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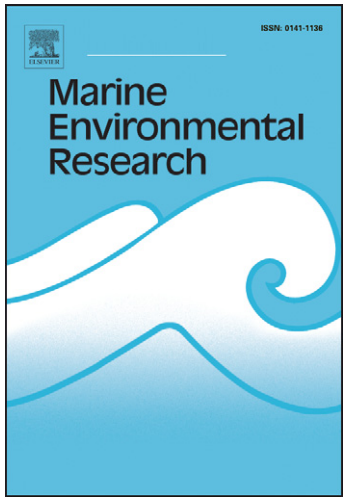

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Natural background and anthropogenic inputs of polycyclic aromatic hydrocarbons (PAH) in sediments of South-Western Barents Sea

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Abstract
Polycyclic aromatic hydrocarbons (PAH) were measured in sediment cores from 13 locations in South-Western Barents Sea as part of a detailed study of the Norwegian seabed under the MAREANO program. The generally low PAH levels found, an average around 200 ng g^{-1} dry weight for sum PAH, indicate low inputs of petroleum hydrocarbons to the marine environment in the area. Differences in PAH composition and various PAH ratios indicate a natural, mostly petrogenic origin of PAH in sediments from the open sea locations, while the fjord locations show higher pyrogenic PAH contents with an increase towards upper sediment layers, indicating low inputs from human activities. Petrogenic PAH levels increase in deeper sediments at open sea locations, also when normalised to total organic carbon (TOC) contents, suggesting natural leakages of oil-related hydrocarbons in the area.
***Key words**: PAH, TOC, sediments, radiodating, ^{210}Pb, ^{137}Cs, petrogenic, biogenic, pyrogenic, human impact, marine environment, MAREANO*

Introduction

The Barents Sea is experiencing an increasing impact from various human activities. Almost 1/3 of all Norwegian undiscovered oil resources may be found in that region (NPD, 2005) Exploitation of a major gas field, Snøhvit, has recently started, while production at a large oil field nearby, Goliat, is due to start in the near future. A considerable part of Russian oil is transported from the Russian Arctic through the Barents Sea: 9.5 to 11.5 x 10^6 tonnes per year in 2005-2008, with an expected annual increase up to 20 mln tonnes in 2009 (Bambulyak and Frantzen, 2009). Fishing, an important activity in the Barents Sea for many years, has an impact on the marine environment due to emissions from fishing vessels and accidental releases of bunker oil. In the year 2008, 451,000 tonnes of cod and 155,000 tonnes of haddock could be legally fished by Norway, Russia and other countries in the Barents Sea (FKD, 2007).

The above-mentioned activities may result in chemical contamination of the marine environment with petroleum hydrocarbons. Among these, PAH are particularly important due to their persistence, ability to bioaccumulate and toxicity to marine organisms (e.g. Neff, 2002).

A recent comparison of the levels of polycyclic aromatic hydrocarbons (PAH) in sediments, measured by various institutions in Barents Sea during the last 2 decades, has indicated a slight increase in the levels of petrogenic PAH in South-Western Barents Sea during recent years

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(Dahle et al., 2009). In four other studied areas of this sea such a trend was not found (*ibid*.) This work describes the results of a new, detailed study of PAH levels and origins in the South-Western Barents Sea.

PAH in the marine environment consist of a complex mixture of compounds consisting of 3 or more fused aromatic rings and may include alkyl chains; similar type of compounds including only 2 aromatic rings (e.g. naphthalene), unsaturated rings (e.g. acenaphthene) and heteroatoms such as sulphur (e.g. dibenzothiophene) are often also considered as PAH. Lighter PAH, like naphthalene, are more water-soluble and volatile than the heavier compounds, and will therefore be less persistent in the environment, being subject to dilution, evaporation and bacterial degradation (Page et al., 1999). Heavier compounds will more likely reach the seabed, often after sorption to organic particles, and undergo deposition or bacterial degradation in sediments (Neff, 2002). PAH compounds are lipophilic and can be taken up by biota. They can be toxic to marine organisms, including acute toxicity and carcinogenicity, particularly so for some PAH of higher molecular weight (Neilson, 1998; Neff, 2002). Benzo[*a*]pyrene is ecotoxicologically the best-studied and one of the most potent carcinogens among PAH (Collins et al., 1991).

PAH can be formed in various processes:

- Combustion. Pyrogenic PAH are mainly non-alkylated compounds, often dominated by 4-6 rings PAH, e.g. pyrene and benzofluoranthenes. The source of these compounds may be both natural (e.g. forest fires, volcano eruptions etc.) and anthropogenic (wood ovens, industry etc.) In the marine environment, pyrogenic PAH may originate from emissions from shipping (e.g. Dalsøren et al., 2007), flaring at offshore oil installations or long-range transport from land areas.

- Oil formation. Petrogenic PAH vary strongly in their composition, each type of oil having its specific profile; high amounts of lighter PAH with a high degree of alkylation are typical, e.g. alkylphenanthrenes. In the marine environment, the sources of these compounds may be both natural, such as oil seeps from oil reservoirs or hydrocarbon source rocks, and anthropogenic, due to oil spills (e.g. Page et al., 1996).

- Biological processes. Biogenic PAH formed in recent biological processes such as microbial activity in plant detritus, e.g. perylene, are not as strongly varied in chemical structure as petrogenic PAH due to restricted pathways of biosynthetic reactions. These compounds of natural origin have been observed to dominate PAH composition in sediments in some places, e.g. Northern Barents Sea (Dahle et al., 2006; Boitsov et al., 2009), or Dvina Bay of the White Sea (Savinov et al., 2000).

