthrenes and dibenzothiophenes). PAH levels in sediments from the Marraat area range from just below 100 µg/kg to above 1500 µg/kg on a dry weight (dw) basis. Lowest values were observed for the shallow sediments just outside the coast of Marraat. One sample (Marraat 1), however, sampled at 10 m depth, showed the largest value of all: 1558 µg/kg dw. Other shallow (down to 25 m depth) samples from up to 500 m from the coast ranged from about 100 µg/kg to about 500 µg/kg dw.

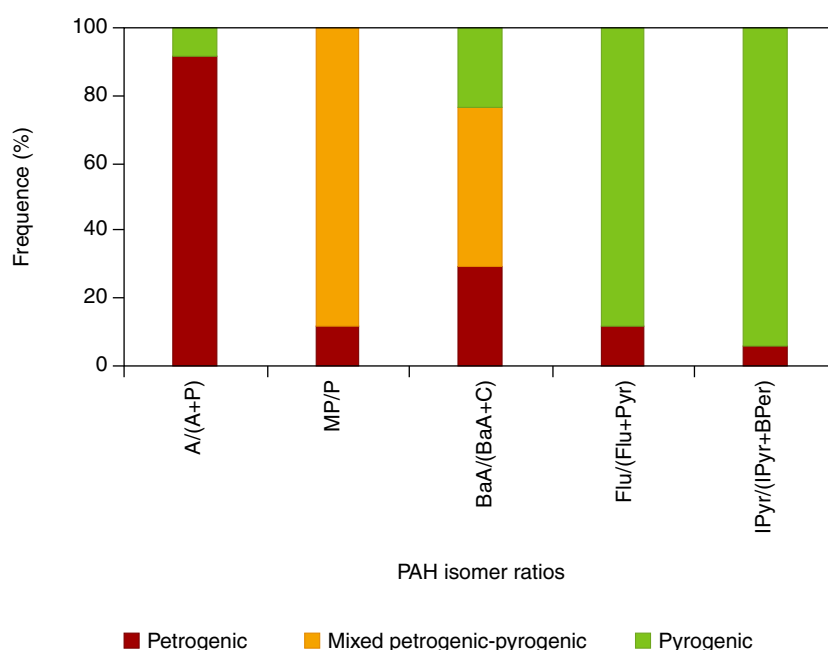
Other samples from greater depths (200-400 m) and more than 1000 m from the coast showed 3 to 4 times higher levels than samples closer to the coast. At present, there is no information about the sea bottom geol-

ogy and currents, and therefore it is difficult to explain whether the observed differences are due to differences in sedimentation rates or other local conditions.

PAH composition in sediments

Specific PAH isomer ratios are often used to allocate PAH to either petrogenic, pyrogenic or mixed petrogenic-pyrogenic sources, e.g. the fluoranthene to pyrene ratio (Oros & Ross, 2005). Here several ratios have been investigated, and except for the anthracene to phenanthrene ($A/(A+P)$) ratio they all indicate that the PAH contents of the sediments off the coast of Marraat are of mixed petrogenic-pyrogenic or primarily pyrogenic origin. Thus no significant indication of natural oil seeps was observed.

Figure 12. Source allocation of PAH in sediments off coast of Marraat based on selected PAH isomer ratios. A = anthracene, P = phenanthrene, MP = methylphenanthrenes, BaA = benzo(a)anthracene, C=Chrysene, Flu = fluoranthene, Pyr = pyrene, IPyr = indeno(123cd)-pyrene, BPer = benzo(ghi)perylene.



On the other hand, the relative content of PAH in the sediment samples, especially the alkylated naphthalenes, phenanthrenes and dibenzothio-phenes, might indicate some input from petrogenic sources as they display bell-shaped distributions typical for crude oils (Figure 13).

TPH levels in biota

The biota samples included blue mussels (*Mytilus edulis*), that were pooled into two size fractions, 36-49 mm and 60-72 mm shell length, respectively, and liver samples from 33 shorthorn sculpins (*Myoxocephalus scorpius*) and 2 Greenland cod (*Gadus ogac*); the liver samples were pooled into nine samples that generally included both sexes and juvenile and adults. Extracts from both types of samples were analysed, and the results are listed in Table 10.

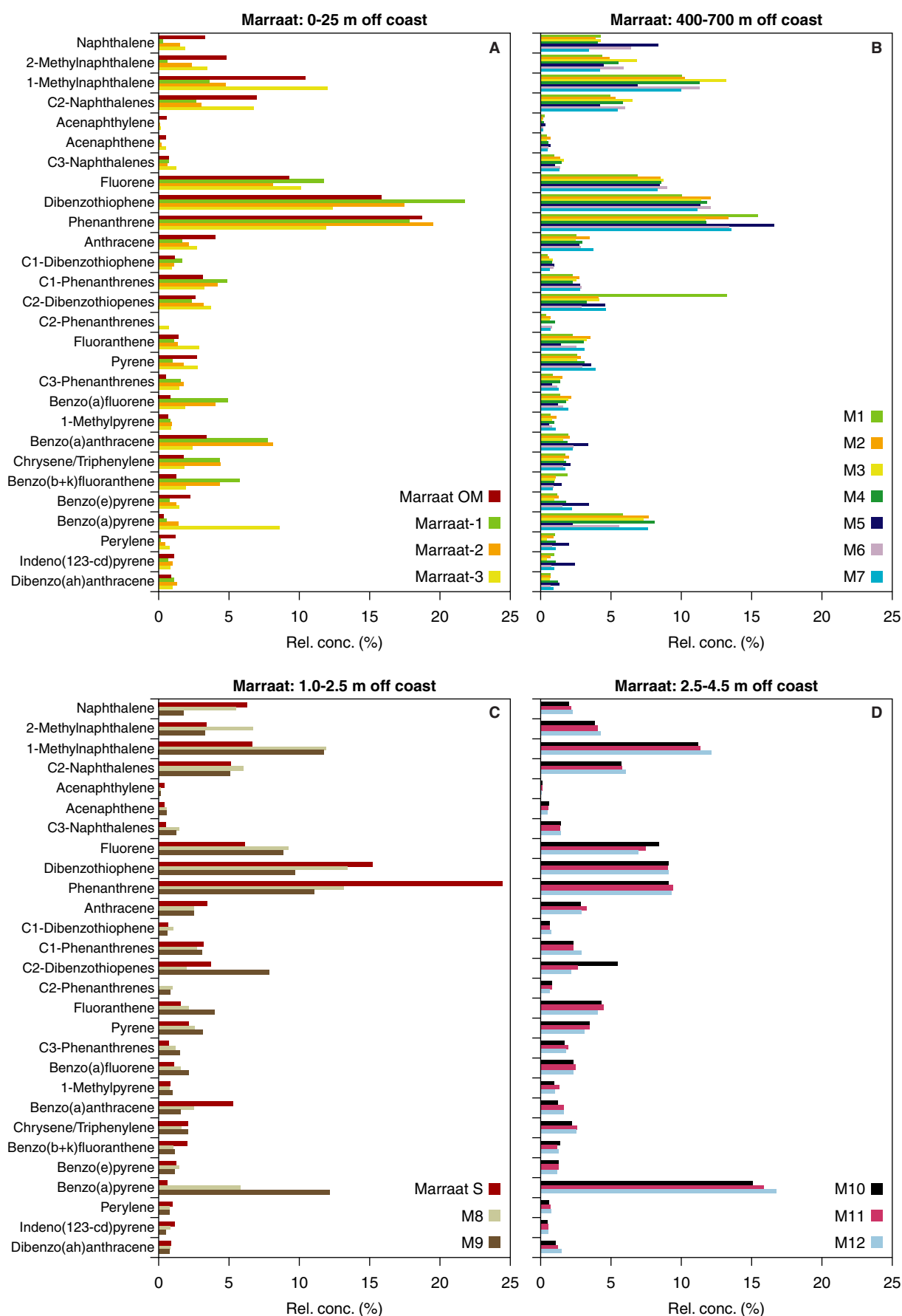


Figure 13. Distribution (rel. conc.) of PAH isomers in sediment samples off the coast of Marraat, West Greenland. A) 0-25 m off the coast, B) 400-700 m off the coast, C) 1-2.5 km off the coast and D) 2.5-4.5 km off the coast.