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PAH from different sources may be present at the same location. The relative amounts of certain PAH compounds may serve to distinguish between different types of origin of the local PAH presence. A number of such PAH ratios have been proposed, as summarized by Yunker et al. (2002). Thus, a predominance of alkylated homologues of naphthalene, phenanthrene and dibenzothiophene over their parent compounds indicates a petrogenic origin of PAH (e.g. Budzinski et al., 1997). Relative contents of thermally less stable PAH in relation to the more stable ones, for example phenanthrene/anthracene ratio (PHE/ANT), may be used to differentiate between pyrogenic and other types of PAH, PHE/ANT ratio below 10 typically corresponding to pyrogenic input, indicating higher temperatures of formation (Gschwend and Hites, 1981; Budzinski et al., 1997). Presence of certain PAH may indicate the source, such as biogenic predecessors in case of perylene (Venkatesan, 1988).

This work has been carried out as part of the ongoing MAREANO[1] program, a long-term, multi-institutional project. The aim is to perform a detailed biological, geological and geochemical mapping of the Norwegian seabed (MAREANO, 2008). Extensive geochemical studies may provide a better understanding of the different sources and pathways of hydrocarbons found in sediments in this area at present. Levels of PAH found in this study will also serve as a baseline for the future when extensive oil exploitation begins in the region. It has been demonstrated on several occasions that in environmental damage assessments it is very useful to have information about sources of hydrocarbons present in the affected area before activities or accidents took place (for example, see Page et al., 1996, and other studies of *Exxon Valdez* disaster).

Methods

Multicorer sampling

The geographical area and sampling stations are shown in Figure 1. Sediment cores were collected at 13 locations during a research cruise in June 2006. Multicorer equipped with 6 tubes 100 mm in diameter and 60 cm long was used for sampling. Length of sediment cores with well-preserved sediment surfaces were measured onboard the ship and sliced to 1 cm-thick slices immediately after sampling. Samples were then kept at -20°C until analyses in the laboratory.

Samples were collected where fine-grain sediments suitable for multicorer sampling were found. Information about the nature of the bed and coring locations was based on multi-beam maps, seismic data and video recordings. A large part of the seabed in the Tromsøflaket area is occupied

[1] Norwegian acronym for "Marine Area Database of Norwegian Ocean Areas".

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by rocks and boulders or by sandwaves and there were only four areas where sediments were of appropriate quality for sampling and analyses. The smaller area of Ingøydjupet contained mostly soft muddy sediments suitable for coring; besides, there were numerous special features on the seabed: a large pockmark field, discovered earlier by multibeam mapping and confirmed by video footage (Chand et al., 2009). Extra samples were therefore collected in the area of pockmarks, including one sample from inside a pockmark (st. 136) and one from an immediate vicinity of the same pockmark (st. 153). Sea depth at sampling stations in Ingøydjupet area is 420-440 m, comprising muddy sediments with high contents of silt and clay, between 86.7 and 95.6% (Jensen et al., 2007). The Tromsøflaket sampling stations were at shallower sea depths, between 249 and 322 m, with more coarse sediments, silt and clay contents of 6.0 to 75.9% (*ibid.*) In fjord areas, sampling stations were at sea depths of 396 to 518 m, with fine-grained sediments with silt and clay contents of 76.1 to 95.4% (*ibid.*)

Materials

Pure standards (95-99.9%) of 22 PAH and 5 deuterated PAH (biphenyl-d_{10}, anthracene-d_{10}, phenanthrene-d_{10}, pyrene-d_{10}, perylene-d_{12}) were from Chiron (Trondheim, Norway). Standard solutions were prepared in hexane. Solvents (methanol, hexane, dichloromethane) were analytical grade from Merck (Oslo, Norway) and Arcus (Vestby, Norway). Potassium hydroxide (KOH), and hydrochloric acid (HCl) were from Merck. Copper powder (99.5%, 40-100 mesh) was from Alfa Aesar (Karlsruhe, Germany). The distilled water used was purified with NANOPURE Ultrapure Water Systems (USA). Bond Elut Silica 3cc 500mg extraction columns were from Varian Inc. (Middelburg, the Netherlands).

PAH analyses in sediments using GC-MS

The chemical analysis of PAH in sediments was carried out according to a method routinely used at IMR and accredited by the official Norwegian accreditation body, Norsk Akkreditering. Sediment samples were dried in open air at room temperature until complete dryness. The samples were then ground in a mortar, and sample of known size was extracted by saponification in methanolic KOH followed by extraction by hexane, removal of sulphur by active copper, clean-up on silica Bond-Elute column and then analysed the hydrocarbon fraction by gas chromatography-mass spectrometry (GC-MS), with gas chromatograph HP-6890 coupled to Micromass Autospec Ultima mass spectrometer, in Selected Ion Recording (SIR) mode. GC-column was HP-5MS, fused silica, 30 m x 0.25 mm, 0.25 µm. Carrier gas was Helium, 1.5 ml min^{-1}, constant flow. Injection was done in splitless mode, injection volume 1 µl, injector

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temperature 280º C. Purge-off time was 1 min. Oven program was 60º C initial temperature held for 1 min, then increased to 100º C by 15º C min^{-1}, and then increased to 280º C by 6º C min^{-1} and held at this temperature for 9 min. Mass spectrometer was used in electron impact (EI) mode and the spectrum was scanned for molecular masses of analytes listed in Table 2 and the deuterated internal standards, biphenyl-d_{10}, anthracene-d_{10}, pyrene-d_{10} and perylene-d_{12}, used for quantification, as well as phenanthrene-d_{10}, used as recovery internal standard. The results were quantified with Opus Quan software package. Limits of quantification (LOQ) were 0.5 ng g^{-1} dry weight for individual PAH. Analytical precision varies from compound to compound but is set to 30% for individual PAH compounds.

TOC and grain size determination.

One set of sediment sub-samples was analysed for weight percentages (wt. %) of total organic carbon (TOC) using a LECO CS 244 analyser. For the TOC analyses, aliquots (~200 mg) of the samples were treated with 10 % (volume) hydrochloric acid (HCl) at 60ºC to remove carbonate, and then washed with distilled water to remove HCl. We caution the reader that the possible loss of organic material by acid leaching is not taken into account. The samples were dried overnight (50ºC) and then analysed.

Grain size analyses of total sediment were obtained from laser diffraction techniques (Coulter LS 2000) (for details, see Xu 2000, and references therein) and wet sieving. The Coulter LS 2000 measured the fractions from 0.4 µm to 2 mm while particles larger than 2 mm were determined by wet sieving. Prior to each analysis, the samples were freeze-dried. The grain size distribution is determined with respect to volume percent and with the assumption of uniform density of the sample.

^{210}Pb and ^{137}Cs measurements.

Levels of lead-210 (^{210}Pb) were measured in 5 of the sediment cores according to the procedure described elsewhere (Pheiffer and Sørensen, 1979). The measured levels were used for determining the sedimentation rates and dating the selected cores.

Levels of radioactive cesium in sediments was determined by gamma-spectroscopy on High-Purity Germanium (HPGe) detector. The sediment samples were dried in open air at room temperature until complete dryness. The samples were then ground in a mortar, and a known sample size was transferred to a container with specific geometry. The sample was gamma-counted for approximately 60,000 sec. on an electrically cooled HPGe-detector. The detector

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used is single-peak calibrated by using a solution of known quantities of ^{137}Cs within identical container geometry and approximately the same density as the sample. The results were decay corrected to the sampling day and reported as activity Cs-137 in dry weight of sediment, Bq kg^{-1} (dry weight).

Principal Component Analysis.

The complete data set of surface sediment levels of PAH was evaluated for the amount of values below the limit of quantification (LOQ, 0.5 ng g^{-1} dry weight), and the components with all the values below LOQ, were excluded from the dataset. For other compounds, the values below LOQ were replaced by a random number between zero and the limit of detection (Yunker and Macdonald, 2003). Principal component analysis (PCA) along two components was then carried out on this data subset, including 13 sampling stations as variables and 26 PAH compounds as objects. All data was block-normalised and weighted to average. A 2-principal components analysis explained 85.4% of the variation. Sirius 7.1 software from PRS AS, Bergen, Norway was used for PCA.

Results & discussion

General results are summarized in Table 1. PAH levels were measured in every 2nd cm slice of each sediment core. Further discussion will consider all the analysed samples as falling into 3 groups, according to geographical areas, as shown in Table 1: those from fjord areas, those from Ingøydjupet area and those from the rest of the studied open sea areas (Tromsøflaket). Ingøydjupet area is deeper than Tromsøflaket, more than 400 m as compared to 200-300 m. It is also special due to presence of pockmarks (depressions approximately 40-60m in diameter and 6 m deep, (Chand et al., 2009)) on the seabed in a part of this area. Pockmarks are geological formations which may signify former or recent hydrocarbon venting activity (seepages of gas or fluids from formations below the sediment surface, e.g. Hovland and Judd, 1988), but it is not known whether those in Ingøydjupet are active at present.

The observed PAH levels are low at all locations, averaging 200 ng g^{-1} dry weight and not exceeding 330 ng g^{-1} dry weight for the sum of PAH concentrations in surface sediments. Average levels of PAH in Barents Sea sediments are known to be relatively low compared to the seas closer to more densely populated and industrialized areas, like the Skagerrak or the Baltic Sea. Recent studies found mean levels of a sum of 20 PAH throughout the Western Barents Sea to be 400-500 ng g^{-1} dry weight (Boitsov et al., 2009), 4 to 5 times lower than the levels observed in Skagerrak for 18 of the same 20 PAH (Longva and Thorsnes, 1997) and 2 to 7 times lower

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than in the Baltic Sea for 13 of the same 20 PAH (Pikkarainen, 2004). These data are in good agreement with earlier measurements of PAH in Barents Sea sediments (Dahle *et al.,* 2006). However, there is a large variation in natural hydrocarbon levels in different areas of the Barents Sea. For example, areas close to Svalbard show naturally high hydrocarbon levels, up to ca. 1400 ng g^{-1} dry weight for the sum of 20 PAH in some places, probably due to erosion of coal-bearing bedrock on Svalbard (Boitsov et al., 2009).

The highest levels are often observed in sample stations with highest TOC-concentrations, due to the fact that PAH are easily bound to organic matter. The linearity of this relation for the studied sediments confirms that the influx of organic matter mostly determines PAH levels in 2-3 cm core depth samples at the 12 stations (Fig. 2). Sampling stations with highest PAH levels and with highest TOC contents, 85, 115, 119 and 128, are placed in the fjords, which are typical sediment sinks. Three stations from the deeper Ingøydjupet area are also relatively high on PAH/TOC scale and are grouped together, reflecting their geographical proximity and similarities in depositional setting. Station 112, also from Ingøydjupet, was outside of the area with pockmarks and show TOC levels closer to those of Tromsøflaket stations, where sedimentation is less active and sediments are more coarse-grained due to stronger ocean currents at Tromsøflaket compared to Ingøydjupet (Jensen et al., 2007).