TPH levels (nC13 to nC38) in biota samples range from 0.13 mg/g ww in mussels to 0.54 mg/g in sculpin liver. For three samples, values just below the detection limit. In blue mussel an average of 0.15 mg/g ww was observed (range: 0.13-0.17 mg/g ww); in sculpin liver it was 0.40 mg/g ww (range: 0.27-0.54 mg/g ww), and in Greenland cod liver it was 0.38 mg/g ww. Values for individual pooled samples are given in Table 10.

As mussels do not have the adequate enzyme system to metabolize aromatic hydrocarbons and hence bioaccumulate these compounds, the mussel data observed here might indicate some kind of petrogenic input to the area.

As for the sediment samples, none of the biota samples analysed by GC-FID chromatograms showed clear signs of regular petroleum compounds (e.g. n-alkanes). However, GC-MS fingerprinting of the mussel and liver extracts showed low concentrations of aliphatic hydrocarbons (e.g. n-alkanes), and as for the sediment samples, a distinct odd-even predominance (nC19 to nC31) was observed. Lighter alkylated PAH (naphthalenes, phenanthrenes and dibenzothiophenes) and petroleum biomarkers (hopanes) showed the regular pattern of light fuel oil. Again, by comparing the hopane pattern with that of extracts from oil-stained stones collected at the beach at Marraat, did not enable the identification of mussel or liver extracts as hydrocarbons originating from the "Marraat" oil. Therefore, the observed hydrocarbons in the biota samples probably indicate input from both immature petrogenic hydrocarbons of possible lacustrine origin and local pollution by fuel oil.

PAH levels in biota

The PAH analyses of biota included the same compounds as in sediments (c.f. Table 10). The following levels were observed: blue mussels, 0.12 µg/g ww (range: 0.10-0.14 µg/g ww); shorthorn sculpin (liver), 0.39 µg/g ww (range: 0.29-0.49 µg/g ww); Greenland cod (liver), 0.39 µg/g ww. Values for individual samples are given in Table 10.

For some of the samples, the recovery of naphthalene and methyl-naphthalene (based on spiked isotopically marked standards) was quite low (< 30%). As this may lead to a considerable overestimation of the content of especially the alkylated naphthalenes, these values have therefore not been reported for those samples having recoveries < 30%.

Compared to previous results, the levels for blue mussels observed here are similar to those reported by Riget et al. (2003) for species sampled at the Qaqortoq area in South Greenland; those values ranged from 0.04 to 0.21 µg/g ww. Also for shorthorn sculpin liver samples, the values observed here are similar to those reported by Riget et al. (2003), where levels ranged from 0.36 to 0.49 µg/g ww.

Similar results were obtained when comparing the PAH levels in the biota samples analysed here with those of another study from the Qaanaaq/Thule Airbase area (Glahder et al., 2002).

As for the sediments samples, source indicative isomer ratios of individual PAH have been calculated for the biota samples. Again these ratios do not seem to indicate input of distinct petrogenic hydrocarbons to the area. Most ratios indicate mostly mixed petrogenic-pyrogenic input.

Table 10. TPH levels (mg/g wet weight) and PAH levels (µg/g wet weight) in biota samples from the Disko area (Marraat), West Greenland, 2005. n.a.: not available; M = male, F = female.

MIMI-no.	5-0734	5-0735	5-0698	5-0699	5-0700	5-0701	5-0702	5-0703	5-0704	5-0705	5-0706
Sample	Blue mussels	Blue mussels	Liver (Sh. sculpin)	Liver (Sh. sculpin)	Liver (Sh. sculpin)	Liver (Sh. sculpin)	Liver (Sh. sculpin)	Liver (Sh. sculpin)	Liver (Sh. sculpin)	Liver (Sh. sculpin)	Liver (Gadus ogac)
Size/pool	Length: 3.6-4.9 mm	Length: 6.0-7.2 mm	2 M+2 F (10.97 g)	1 M (25.99 g)	8 M+2 F (9.543 g)	5 M+2 F (9.675 g)	2 F (10.45 g)	3 F (12.02 g)	3 F (13.23 g)	3 F (10.16 g)	1 M+1 F (4.165 g)
TPH (nC13-nC38)	0.17	0.13	0.43	< 0.37	< 0.37	0.38	0.46	< 0.37	0.54	0.51	0.38
Naphthalen	n.a.	n.a.	0,021	0,016	n.a.	0,027	0,021	0,021	n.a.	0.017	n.a.
2-Methylnaphthalene	n.a.	n.a.	0,009	0,008	n.a.	0,013	0,011	0,009	n.a.	n.a.	n.a.
1-Methylnaphthalene	n.a.	n.a.	0,006	0,006	n.a.	0,007	0,008	0,006	n.a.	n.a.	n.a.
C2-Naphthalenes	n.a.	n.a.	0,032	0,029	n.a.	0,036	0,040	0,029	n.a.	n.a.	n.a.
C3-Naphthalenes	n.a.	n.a.	0,079	0,079	n.a.	0,087	0,101	0,069	n.a.	n.a.	n.a.
Acenaphthylene	n.a.	0,000	0,001	0,001	0,001	0,001	0,001	0,001	0,001	0,001	0,000
Acenaphthene	0,010	0,005	0,017	0,017	0,025	0,019	0,021	0,015	0,017	0,021	0,019
Fluorene	0,012	0,008	0,039	0,054	0,035	0,028	0,025	0,025	0,022	0,029	0,075
Phenanthrene	0,016	0,014	0,054	0,043	0,053	0,057	0,044	0,041	0,044	0,048	0,049
C1-Phenanthrenes	0,010	0,009	0,030	0,025	0,031	0,035	0,028	0,025	0,028	0,030	0,026
C2-Phenanthrenes	0,008	0,007	0,024	0,021	0,025	0,030	0,023	0,021	0,026	0,025	0,031
C3-Phenanthrenes	0,001	0,001	0,006	0,003	0,003	0,010	0,002	0,005	0,002	0,005	0,032
Dibenzothiophene	0,002	0,002	0,005	0,004	0,005	0,006	0,005	0,004	0,004	0,004	0,005
C1-Dibenzothiophenes	0,006	0,006	0,018	0,015	0,019	0,022	0,018	0,014	0,018	0,016	0,018
C2-Dibenzothiophenes	0,008	0,010	0,033	0,030	0,030	0,030	0,029	0,028	0,032	0,029	0,066
Anthracene	0,000	0,000	0,001	0,001	0,001	0,001	0,001	0,001	0,000	0,001	0,001
Fluoranthene	0,007	0,013	0,037	0,025	0,035	0,028	0,027	0,030	0,024	0,022	0,022
Pyrene	0,005	0,007	0,024	0,016	0,023	0,021	0,021	0,021	0,022	0,017	0,018
1-Methylpyrene	0,000	0,000	0,001	0,000	0,001	0,000	0,000	0,000	0,001	0,000	0,000
Benzo(a)fluorene	0,001	0,001	0,002	0,001	0,002	0,002	0,001	0,002	0,002	0,002	0,001
Benzo(a)anthracene	0,001	0,001	0,002	0,002	0,004	0,002	0,002	0,002	0,003	0,002	0,003
Chrysene/Triphenylene	0,002	0,002	0,004	0,003	0,008	0,004	0,003	0,004	0,006	0,004	0,005
Benzo(b+k)fluoranthene	0,001	0,001	0,003	0,004	0,004	0,004	0,004	0,004	0,004	0,005	0,004
Benzo(e)pyrene	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000
Benzo(a)pyrene	0,001	0,001	0,001	0,001	0,002	0,002	0,001	0,001	0,002	0,002	0,001
Perylene	0,001	0,001	0,002	0,003	0,003	0,003	0,003	0,003	0,003	0,002	0,003
Indeno(123-cd)pyrene	0,000	0,000	0,002	0,002	0,002	0,002	0,002	0,002	0,002	0,002	0,002
Dibenzo(ah)anthracene	0,000	0,000	0,000	0,001	0,000	0,000	0,001	0,000	0,001	0,001	0,001
Benzo(ghi)perylene	0,000	0,000	0,001	0,001	0,001	0,001	0,001	0,001	0,001	0,001	0,001
PAH sum	0,09	0,09	0,46	0,41	0,31	0,48	0,45	0,38	0,26	0,28	0,38