Using ^{210}Pb dating, sedimentation rates for open sea stations were found to be 0.7 mm $year^{-1}$ for station 112 (Ingøydjupet), 1.0 mm $year^{-1}$ for station 102 (Tromsøflaket) and 1.2 mm $year^{-1}$ for station 153 (Ingøydjupet), while the fjord station 85 had a higher sedimentation rate of 2.2 mm $year^{-1}$. This is an expected distribution of sedimentation rates which tend to be higher in fjord areas. Relevant measurements in another part of the Barents Sea, close to Kola Bay, revealed sedimentation rates of 0.5 mm $year^{-1}$ in the open sea and between 0.6 and 2.5 mm $year^{-1}$ in various parts of Kola Bay, decreasing towards the open sea (Petrova, 2008); while measurements in North-Western Barents Sea, South of Spitsbergen, found sedimentation rates at 2.8 mm year $^{-1}$ (Heldal et al, 2002). Station 136, situated within one of the pockmarks in Ingøydjupet, close to station 153 outside of this pockmark showed a high sedimentation rate, above 4 mm per year, which put a question mark to the quality of this core (see discussion below). ^{210}Pb dating is known to be reliable for areas with undisturbed sedimentation but may be problematic for dating short time periods if a disturbance in the sediments has occurred (e.g. Stepanets et al., 2001).

Concentration profiles of PAH were determined for all sediment cores and the values were then normalized to 1% TOC. Normalization of PAH levels to TOC contents allows comparing

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differences in PAH inputs unrelated to variability in influx of organic matter. Five of the sediment cores have been dated by ^{210}Pb-radiodating, to various depths of up to 20 cm. Fig. 3 shows the PAH levels normalised to 1% TOC for dated cores, divided into 3 groups according to the possible source of the compounds: plots for perylene as the tracer of biogenic origin, for pyrogenic PAH (PyrPAH) defined as all the four- to six-ring PAH except perylene, and for petrogenic PAH shown as NPD (naphthalene, dibenzothiophene, phenanthrene and their C_1-C_3 alkylated homologues). Dates are shown for 3 of the 5 dated cores, the remaining two either having too few data points to reveal any trends (core from station 112) or showing atypical trends (core from station 136).

Levels of the radioisotope ^{137}Cs, which has only anthropogenic sources in the environment, were measured in three sediment cores, one from each area (Fig. 4.) The highest levels observed for station 85 are explained by terrestrial runoff. This is based on mapping of ^{137}Cs in topsoil in coastal parts of north-eastern Finnmark, which show higher levels, up to 2000 Bq m^{-2}, as compared to Northern Finland and western part of the Kola peninsula (Reimann et al., 1998). Although fjord areas discussed in this article lie to the west of the above-mentioned areas of Finnmark, it is reasonable to assume that comparable ^{137}Cs-levels could be present there. This may also account for the peak observed at ca. 8 cm depth, corresponding to 1960-s according to ^{210}Pb-dating (Fig. 3). The peak may be mostly due to atmospheric nuclear tests, conducted at Novaya Zemlya in 1950-s and the beginning of 1960-s and resulting in similar peaks in ^{137}Cs levels in sediments from other locations in the Arctic (Sayles et al., 1997). The top of the observed peak is dated by ^{210}Pb to ca. 1970, 7 years later than the ban on atmospheric nuclear tests (1963), which may be the time required for radioactive fallout deposited on land to reach the sea. However, several other significant inputs of ^{137}Cs to the environment of the North Atlantic, such as Chernobyl disaster and releases from the Sellafield and La Hague nuclear reprocessing plants, may also contribute to the observed levels (Heldal et al., 2002). The ^{210}Pb dating of the core from station 85 is thus only tentatively confirmed by the ^{137}Cs measurements. The levels of ^{137}Cs in the two other cores are low, although the core from station 136 seems to show a peak similar to that of station 85, thus confirming our suspicions with regard to the dating of this core. Trends displayed in all 3 cores seem to bear no evidence of any significant bioturbation.

Levels of individual PAH compounds are shown in Table 2 for surface sediments and for 14-15 cm depth, which was the depth of the shortest core (from station 109). Concentration profiles of perylene (see Fig. 3) and petrogenic PAH (shown as NPD in Fig. 3) are rather similar, with small variation and low levels in recent sediments. These levels could be mostly due to long-range

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transport, which is known to play a significant role in defining PAH levels at many locations throughout the Arctic (e.g. Halsall et al., 1997). There is, however, a strong increase in the concentrations of the same compounds in deep sediment layers (outside of the dated range). The trend is observed at most open-sea locations and is strongest at some Ingøydjupet stations, but is absent in the cores from fjord stations (Fig. 3). A study of heavy metals in the same sediment samples from two of the Ingøydjupet stations revealed an increase of mercury and lead in upper sediment layers, indicating pollution by long-range transport (Jensen et al., 2009). The opposite trend observed for these samples in case of PAH suggests a contribution from a local natural source for these compounds. For perylene this trend may be due to formation as a result of diagenetic processes (Wakeham et al., 1980; Yunker and Macdonald, 2003). However, the similarity of nearly all the profiles at open-sea stations for alkylated PAH as well as parent compounds, and the apparent increase in the levels of two- and three-ring alkylated PAH in the depth, similar to or exceeding that of perylene, suggests a natural petroleum source (similarly observed by Yunker and Macdonald, 2003). Presence of local petroleum sources should be of little surprise in the whole region of South-Western Barents Sea; the Goliat oil field is placed just a few kilometres from the investigated area. In the case of Ingøydjupet, such a natural source may be associated with the presence of pockmarks (MAREANO, 2008; Chand et al., 2009). Levels of alkylated PAH are indeed somewhat higher in this area than in the other studied areas, and dominate over their parent compounds at most of the open-sea stations, in contrast to fjord stations. A likely mechanism is a seepage of petroleum hydrocarbons to the surface sediments from deeper strata, e.g. a petroleum reservoir or from hydrocoarbon source rocks. Perylene levels increasing in the depth together with those of alkylated PAH (at open-sea locations but not at fjord locations) may then be hypothetically explained by increased microbial activity due to hydrocarbon fluids (Silliman et al., 2001; Hovland and Judd, 1988).

The heavier PAH (4-6-ring) are found in highest concentrations in the samples from fjord areas. Moreover, there is an apparent increase in concentrations (up to nearly 10 times when normalized to TOC, see PyrPAH profiles in Fig. 3) towards recent times (continuing until approximately 1940-s in the dated core from station 85). The concentrations then level off and, from approximately 1980-s decrease slightly in surface sediments. No such increase is observed at Ingøydjupet stations, while at Tromsøflaket there seems to be a modest increase, only occurring in the most recent sediments.

The pyrogenic origin of these inputs has been confirmed using PHE/ANT ratio, which is below 10 in surface sediments from all the fjord locations (Table 3). The ratios increase in deeper

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sediments, implying weaker pyrogenic inputs. Sediment cores from open sea locations have no samples with PHE/ANT below 10, except for a single surface sediment sample from station 102 at Tromsøflaket. This suggests that pyrogenic PAHs contribute less to the sediments at the open sea stations at Tromsøflaket and Ingødydjupet.

The increase in pyrogenic inputs with time at fjord locations may be attributed to either a natural source like forest fires, or from various anthropogenic sources. Both types of sources are of low importance in this area, and, despite the increase, the PAH levels are still low.

Distinguishing between different combustion sources is difficult. One method is to study PAH fingerprints, which may differ depending on the source and conditions of PAH formation (Pozzoli et al., 2004; Uhler et al., 2005). The profile observed in the fjord samples (Fig. 5) seems to be different from those reported for forest fires (Khalili et al., 1995; Masclet et al., 1995; Olivella et al., 2006), with benzofluoranthenes, indeno[1,2,3-*cd*]pyrene and benzo[*ghi*]perylene dominating strongly all 4 samples. The latter two compounds have been shown to predominate in Paris air samples enriched with vehicle exhaust (Masclet et al., 1995).

Various PAH ratios have been proposed to differentiate between combustion sources, but do not always provide a definitive answer (Maher and Aislabie, 1992; Yunker et al., 2002). PHE/ANT values between 5.8 and 6.1 for the fjord samples (Table 3) were far from the value of 3.0 proposed for forest fires (Gschwend and Hites, 1981). Benzo[*a*]pyrene to benzo[*ghi*]perylene ratio (denoted as BAP/BGP) did not exceed 0.3 at the fjord stations. Such values have been attributed to vehicles and gasoline exhaust (Simcik et al., 1999).

Most probable sources of PAH in fjord sediments may thus be traffic exhaust (soot) and other human activities in the towns of Hammerfest and Alta nearby (see Fig. 1), as well as the shipping traffic in this area. The suggestion of anthropogenic sources is further strengthened by the slight decrease in pyrogenic PAH in the upper few centimetres in all the fjord samples (see Fig. 3). This has been previously observed and linked to a reduction in coal burning in the last decades (Gschwend and Hites 1981). An earlier study of sediments in the proximity of 4 Norwegian harbours in the Barents Sea revealed elevated levels of pyrogenic PAH from anthropogenic sources, such as soot and others (AMAP, 2009).

Principal component analysis (PCA) was carried out to check the similarity of samples based on their composition. The loading plot (Fig. 6a) reveals a separation between fjord areas and the open sea, with sampling station 102 not belonging to either of the two groups, possibly indicating

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a local contamination of surface sediments, as is also shown in Table 3 and Fig. 4. The main objects explaining the separation of the fjord stations from the rest are pyrogenic PAH (Fig. 6b), while open-sea stations are clearly defined by perylene and petrogenic alkylated PAH.

Thus, we could not find any difference in chemical composition of the samples from inside the pockmarks (station 136) compared to the samples from outside All samples from the pockmark part of Ingøydjupet showed similar chemical profile. At station 136, there has likely been a disturbance of the sediments. This is concluded due to abnormalities in the determined sedimentation rate and the disagreement between ^{210}Pb-dating and ^{137}Cs-dating, and because there was observed a turning point in PAH/TOC ratios at about 12 cm depth for the core. This disturbance may be caused by bottom trawling, as numerous traces from trawl gear were observed on the seabed in 90% of the investigated open-sea areas, averaging 42 traces per studied kilometre of seabed, i.e. one trace every 25 m (Buhl-Mortensen et al., 2009). In some places the density of traces of bottom trawling was as high as one trace every 10 m (*ibid.*) However, the disturbance may also be due to a natural process, e.g. sliding of sediments, or pockmark-forming seepages of hydrocarbons or other fluids from deeper formations. A reduction or complete stop of this process in the past might then lead to the observed compositional similarity of the sediments from inside the pockmark to those from other locations at the surface.

Conclusions

Generally low hydrocarbon levels in surface sediments were observed at all the studied locations. There is a difference in composition and depth profiles between fjord areas and open-sea areas, suggesting different sources of PAH. A combination of long-range transport and local natural petrogenic and biogenic inputs may explain the background levels at the surface and increased levels in deep sediments observed in the samples from open sea areas, i.e. Tromsøflaket and Ingøydjupet. Pyrogenic inputs due to local inputs are apparent in the samples from fjord areas, with indications of anthropogenic influence increasing over time in these regions. Indications of a physical disturbance of sediments in one core from the “pockmark area” in Ingøydjupet may be caused by human activity like bottom trawling, or due to natural processes such as sliding of sediments or pockmark-forming seepages of hydrocarbons or other fluids from deeper formations. Thus, although low levels of PAH in the studied part of the Arctic were detected, it was still possible to link the PAH fingerprints in sediments at the different locations to specific natural and anthropogenic sources.