West Greenland (2006)

In 2006 another study was conducted off West Greenland, where several sediment samples were collected and analysed. Table 11 summarizes the results of that study. Evaluated on a dry weight basis most samples are close to or slightly above background levels with regard to sumPAH (approx. 100 µg/kg dw). Only three samples, one from the Aasiaat Basin and two from the Nuussuaq Basin are distinctly above background levels with sumPAH close to 900 µg/kg dw. However, none of the calculated diagnostic PAH source ratios (e.g. A/(A+P), Fl/(Fl+Py), BaA/(BaA+C) and IPy/(IPy+BPer)) give a clear indication of prevalent petrogenic

PAHs. Most ratios indicate mixed petrogenic-pyrogenic or prevalent pyrogenic sources. Also when calculated on the basis of loss-on-ignition the same data (c.f. Table 12) confirms that the highest accumulations of PAHs are present at the Aassiaat and the Nuussuaq Basins.

Table 11. PAH concentration in sediment samples off West Greenland (2006) on dry weight (dw) basis.

Location	Hecla High		Nuuk diaper		Aasiaat Structural Trend		Aasiaat Basin			Aasiaar Structural Trend			Nuussuaq Basin				
Position	64°20'N- 057°03'W		64°27'N- 052°47'W		69°00'N- 059°47'W	68°05'N- 058°03'W	68°05'N- 058°03'W	70°08'N- 059°36'W	70°08'N- 059°39'W	71°00'N- 058°46'W	69°19'N- 059°20'W	70°58'N- 061°18'W	69°13'N- 051°12'W	69°51'N- 051°42'W	70°18'N- 053°32'W	70°22'N- 054°06'W	70°51'N- 054°12'W
Depth (m)	753-759																
Sample no.	016R-01	016R-02	009R-01	009R-02	101R	045R-01	045R-02	062R	065R	112R	089R	084R-01	150R	143R	136R	127R	116R
PAH conc. (µg/kg ts)																	
Naphthalene	0,3	0,9	3,9	4,3	15,4	3,7	3,0	3,7	7,2	33,0	7,9	12,9	2,2	18,8	16,0	5,6	
2-Methylnaphthalene	1,1	1,3	2,7	3,5	3,6	3,4	3,3	5,0	8,6	41,5	3,8	9,9	3,0	17,6	14,7	5,9	
1-Methylnaphthalene	0,7	0,7	1,9	2,6	3,8	2,2	2,3	4,0	6,7	32,5	3,4	7,4	3,2	15,8	14,6	5,8	
C2-Naphthalenes	4,6	3,4	12,5	32,7	11,9	6,0	8,0	12,4	18,4	102,0	13,8	18,8	12,0	45,7	59,8	26,5	
C3-Naphthalenes	3,1	2,5	6,1	13,8	4,5	2,1	4,2	7,2	7,6	49,0	9,5	9,8	10,7	49,3	57,3	22,9	
Acenaphthylene	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	
Acenaphthene	0,8	0,7	0,9	1,1	<0,1	0,9	<0,1	<0,1	<0,1	3,5	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	
Fluorene	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	
Dibenzothiophene	1,3	1,6	2,4	2,8	3,6	1,6	1,5	1,8	3,5	11,8	2,4	4,3	1,3	6,2	6,0	2,4	
C1-Dibenzothiophenes	5,9	6,5	10,4	12,3	11,1	4,1	5,0	5,5	7,1	29,9	7,4	16,1	16,1	34,9	20,6	10,1	
C2-Dibenzothiopenes	3,6	2,1	5,3	8,2	10,4	2,1	2,9	3,7	4,0	9,4	6,5	11,9	7,0	78,7	10,7	4,7	
Phenanthrene	0,2	5,2	14,4	20,0	30,2	3,8	4,0	10,7	21,7	90,1	15,3	25,6	5,3	32,1	42,4	9,3	
C1-Phenathrenes	11,4	13,3	23,8	31,3	29,8	10,2	10,7	15,4	24,7	129,0	17,7	32,3	18,3	74,7	66,6	25,2	
C2-Phenanthrenes	8,4	9,5	18,7	23,0	27,1	8,7	7,7	12,7	16,6	107,1	17,8	34,3	18,4	117,7	86,3	29,2	
C3-Phenanthrenes	0,5	0,2	0,6	0,6	1,1	0,6	0,3	1,0	3,1	11,1	0,9	2,3	1,3	35,7	32,3	8,3	
Anthracene	2,2	3,0	1,0	3,0	7,2	0,5	N/A	N/A	N/A	5,1	14,1	2,8	N/A	6,5	6,6	3,7	
Benzo(a)fluorene	0,8	0,7	1,6	1,9	1,4	1,2	1,2	1,6	3,1	11,7	1,3	1,9	1,0	14,9	17,0	4,8	
Fluoranthene	7,1	8,6	21,4	24,1	21,3	7,5	7,7	9,1	10,4	24,5	22,1	24,2	4,4	31,2	29,0	11,5	
Pyrene	7,8	8,9	18,6	20,1	30,2	7,8	8,9	10,6	13,5	39,1	24,6	31,6	9,3	41,0	44,7	13,0	
1-Methylpyrene	0,4	0,4	0,4	0,5	0,7	0,4	0,4	0,5	1,0	4,6	0,7	1,1	0,6	5,2	5,0	1,6	
Benzo(a)anthracene	1,2	0,8	2,8	2,6	2,8	1,0	1,1	1,4	3,3	10,3	2,6	4,3	1,7	8,4	9,9	2,1	
Chrysene_Triphenyl.	2,6	2,8	7,9	8,6	8,3	2,8	3,5	4,8	9,0	32,2	7,8	12,0	2,4	19,9	17,5	7,2	
Benzo(bk)fluoranthene	5,9	6,4	13,0	17,3	13,9	5,1	5,8	8,6	11,3	42,5	11,5	14,3	4,8	34,1	34,7	8,9	
Benzo(e)pyrene	1,7	1,8	3,8	6,1	3,8	1,5	2,1	2,8	6,4	20,1	3,2	4,3	1,5	11,7	11,3	3,8	
Benzo(a)pyrene	<0,5	<0,5	1,4	2,1	3,5	<0,5	N/A	N/A	N/A	9,4	2,9	4,0	1,5	8,0	11,2	1,9	
Perylene	1,1	1,2	4,0	5,2	7,6	4,1	N/A	N/A	N/A	50,1	7,4	6,4	14,7	184,5	228,4	38,3	
Indeno(123-cd)pyrene	3,0	3,3	7,2	9,9	6,1	2,0	2,4	3,4	3,0	11,5	5,4	6,3	3,1	9,5	8,5	2,5	
Benzo(ghi)perylene	2,3	2,5	7,0	8,8	4,7	2,9	3,6	3,4	6,1	18,7	4,7	5,6	3,0	14,6	11,8	3,9	
Dibenzo(ah)anthracene	0,9	0,9	1,6	1,9	1,8	1,1	1,1	0,9	1,6	5,0	1,5	2,4	0,7	3,0	2,2	0,7	
sum PAH	79	89	195	268	266	87	91	130	198	935	216	306	147	920	865	260	

Table 12. PAH concentration in sediment samples off West Greenland (2006) on loss-of-ignition (LOI) basis.