Acknowledgements

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Table 1. PAH levels in sediment samples from the studied locations.

Sampling station / Location	Sum PAH*, ng g^{-1} d.w.	
	0-1 cm	14-15 cm
1. Fjord areas		
85	250	310
115	209	68.3
119	326	363
128	272	226
2. Tromsøflaket		
96	97.2	143
102	224	42.1
105	58.8	63.8
127	82.8	20.0
3. Ingøydjupet		
109	211	146
112	157	156
136	208	174
153	209	195
154	217	161
Min	58.8	20.0
Max	326	363
Mean	194	159
SD	76.7	101

* PAH levels are given as a sum of concentrations of all studied compounds, including 22 compounds quantified separately and 8 groups of alkylated PAH quantified by cluster of peaks in the chromatogram. Table 2 gives the detailed list of compounds analysed.

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Table 2. Concentrations of selected PAH compounds at 13 sampling locations in surface and deep sediments, ng g^{-1} dry weight. Limits of quantification were 0.5 ng g^{-1} dry weight for each individual compound.

Compound	Surface sediments (0-1 cm)				Deep sediments (14-15 cm)			
	Mean	Min	Max	SD	Mean	Min	Max	SD
Naphthalene	1.59	0.74	2.45	0.55	1.32	0.68	2.46	0.56
2-methylnaphthalene	3.37	1.39	5.51	1.42	2.94	1.09	5.75	1.57
1-methylnaphthalene	2.52	1.10	4.26	1.11	2.09	0.58	4.57	1.36
C2-naphthalenes	14.0	6.66	21.2	4.77	10.5	2.33	21.3	6.18
C3-naphthalenes	12.4	4.26	20.5	5.43	10.6	1.81	20.3	6.36
Acenaphtylene	<0.5	<0.5	<0.5	-	<0.5	<0.5	<0.5	-
Acenaphthene	<0.5	<0.5	<0.5	-	<0.5	<0.5	<0.5	-
Fluorene	1.07	<0.5	1.62	0.40	0.72	<0.5	1.46	0.36
Anthracene	0.53	<0.5	1.37	0.37	<0.5	<0.5	0.96	0.29
Phenanthrene	6.38	2.32	11.5	2.57	4.95	2.08	7.68	1.88
C1-phenanthrenes	8.58	3.06	12.7	3.43	8.25	1.99	19.5	4.95
C2-phenanthrenes	6.71	2.15	10.1	2.47	7.34	1.16	30.7	7.49
C3-phenanthrenes	6.91	2.12	10.8	2.70	7.37	0.84	31.4	7.76
Dibenzothiophene	<0.5	<0.5	0.76	0.21	<0.5	<0.5	0.53	0.16
C1-dibenzothiophenes	0.89	<0.5	1.50	0.39	0.83	<0.5	2.21	0.55
C2-dibenzothiophenes	1.67	<0.5	3.09	0.73	1.86	<0.5	8.09	1.98
C3-dibenzothiophenes	1.61	<0.5	3.62	0.84	1.65	<0.5	7.56	1.87
Fluoranthene	5.94	1.45	11.7	3.65	4.84	<0.5	16.5	5.07
Pyrene	4.09	1.19	8.15	1.91	3.42	0.54	7.76	2.06
Benz[*a*]anthracene	3.37	0.77	6.75	2.02	2.15	<0.5	6.12	1.87
Chrysene	6.05	1.75	10.3	2.65	2.73	<0.5	7.35	2.09
Benzo[*b,j,k*]fluoranthenes	37.5	10.5	76.7	19.9	29.1	1.6	105	32.8
Benzo[*e*]pyrene	10.8	2.88	20.8	5.39	10.5	1.01	33.4	9.43
Benzo[*a*]pyrene	3.69	0.99	7.41	1.99	2.43	<0.5	6.46	1.95
Perylene	10.7	3.83	19.8	5.74	11.4	1.09	32.8	8.52
Indeno[*1,2,3-cd*]pyrene	24.9	6.00	62.3	17.8	20.4	<0.5	73.0	26.2

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Dibenz[*a,h*]anthracene	3.12	0.69	7.81	2.05	2.72	<0.5	8.45	2.87
Benzo[*g,h,i*]perylene	14.9	3.24	36.1	10.2	13.4	0.64	43.4	13.6
Sum PAH	194	58.8	326	76.7	164	20.0	363	102
THC, μg g^{-1}	6.68	2.70	14.8	4.03	194	58.8	326	76.7

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Table 3. Phenanthrene/anthracene (PHE/ANT) and benzo[*a*]pyrene/benzo[*ghi*]perylene (BAP/BGP) ratios at the studied locations.

Station	BAP/BGP				PHE/ANT			
	Surface sediment (0-1 cm)	Whole core			Surface sediment (0-1 cm)	Whole core		
		min	max	mean		min	max	mean
1. Fjord areas								
85	0.2	0.1	0.2	0.2	8.8	6.1	9.7	7.2
115	0.3	0.1	0.3	0.2	7.1	5.9	15.1	9.0
119	0.2	0.1	0.2	0.2	8.5	6.0	8.5	7.2
128	0.3	0.1	0.3	0.2	14.4	5.8	15.6	9.2
2. Tromsøflaket								
96	0.3	0.2	0.4	0.3	21.4	15.5	26.3	19.2
102	0.5	0.2	0.5	0.3	8.4	8.4	50.0	29.4
105	0.3	0.1	0.4	0.3	20.0	14.6	25.4	19.2
127	0.2	0.2	0.3	0.2	8.2	12.5	30.5	19.8
3. Ingøydjupet								
109	0.3	0.2	0.3	0.3	19.5	12.4	32.7	24.7
112	0.3	0.2	0.4	0.3	11.2	10.4	14.2	12.2
136	0.2	0.2	0.5	0.3	20.8	7.1	20.8	15.3
153	0.3	0.1	0.3	0.2	21.9	16.9	41.5	26.5
154	0.2	0.2	0.9	0.3	29.0	18.9	47.9	32.4

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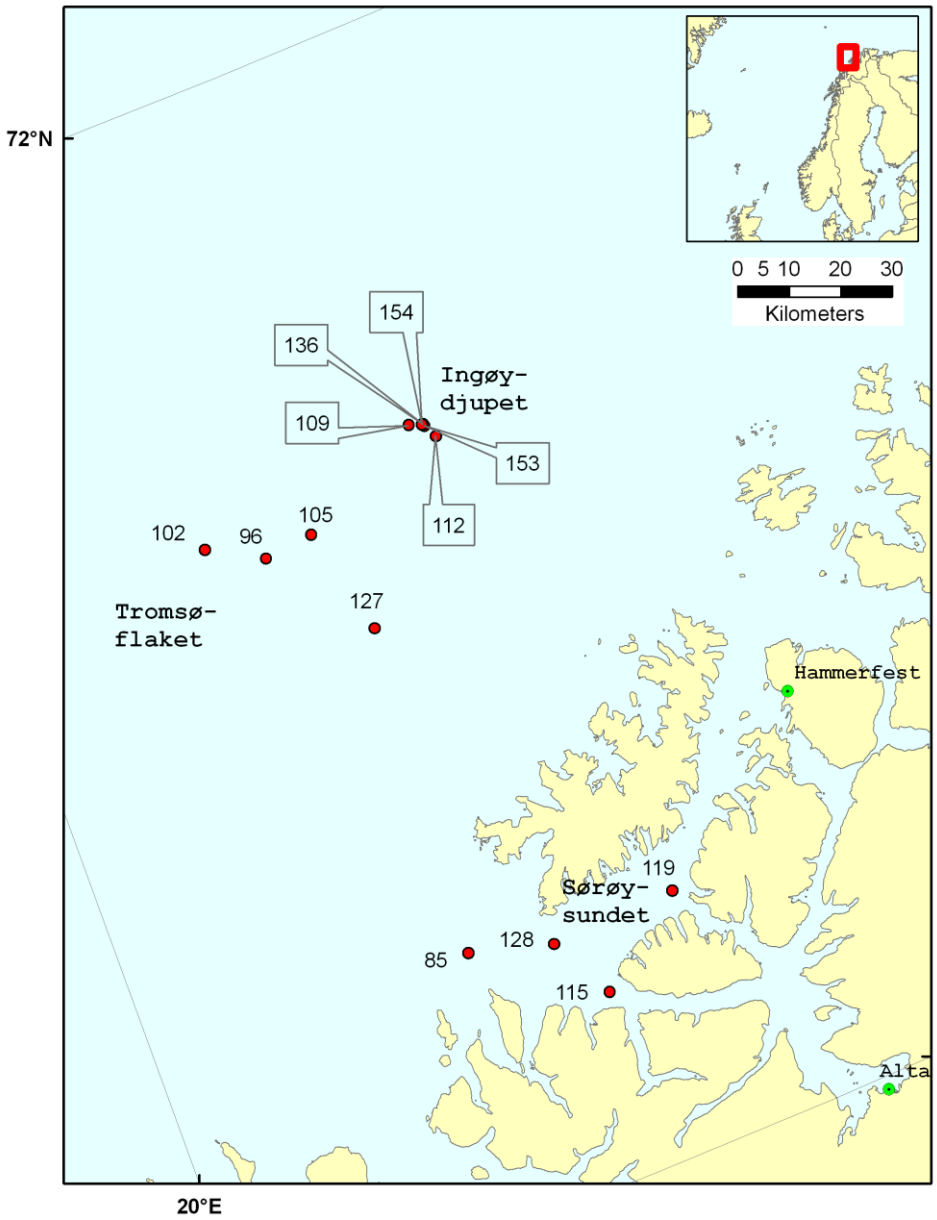