Location	Hecla High		Nuuk diapiir		Aasiaat Structural Trend		Aasiaat Basin			Aasiaar Structural Trend			Nuussuaq Basin				
Position	64°20'N-057°03'W		64°27'N-052°47'W		69°00'N-059°47'W	68°05'N-058°03'W	68°05'N-058°03'W	70°08'N-059°36'W	70°08'N-059°39'W	71°00'N-058°46'W	69°19'N-059°20'W	70°58'N-061°18'W	69°13'N-051°12'W	69°51'N-051°42'W	70°18'N-053°32'W	70°22'N-054°06'W	70°51'N-054°12'W
Depth (m)	753-759																
Sample no.	016R-01	016R-02	009R-01	009R-02	101R	045R-01	045R-02	062R	065R	112R	089R	084R-01	150R	143R	136R	127R	116R
Loss on ignition (%)	2.0	2.1	4.7	5.2	7.0	1.8	2.6	2.3	1.4	5.5	4.8	4.8	1.3	5.6	5.2	2.1	3.3
%<63μ	68.52	68.43	90.54	91.64	98.9	74.95	83.13	61.77	55.89	92.73	97.52	97.24	90.04	96.93	93.52	42.53	71.15
PAH conc. (μg/kg loi)																	
Naphthalene	15,9	41,4	83,3	82,9	218	210	118	161	506	598	167	270	170	514	306	275	
Methylnaphthalenes	95,7	94,2	97,1	117	106	311	219	390	1082	1342	151	363	474	914	559	566	
C2-Naphthalenes	234	162	266	629	169	336	315	537	1294	1850	291	395	922	1253	1141	1292	
C3-Naphthalenes	158	119	129	265	63,8	115	164	314	532	888	200	206	820	1351	1093	1117	
Acenaphthylene	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	
Acenaphthene	39,9	35,2	18,6	20,3	<5	51,8	<5	<5	<5	63,1	<5	<5	<5	<5	<5	<5	
Fluorene	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	
Dibenzothiophene	67,0	75,7	51,3	54,5	51,3	89,8	57,4	79,3	244	214	49,4	91,4	102	171	114	117	
C1-Dibenzothiophenes	303	315	221	237	158	232	195	238	502	543	156	338	1237	958	393	493	
C2-Dibenzothiopenes	186	102	111	158	148	117	115	159	283	171	136	250	534	2157	204	231	
Phenanthrene	9,45	251	304	384	429	211	157	466	1527	1635	321	538	406	879	809	451	
C1-Phenathrenes	585	642	505	601	423	573	419	668	1735	2339	372	680	1405	2048	1269	1228	
C2-Phenanthrenes	431	461	396	442	384	490	303	550	1165	1943	373	720	1414	3224	1645	1422	
C3-Phenanthrenes	27,1	7,5	13,0	11,9	15,8	35,2	12,5	42,1	219	202	19,3	47,7	96,8	979	616	403	
Anthracene	113	145	20,3	58,3	103	29,5	N/A	N/A	N/A	91,8	295	58,2	N/A	177	126	180	
Benzo(a)fluorene	42,8	35,5	34,5	37,3	19,8	69,3	45,9	69,3	221	213	27,1	40,2	73,4	408	325	236	
Fluoranthene	362	417	452	463	301	420	301	394	732	444	464	510	337	856	552	562	
Pyrene	401	432	393	387	429	436	347	460	950	709	518	665	715	1125	852	635	
Benzo(a)anthracene	59,3	38,1	58,3	50,9	40,1	56,9	44,8	60,3	234	186	54,2	89,7	132	231	188	101	
Chrysene_Triphenyl.	134	133	166	166	117	154	135	209	635	584	164	253	186	546	334	353	
Benzo(bk)fluoranthene	300	309	276	333	198	284	228	373	792	772	242	301	367	934	663	432	
Benzo(e)pyrene	88,0	89,0	81,0	117	54,3	83,9	82,7	121	452	364	67,8	90,6	118	320	216	186	
Benzo(a)pyrene	<25	<25	30,4	40,0	50,1	<25	N/A	N/A	N/A	170,8	61,8	83,0	112	218	214	90,2	
Perylene	55,0	59,6	83,9	99,2	108	228	N/A	N/A	N/A	908	156	134	1127	5055	4354	1867	
Indeno(123-cd)pyrene	154	160	152	190	86,0	115	95,7	147	213	209	114	132	236	261	161	122	
Benzo(ghi)perylene	118	122	149	169	66,7	160	139	149	432	340	98,4	117	231	400	225	191	
Dibenzo(ah)anthracene	44,8	44,6	33,3	36,0	25,3	58,9	41,8	40,1	116	90,3	32,1	49,5	53,0	82,7	42,8	31,7	
sum PAH	4023	4290	4124	5151	3765	4870	3537	5627	13867	16866	4530	6421	11269	25061	16403	12582	

Appendix 3. Polycyclic Aromatic Hydrocarbons (PAHs) in the Greenland Environment – Summary of other studies

The AMAP assessment report for Greenland and the Faroe Islands 1997-2001, Vol. 2 Greenland, by Riget et al. (2003) reports levels of PAHs from the NOSGE study under the Danish AMAP pro-gramme. Various samples from both the terrestrial and the marine environment of South Greenland were collected in 1999-2001 and analysed, and the study covered a suite of PAHs including both unsubstituted and alkylated 2-6 rings PAHs.

PAHs in Precipitation

Precipitation data for total PAHs from three stations in South Greenland: a background area (Usuk, 64°58' N – 51°30' W), near Igaliko (a settlement with 40 people) and the town of Qaqortoq (60°43' N – 46°02' W) with 3200 inhabitants, were measured in the summer of 2001 and the winter of 2001 (Riget et al., 2003). Average levels were about 50 ng/L, lowest at Usuk (background) and highest at Qaqortoq (town). At Qaqortoq, concentrations were 2-3 times higher than average levels at background sites in France during summer (Masclet et al., 2000). Prior to that, Masclet et al. (2000) studied the deposition of PAH in Greenland by monitoring the concentration in superficial snow during 1993-1996 as part of the TAGGSI study. An average value for Σ PAH of 2.1 $\mu\text{g}/\text{kg}$ snow was observed.

PAHs in the Terrestrial Environment

Soil and lichen (*Cetraria nivalis*) samples from southern Greenland near the small town of Qaqortoq (60°43' N – 46°02' W) were collected during 1999 -2000 and analysed. For the soil samples, average levels were about 113 $\mu\text{g}/\text{kg}$ dw, while they were about 80 $\mu\text{g}/\text{kg}$ ww¹ for lichen.

Table 13. Concentration of Σ PAH in soil ($\mu\text{g}/\text{kg}$ dw) and lichens ($\mu\text{g}/\text{kg}$ ww) samples from the area of Qaqortoq (60°43' N – 46°02' W), South Greenland (Riget et al., 2003).

	Location	Σ PAH (1999)	Σ PAH (2000)
Soil	Usuk (background)	--	106
	Igaliko (farm site)	--	128
	Igaliko (near lake)	--	105
Lichens (<i>Cetraria nivalis</i>)	Usuk (background)	74	79
	Igaliko (farm site)	--	--
	Igaliko (near lake)	--	93

¹ ww = wet weight

PAHs in the Freshwater Environment

Sediments

In 2000, a sample from South Greenland, from a small lake near the town of Qaqortoq (60°43' N – 46°02' W), was analysed (Riget et al., 2003). The Σ PAH level was 120 µg/kg dw.

Biota

Biota samples from the freshwater environment included liver samples of arctic char (*Salvelinus alpinus*) from a small lake (Igaliko) and an open fjord (Itilleq), both near Qaqortoq (60°43' N – 46°02' W), South Greenland. The samples were collected in 2000, and average values of Σ PAH were 205 µg/kg ww and 250 µg/kg ww for Igaliko (lake) and Itilleq (fjord), respectively (Riget et al., 2003).

PAHs in the Marine Environment

Biota

From the marine environment, four types of biota samples have been collected and analysed for PAHs: macroalgae, invertebrates, mussels and fish. These samples were collected and analysed in 1999-2000, *c.f.* Tables 14, 15, and 16 (Riget et al., 2003).

Table 14. Concentration of Σ PAH (µg/kg ww) in macroalgae and invertebrates from the Qaqortoq area (60°43' N – 46°02' W), South Greenland (Riget et al., 2003).

Species	Macroalgae					Invertebrates				
	Periwinkle (<i>Littorina saxatilis</i>) (n=2)	Bladder wrack (<i>Fucus vesiculosus</i>) (n=1)		Arctic wrack (<i>Fucus disticus</i>) (n=1)	Sweet tangle (<i>Laminaria saccharina</i>) (n=1)	Sea lettuce (<i>Ulva lactuca</i>) (n=1)	Sea weed (<i>Enteromorpha</i>) (n=1)	Sand hopper (<i>Gammarus</i> sp.) (n=1)	Lugworm (<i>Arenicola cristata</i>) (n=1)	
Site	Igaliko	Usuk	Igaliko	Qaqor-toq	Usuk	Usuk	Usuk	Usuk	Usuk	Igaliko
Year	1999	2000	2000	2000	2000	2000	2000	2000	1999	1999
Σ PAH	45	66	66	41	43	43	52	24	98	370

The data in Table 14 show that the invertebrates, especially the lugworm, have a significantly higher level of PAHs than the macroalgae. This is might be due to biomagnification and the fact that while macroalgae live in the water phase, the invertebrates live in the sediment, where the concentration of PAHs generally are higher than in water.

Blue mussels were collected and analysed from 14 different sites in South Greenland. The levels were observed to depend on mussel size. Average values shown in Table 15 were about 90 µg/kg ww (range: 32-210 µg/kg ww). These levels are similar to those observed for blue mussels in the Baltic Sea.

The data in Table 15 from each site represent average values for species of different sizes. No obvious differences in Σ PAH levels were observed between different size groups, while year-to-year variations seem to be more dominant. Levels were higher for the samples collected at Qaqor-

toq, and this may indicate that pollution is more pronounced here, probably due to boat traffic.

Table 15. Concentrations of Σ PAH ($\mu\text{g/kg ww}$) in blue mussels (*Mytilus edulis*) from three locations in South Greenland, near the small town of Qaqortoq ($60^{\circ}43' \text{ N} - 46^{\circ}02' \text{ W}$), 1999-2000 (Riget et al., 2003).

Location	Usuk		Igaliko		Usuk	Igaliko	Qaqortoq
Sites	Harbour		Outside harbour				
Year	1999 (n=2)		1999 (n=1)		2000 (n=2)	2000 (n=1)	2000 (n=1)
Σ PAH	42		76		115	130	210

One sample of each sex from each location was analysed, and each sample was pooled of 4-5 individuals.

In 1999-2000, 19 liver samples from shorthorn sculpins were also collected and analysed. Fish of different age and sex were collected, but no obvious differences were observed between the different groups, *i.e.* young-old and male-female. Average values of $425 \mu\text{g/kg ww}$ were observed (range: $270-600 \mu\text{g/kg ww}$), as shown in Table 16. The slight differences observed for the blue mussels with higher levels in areas with higher population are not found for the sculpins. Here no differences are observed between samples from the background station at Usuk and those from the small town of Qaqortoq. The difference observed between mussels and fish probably reflect the difference in these two species' efficiency to metabolize PAHs; mussels metabolize PAHs rather poorly and therefore experience a higher degree of bioconcentration than fish.

Table 16. Concentration of Σ PAH ($\mu\text{g/kg ww}$) in liver of shorthorn sculpin (*Myoxocephalus scorpius*) from three locations in South Greenland, near the small town of Qaqortoq ($60^{\circ}43' \text{ N} - 46^{\circ}02' \text{ W}$), 1999-2000 (Riget et al., 2003).

Location	Usuk		Igaliko		Usuk		Igaliko		Qaqortoq	
Sex	female	Male	female	male	female	male	female	Male	female	Male
Year	1999	1999	1999	1999	2000	2000	2000	2000	2000	2000
Σ PAH	460-510	380-440	340-600	430-470	270-450	380	370-430	320-520	440	370-430

Appendix 4. PAHs in Marine Recipients at Thule Airbase 2002

In 2002, a study of the marine recipients at Thule Airbase (76°32' N – 68°52' W) were carried out. As part of this study PAH levels of sediment, blue mussels and liver of shorthorn sculpins were measured (Glahder et al., 2002).

Sediments

Surface sediment samples from five different sites (11 samples in total) around coastal dump sites at Thule Air Base and a reference site at Qaanaaq were collected and analysed. Levels of total PAH ranged from 97 to 485 µg/kg dw with an average of about 260 µg/kg dw, *c.f.* Table 17.

Table 17. Concentrations of PAHs (µg/kg dw; average and geometric mean) in surface sediment samples from an area close to 4 coastal dump sites at Thule Air Base (North Star Bay, TAB1, TAB31 and TAB37) and a reference site at Qaanaaq, 2002 (Glahder et al., 2002).

Location	North Star Bay (n=2)		TAB 1 (n=2)		TAB 31 (n=2)		TAB 37 (n=2)		Qaanaaq (n=1)
	avg	geom.	avg	geom.	avg	geom.	avg	geom.	avg
Naphthalene	12.8	12.8	12.9	12.9	10.4	10.3	7.33	7.32	7.78
C1-Naphthalenes	36.8	36.6	18.1	18.1	17.9	17.7	4.38	4.36	3.46
C2-Naphthalenes	144	142	93.8	92.4	62.9	59.0	11.1	11.0	10.9
C3-Naphthalenes	82.2	82.1	28.0	27.9	62.2	62.2	5.59	5.46	9.23
Acenaphthylene	0.96	0.91	1.55	1.54	< 0.5	< 0.5	0.57	0.57	0.73
Acenaphthene	1.96	1.90	1.22	1.21	3.14	3.14	< 0.5	< 0.5	0.57
Fluorene	5.91	5.88	5.70	5.69	3.51	3.47	2.22	2.21	3.26
Dibenzothiophene	2.14	2.13	2.05	2.04	1.79	1.79	1.20	1.19	1.11
C1-Dibenzothiophenes	23.1	21.8	10.8	10.5	31.2	23.5	3.57	3.45	11.5
Phenanthrene	12.2	12.1	17.6	17.5	15.6	15.5	11.8	11.7	12.7
C1-Phenanthrenes	17.9	17.9	20.2	20.2	9.51	9.50	8.29	8.20	15.3
C2-Phenanthrenes	46.3	46.0	63.6	63.6	32.3	32.1	21.6	19.7	27.2
C3-Phenanthrenes	2.66	2.65	1.59	1.57	1.02	1.01	1.67	1.67	0.70
Anthracene	2.03	2.02	2.23	2.23	1.97	1.93	1.96	1.83	2.29
Fluoranthene	11.0	10.9	16.8	16.7	7.74	7.69	7.11	7.11	6.81
Pyrene	10.1	10.1	13.0	13.0	4.77	4.73	8.71	8.50	6.13
1-Methylpyrene	0.77	0.77	1.00	0.98	0.57	0.57	0.54	0.54	< 0.5
Benzo(a)fluoren	0.59	0.59	1.07	1.07	0.83	0.80	< 0.5	< 0.5	< 0.5
Benzo(a)anthracene	9.06	9.02	11.4	11.3	1.78	1.74	7.07	7.06	5.60
Chrysene/Triphenylene	4.81	4.81	5.27	5.18	< 0.5	< 0.5	2.33	2.31	2.45
Benzo(bjk)fluoranthene	7.17	7.01	8.64	8.19	4.55	4.47	2.89	2.85	2.43
Benzo(e)pyrene	4.51	4.42	4.08	3.91	1.93	1.90	0.98	0.88	1.09
Benzo(a)pyrene	5.01	4.93	6.13	5.93	4.62	4.58	3.21	3.20	2.32
Perylene	18.8	18.7	12.9	12.5	6.89	6.86	0.99	0.93	1.93
Indeno(123cd)pyrene	2.74	2.47	4.24	3.77	2.42	2.40	0.92	0.91	< 0.5
Benzo(ghi)perylene	3.33	3.24	2.76	2.33	1.41	1.31	0.56	0.56	< 0.5
ΣPAH	469	464	367	362	291	278	116	114	135

Mussels

Two species of mussels were sampled and analysed; 15 samples of Iceland scallops (*Chlamys islandica*) from six different sites (15 stations) and five samples of Greenland cockles (*Serripes groenlandicus*) from four sites (five stations). Levels of 90 to 282 µg/kg ww were observed; the average level was about 125 µg/kg ww, *c.f.* Tables 18 and 19. There are no significant variations within the area, and the levels are within the range observed for blue mussels (*Mytilus edulis*) in temperate marine environment. However, blue mussels at Disko, another site previously studied, had average concentrations of ΣPAH about 80 µg/kg ww (Aarkrog et al., 1997).

Table 18. Concentrations of PAHs (µg/kg dw; average and geometric mean) in mussels sampled an area close to 4 coastal dump sites at Thule Air Base (North Star Bay, TAB1, TAB31 and TAB37) and two reference sites (Qaanaaq and Bylot Sound) 2002 (Glahder et al., 2002).

Location	TAB1				North Star Bay		Bylot Sound	
Species	Iceland scallop (<i>Chlamys islandica</i>) (n=4)	Greenland cockle (<i>Serripes groenlandicus</i>) (n=2)			Iceland scallop (<i>Chlamys islandica</i>) (n=1)	Greenland cockle (<i>Serripes groenlandicus</i>) (n=1)	Iceland scallop (<i>Chlamys islandica</i>) (n=2)	
	average	geomean	Average	geomean			average	Geomean
Naphthalene	4,22	4,19	7,60	7,21	5,81	6,41	5,15	5,13
C1-Naphthalenes	4,03	3,92	4,01	3,79	6,24	3,62	2,96	2,87
C2-Naphthalenes	4,00	3,89	7,80	7,79	6,93	8,11	6,21	6,14
C3-Naphthalenes	4,03	3,90	25,9	17,8	5,81	16,4	5,49	5,40
Acenaphthylene	0,64	0,61	1,27	1,26	0,67	0,89	0,71	0,69
Acenaphthene	1,09	0,93	1,41	1,40	1,08	0,73	0,78	0,74
Fluorene	5,77	4,82	1,96	1,91	9,79	4,27	4,37	4,16
Dibenzothiophene	0,83	0,83	0,85	0,85	1,13	1,04	0,70	0,66
C1-Dibenzothiophenes	12,7	12,4	12,1	12,0	I/K	8,25	8,18	8,05
Phenanthrene	11,9	9,83	23,0	18,8	11,1	9,11	8,06	7,86
C1-Phenanthrenes	3,08	2,93	4,35	4,05	3,96	2,5	3,69	3,61
Anthracene	0,59	0,53	0,35	0,28	0,43	0,3	0,22	0,21
Benzo(a)fluoren	< 0,1	< 0,1	< 0,1	< 0,1	<0,1	<0,1	< 0,1	< 0,1
Fluoranthene	6,62	6,45	7,81	7,79	8,08	6,6	5,61	5,42
Pyrene	7,05	6,89	11,4	11,3	8,76	9,41	4,51	4,48
1-Methylpyrene	2,16	2,15	3,95	3,93	2,09	3,03	2,02	2,02
Benzo(a)anthracene	4,31	4,10	5,08	5,07	3,22	2,99	2,70	2,65
Chrysene/Triphenylene	1,77	1,77	2,47	2,45	1,7	1,25	1,57	1,56
5-Methylchrysene	1,79	1,79	1,69	1,68	1,67	1,19	1,22	1,22
Benzo(bjk)fluoranthene	10,8	10,5	10,7	10,6	7,84	6,15	6,44	6,34
Benzo(e)pyrene	8,94	8,90	7,02	6,95	7,14	2,86	5,44	5,15
Benzo(a)pyrene	4,29	4,20	6,58	6,55	3,75	5,75	3,34	3,07
Perylene	4,28	4,23	7,34	7,08	4,38	4,75	4,60	4,60
Indeno(123cd)pyrene	3,45	3,22	5,55	5,48	2,86	2,7	5,01	4,99
Benzo(ghi)perylene	< 0,5	< 0,5	< 0,5	< 0,5	<0,5	<0,5	0,72	0,72
ΣPAH	108	107	160	155	104	108	87,7	87,7

Table 19. Concentrations of PAHs ($\mu\text{g/kg dw}$; average and geometric mean) in mussels sampled in an area close to an open dump site at Thule Airbase and a reference site at Qaanaaq, 2002 (Glahder et al., 2002).

Location	TAB31		TAB 37		Qaanaaq			
Species	Iceland scallop (<i>Chlamys islandica</i>) (n=3)	Greenland cockle (<i>Serripes groenlan- dicus</i>) (n=1)	Iceland scallop (<i>Chlamys islandica</i>) (n=2)	Greenland cockle (<i>Serripes groenlan- dicus</i>) (n=1)	Iceland scallop (<i>Chlamys islandica</i>) (n=3)			
	average	geomean	average	geomean	average	Geomean		
Naphthalene	6,61	6,53	17,4	8,37	8,37	10,2	6,70	6,68
C1-Naphthalenes	5,78	5,68	4,65	6,49	6,38	9,10	5,39	5,20
C2-Naphthalenes	10,1	7,66	16,8	7,43	7,11	11,4	8,66	8,39
C3-Naphthalenes	15,0	11,7	34,8	11,0	9,85	18,9	8,85	8,15
Acenaphthylene	0,80	0,79	0,90	0,65	0,65	0,66	0,45	0,45
Acenaphthene	0,91	0,82	0,31	0,78	0,69	0,40	1,21	1,19
Fluorene	3,36	3,24	2,37	7,71	6,96	12,0	5,54	5,29
Dibenzothiophene	0,99	0,96	1,77	1,74	1,64	2,35	1,02	0,93
C1-Dibenzothiophenes	33,4	26,0	22,6	10,1	10,0	11,5	16,5	15,3
Phenanthrene	11,4	10,7	26,0	19,8	16,4	18,4	12,8	11,1
C1-Phenanthrenes	6,30	4,32	16,5	11,1	7,47	11,6	5,83	4,38
Anthracene	0,41	0,41	1,01	0,57	0,56	0,58	0,42	0,42
Benzo(a)fluoren	2,06	2,06	0,86	0,67	0,67	0,86	0,46	0,46
Fluoranthene	8,49	7,18	15,8	10,1	9,21	14,8	9,12	8,28
Pyrene	7,62	7,27	16,8	12,0	11,1	17,3	9,67	8,62
1-Methylpyrene	1,70	1,60	1,03	1,44	1,35	0,98	1,72	1,61
Benzo(a)anthracene	5,42	4,67	11,3	5,17	4,68	8,01	4,01	3,72
Chrysene/Triphenylene	3,08	2,59	10,9	2,77	2,67	4,01	1,87	1,84
5-Methylchrysene	2,36	2,18	2,61	1,86	1,80	2,65	2,02	1,95
Benzo(bjk)fluoranthene	6,84	6,22	13,9	12,1	12,0	11,0	5,41	5,25
Benzo(e)pyrene	9,99	8,38	35,9	18,1	14,1	26,8	9,88	7,23
Benzo(a)pyrene	3,49	3,48	3,24	4,44	4,36	3,38	3,73	3,71
Perylene	6,38	6,04	10,9	5,66	5,62	5,99	5,31	4,61
Indeno(123cd)pyrene	4,26	4,08	4,75	3,34	3,20	2,50	3,99	3,34
Benzo(ghi)perylene	6,75	6,75	9,34	4,68	4,68	4,93	4,21	4,21
ΣPAH	157	140	282	165	156	210	132	125

Shorthorn sculpin

Liver samples of shorthorn sculpins were sampled at three different dump sites (TAB 1, TAB 37 and TAB 31), in North Star Bay at Thule Air Base and two reference sites (Bylot Sund and Qaanaaq) near Qaanaaq/Thule. The samples from each site were pooled and analysed. Levels ranged from 289 to 1379 $\mu\text{g/kg ww}$ with one sample being extremely high (1379 $\mu\text{g/kg ww}$). The average level was 335 $\mu\text{g/kg ww}$ when excluding the highest value. There were no significant differences between the levels of Σ PAH for the dump sites and reference sites. The levels here, however, are only about half the levels observed in shorthorn sculpins at the Disko area (Aarkrog et al., 1997).

Table 20. Concentrations of PAHs (µg/kg ww; average and geometric mean) in liver samples of shorthorn sculpins sampled close to open dump sites, at Thule Airbase and at reference sites at Bylot Sund and Qaanaaq, 2002 (Glahder et al., 2002).

Location	TAB1 (n=5)		TAB 37 (n=5)		TAB 31 (n=3)		North Star Bay (n=2)	Bylot Sund (n=2)	Qaanaaq (n=3)	
Site description	Dumps				Air Base		Reference			
	Average	geomean	average	geomean	average	geomean	average	average	average	geomean
Naphthalene	22,7	22,3	19,4	19,2	17,2	17,2	24,2	26,8	29,5	29,1
C1-Naphthalenes	9,53	9,38	9,98	9,78	10,8	10,3	14,1	9,95	20,3	19,2
C2-Naphthalenes	29,9	29,6	37,9	36,6	39,0	37,4	44,7	23,6	44,4	43,9
C3-Naphthalenes	19,1	18,8	34,7	29,1	24,8	22,7	18,9	18,1	27,2	26,3
Acenaphthylene	4,86	4,80	5,21	5,11	2,64	2,51	5,03	4,23	5,76	4,95
Acenaphthene	5,41	5,22	5,16	5,04	3,81	3,77	5,46	8,01	114	22,3
Fluorene	16,3	13,7	14,0	13,2	20,6	16,7	19,5	20,6	30,4	28,3
Dibenzothiophene	1,82	1,72	6,58	3,54	3,80	3,15	1,68	2,14	2,78	2,67
C1-Dibenzothiophenes	50,1	47,3	52,0	49,6	51,1	41,6	36,2	57,8	56,7	55,62
Phenanthrene	20,0	19,6	32,4	27,0	23,9	22,9	17,1	20,4	20,5	18,1
C1-Phenanthrenes	20,1	19,6	41,3	30,0	26,8	25,2	19,2	21,1	18,4	18,3
Anthracene	1,25	1,14	2,63	2,00	1,40	1,26	1,28	1,18	1,81	1,65
Benzo(a)fluoren	0,16	0,08	2,14	0,75	2,08	1,22	0,70	0,61	2,15	2,06
Fluoranthene	20,0	18,4	42,1	26,6	21,9	19,3	8,15	14,1	13,7	12,2
Pyrene	16,8	16,2	81,7	36,0	64,6	48,5	11,1	14,2	61,3	45,1
1-Methylpyrene	1,32	1,27	4,04	1,68	2,14	2,08	2,80	1,44	2,57	2,29
Benzo(a)anthracene	21,2	19,4	13,0	12,1	17,9	16,9	31,5	36,6	27,0	23,5
Chrysene/Triphenylene	13,1	12,7	31,6	20,6	8,66	8,61	13,6	18,2	9,22	8,92
5-Methylchrysen	1,83	0,24	14,1	3,09	17,1	11,0	26,2	0,1	39,1	35,4
Benzo(bjk)fluoranthene	7,03	6,69	8,21	7,66	8,79	8,45	7,02	11,7	10,8	10,7
Benzo(e)pyrene	11,7	10,5	16,8	14,8	20,4	20,1	7,84	6,98	10,7	10,3
Benzo(a)pyrene	11,6	10,8	15,3	14,7	18,8	18,3	13,1	11,9	19,9	19,8
Perylene	13,0	12,8	13,8	13,0	14,1	13,9	14,1	11,6	15,0	14,1
Indeno(123cd)pyrene	16,0	16,0	29,5	23,4	25,2	24,2	18,6	13,1	19,8	19,1
Benzo(ghi)perylene	2,08	1,52	20,6	4,81	15,03	7,61	3,02	1,98	7,89	6,68
ΣPAH	337	320	554	409	463	405	364	356	611	481

Appendix 5. Marine recipients at waste dumps in West Greenland 2003

In 2003, a study of the marine recipients of municipal waste dumps in West Greenland was carried out (Asmund 2007). Among other pollutants, this study included PAH levels in the marine sediments and biota at the waste dumps.

Sediments

Table 21. PAH concentrations ($\mu\text{g/kg dw}$) in sediment samples ($n=1$) at municipal waste dump sites in West Greenland and a reference site (Uunartoq) (Asmund 2007).

Location	Aasiaat	Aasiaat	Nanortalik	Egalugarsuit	Attu	Uunartoq
(Latitude, longitude)	68°43' N – 52°52' W	68°43' N – 52°52' W	60°07' N – 45°12' W	67°34' N - 53°16' W	67°57' N- 53°44' W	69°54' N - 52°36' W
Depth	10m	20 m	10m	10m	13 m	Reference
Naphthalene	3.4	3.5	40.0	5.7	5.8	11.5
C1-Naphthalenes	1.9	3.0	32.4	5.2	4.9	13.5
C2-Naphthalenes	3.1	16.0	188	14.3	11.3	33.6
C3-Naphthalenes	3.0	20.5	68.1	20.6	10.4	24
Acenaphthylene	0.3	0.3	4.0	0.4	<0.2	0.9
Acenaphthene	0.9	0.9	9.2	1.4	1.8	4.8
Fluorene	2.7	3.9	25.9	4.3	21.4	8.5
Dibenzothiophene	0.9	1.1	14.6	1.6	0.9	2.5
C1-Dibenzothiophene	4.0	4.0	50.9	8.7	6.6	8.5
Phenanthrene	8.3	16.8	104	11.4	13.3	23.4
C1-Phenathrenes	9.1	22.6	174	12.5	7.9	39.2
C2-Phenanthrenes	6.1	20.3	71.0	10.8	6.7	19.4
C3-Phenanthrenes	<1	2.2	5.9	0.7	0.6	1.3
Anthracene	2.5	5.9	26.0	2.3	13.8	16.4
Benzo(a)fluorene	0.3	2.2	17.3	0.3	0.3	5.6
Fluoranthene	8.5	13.5	117	10.0	7.0	27.4
Pyrene	9.9	15.4	119	12.7	8.7	32.1
1-Methylpyrene	1.5	6.7	19.3	0.8	0.5	6.1
Benzo(a)anthracene	2.8	5.5	33.6	1.8	1.2	11.4
Chrysene/Triphenylene	2.5	5.6	36.8	2.3	1.5	11.8
Benzo(b+k)fluoranthene	3.7	8.2	54.2	2.3	1.4	15.7
Benzo(e)pyrene	1.3	3.9	22.7	0.7	<0.5	6.2
Benzo(a)pyrene	2.9	5.5	33.7	2.5	1.7	10.7
Perylene	1.1	2.4	47.8	0.7	1.8	7.5
Indeno(123-cd)pyrene	1.8	3.6	22.8	1.4	1.0	8.3
Benzo(ghi)perylene	1.5	4.2	21.4	1.4	0.8	6.1
Dibenzo(ah)anthracene	1.4	2.5	15.5	1.1	0.9	4.5
Σ PAH	85	200	1373	138	132	361

The PAH levels of the sediments at these dump sites are similar or slightly lower than observed elsewhere in Greenland (Asmund 2007). This may be due to the fact that the analysed sediment samples from the dump sites were relative coarse (from shallow water), while other sediment samples generally were sampled at deep sea and of much finer grain size.

Shorthorn sculpin

Liver from shorthorn sculpins collected near the dump sites showed significantly lower levels (about 257 µg/kg ww) than similar samples collected at Kronprinsens Ejland; these samples had average values about 897 µg/kg ww.

Table 22. PAH concentrations (µg/kg dw) in liver samples* from shorthorn sculpins collected close to municipal waste dump site areas in West Greenland and a reference site at Nanortalik (Asmund 2007).

Location	Aasiaat	Attu	Nanortalik	Nanortalik	Eqaluarsuit - W
(Latitude, longitude)	68°43' N – 52°52' W	67°57' N- 53°44' W	60°07' N – 45°12' W	60°07' N – 45°12' W	67°34' N - 53°16' W
Station	dump	Dump	Nan-1	Reference	EQA-4
Naphthalene	17,2	17.4	19.0	16.8	20.3
C1-Naphthalenes	11,9	11.9	11.4	12.7	15.6
C2-Naphthalenes	29,3	23.4	25.6	22.4	23.8
C3-Naphthalenes	15,7	17.0	33.2	24.6	13.5
Acenaphthylene	2,3	1.1	1.6	0.9	1.0
Acenaphthene	14,5	12.2	12.6	10.4	12.6
Fluorene	10,7	12.2	9.1	9.4	14.8
Dibenzothiophene	3.0	2.3	4.2	3.4	4.0
C1-Dibenzothiophene	11,4	11.9	10.9	9.0	11.9
Phenanthrene	27,7	22.3	23.5	22.8	28.3
C1-Phenathrenes	23.0	18.5	19.1	21.7	20.4
C2-Phenanthrenes	13.2	15.7	12.0	13.2	19.0
C3-Phenanthrenes	1.7	2.5	2.7	0.7	1.9
Anthracene	3.3	1.9	2.4	2.9	2.9
Benzo(a)fluorene	0.4	0.4	0.3	0.4	0.6
Fluoranthene	25.2	18.9	21.5	15.1	20.6
Pyrene	26.2	21.9	24.8	21.3	26.0
1-Methylpyrene	2.2	4.1	3.4	1.4	3.7
Benzo(a)anthracene	2.4	2.2	2.5	2.1	3.0
Chrysene/Triphenylene	4.1	3.8	4.0	3.3	4.7
Benzo(b+k)fluoranthene	4.6	3.9	4.8	4.0	4.2
Benzo(e)pyrene	1.9	1.2	1.6	1.2	1.5
Benzo(a)pyrene	6.7	6.1	6.1	7.5	6.9
Perylene	1.6	1.9	1.2	0.5	1.8
Indeno(123-cd)pyrene	3.0	2.9	2.9	3.0	3.5
Benzo(ghi)perylene	1.4	1.4	1.3	1.3	1.8
Dibenzo(ah)anthracene	4.3	4.5	4.5	4.3	3.9
ΣPAH	269	244	266	236	272

*(n=1, each sample is pooled of 4-5 individuals).

Appendix 6. Analytical methods

All samples were Soxhlet extracted with toluene, cleaned on SPE (Si-columns) and analysed by GC-MS in SIM mode. Prior to the extraction, all samples were spiked with a deuterium- and ^{13}C -labelled recovery spike mix comprising 17 unsubstituted PAHs and one methylated PAH (2-6-ring PAHs).

Extraction and clean-up

Sediment samples (approx. 10 g ww) were Soxhlet extracted with 500 mL toluene and HCl activated copper powder for 24 hrs. Water was successively removed using a Dean-Stark condenser. After concentration on a rotary evaporator the solvent was exchanged to n-hexane, and the extracts eluted through 2 g activated SiO_2 with hexane and dichloromethane, successively, for recovery of the aliphatic and aromatic fractions, respectively.

Alternatively, sediment samples were mixed with pre-cleaned sodium sulphate and subjected to accelerated solvent extraction (ASE) using dichloromethane-acetone (1:1 v:v) as solvent and activated copper powder for sulphur removal. Samples were extracted in two cycles at 125°C and 102 atm. (1500 psi).

Homogenised tissue samples (2-5 g ww) were Soxhlet extracted with 500 mL toluene and HCl activated copper powder for 24 hrs. Water was successively removed using a Dean-Stark condenser. Toluene was removed on a rotary evaporator, and the extracts successively refluxed for 4 hrs. with 50 mL 20% KOH in methanol, neutralised with HCl, extracted with n-hexane eluted through 2 g activated SiO_2 with dichloromethane.

GC-FID analysis

Equal amounts of the aliphatic and aromatic fractions were recombined and analysed with GC-FID using a Hewlett Packard 5890 GC equipped with an automatic sample injector, a 30 m \times 0,25 mm ID \times 0,25 μm apolar film (Restek RTX-1) and operated in the splitless injection mode. Oven program from 40 to 320°C in 40 min. Quantification of TPH was achieved using five-point external calibration based on the Brent crude oil solutions. All samples were analyzed in duplicates and corrected for blank values.

GC-MS analysis

The dichloromethane eluents were evaporated under nitrogen and redissolved in 1 mL toluene. 100 μL of the concentrated extracts were mixed with 100 μL volume spike comprising seven deuterium-labelled unsubstituted PAHs (2-6-ring PAHs).

GC-MS analysis was performed on a HP 5890 GC connected to an IN-COS 50 mass spectrometer. Separation was achieved using a 30 m × 0.2 mm ID × 0.1 µm film (DB-1701) capillary column with helium as carrier gas. The GC-oven was programmed from 90 to 290°C.

Quantifications were achieved using a five or six level calibration including all reported PAHs. Calibration standards were added spikes in the same concentration as the samples, and the calculations were performed using the area ratios and linear fits.

Recovery standards were added to all samples to correct for any loss during clean up. Methods blanks were run with each batch of samples to check for laboratory contamination. Similarly, control samples with certified reference values were run with each batch to check for the quantification.

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These studies were conducted on the Nuussuaq Peninsula at Marraat, where GEUS discovered oil in porous volcanics in the early 1990ies. This oil was also found in the Marraat-1 core drilled in 1993. At Marraat the presence of oil stained stones scattered along the coast indicates oil bearing strata and the existence of potential oil seeps. The studies reported here had the objective to see, if the suspected seep had a local impact on the chemistry and biological communities in the marine environment at Marraat. The study included sediments, blue mussels and fish that were analyzed for hydrocarbons, a Pollution Induced Community Test (PICT), a sediment toxicity test and a measurement of PAH metabolites in fish gall. The hydrocarbon pattern found in sediment and biota samples indicates input from both immature petrogenic hydrocarbons of possible terrestrial origin and local pollution by fuel oil. But the hydrocarbon levels found were low and do not indicate an input from a natural local oil seep at Marraat. The results of the PICT, the sediment toxicity test and the PAH metabolite study do not either indicate the presence of an oil seep. However, compared to sediments from a larger area of West Greenland the sediments close to Nuussuaq and Disko have higher concentrations of PAH expressed on basis of their content of organic matter. This could be a result of natural seepage of oil in the Nuussuaq/Disko region.

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