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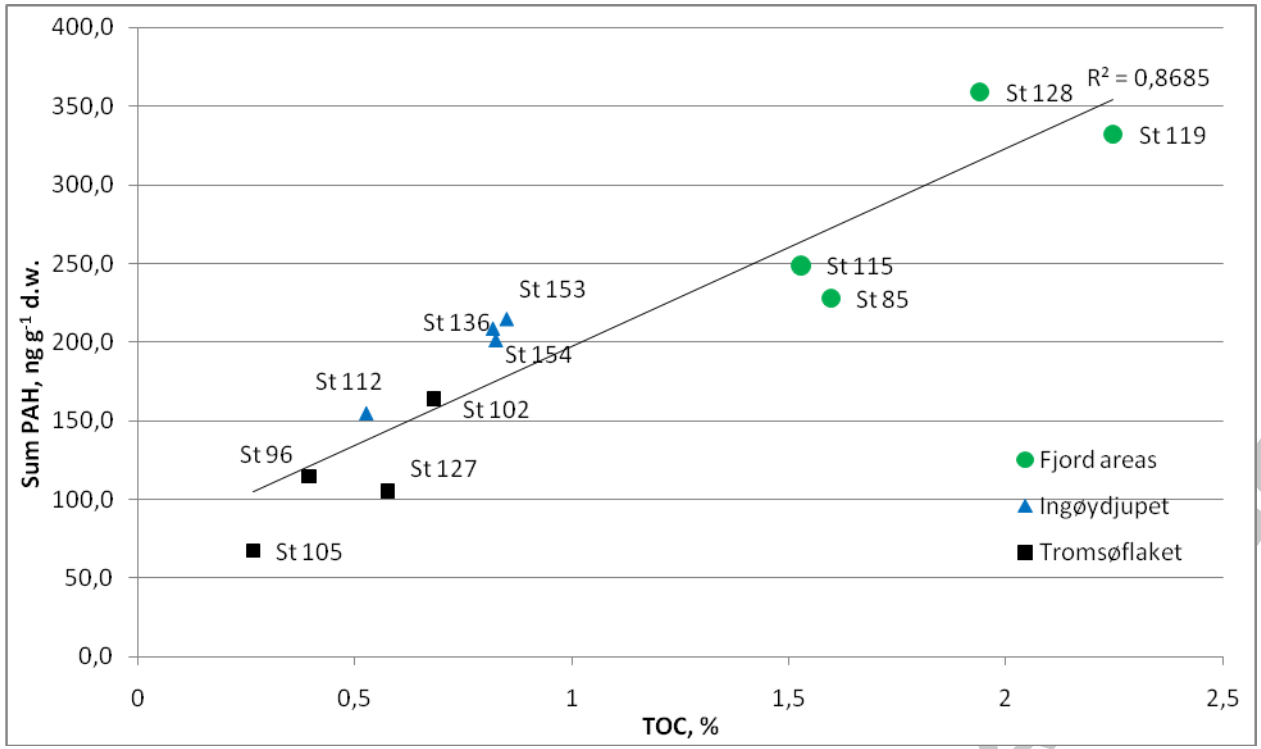

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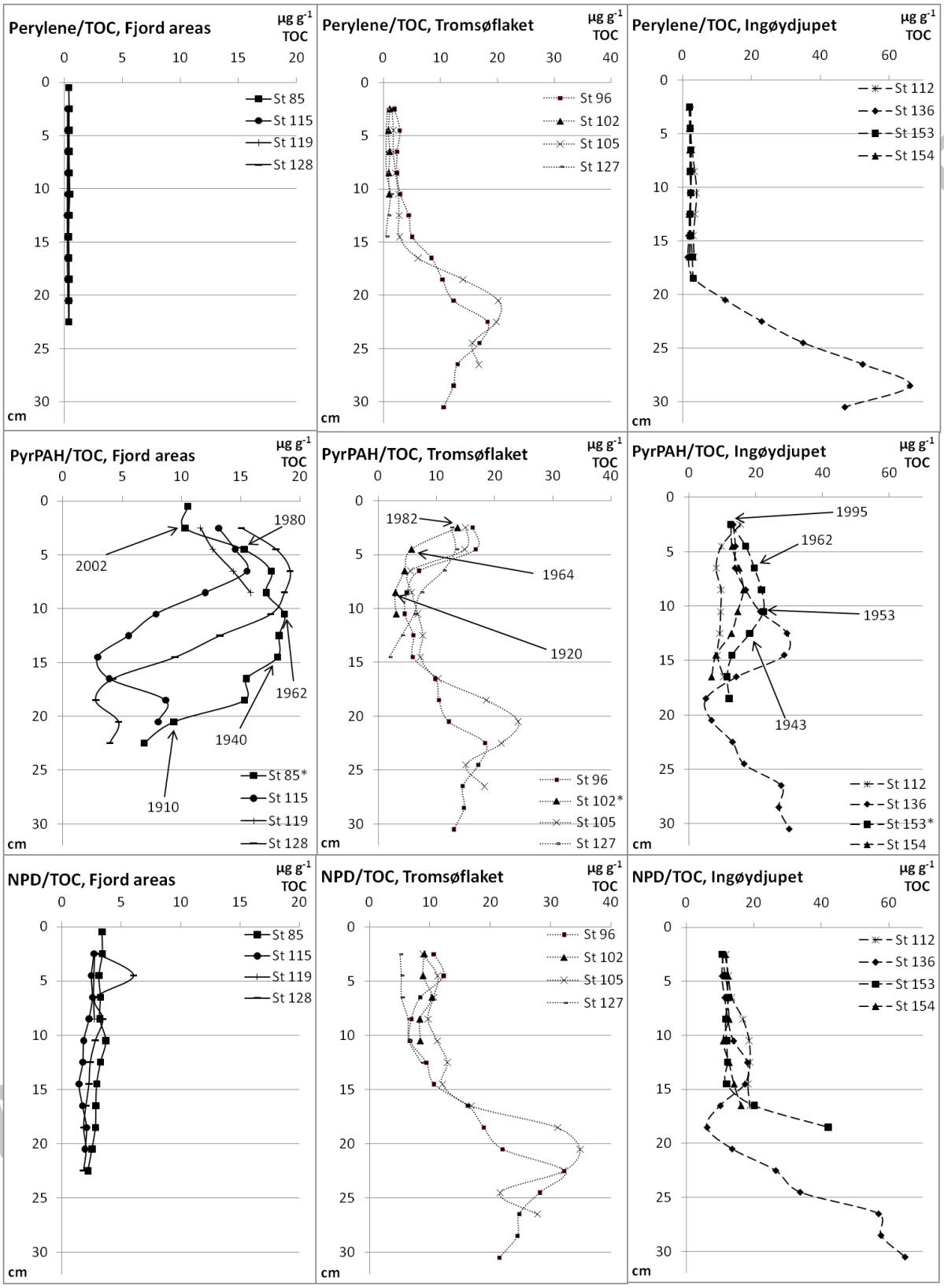

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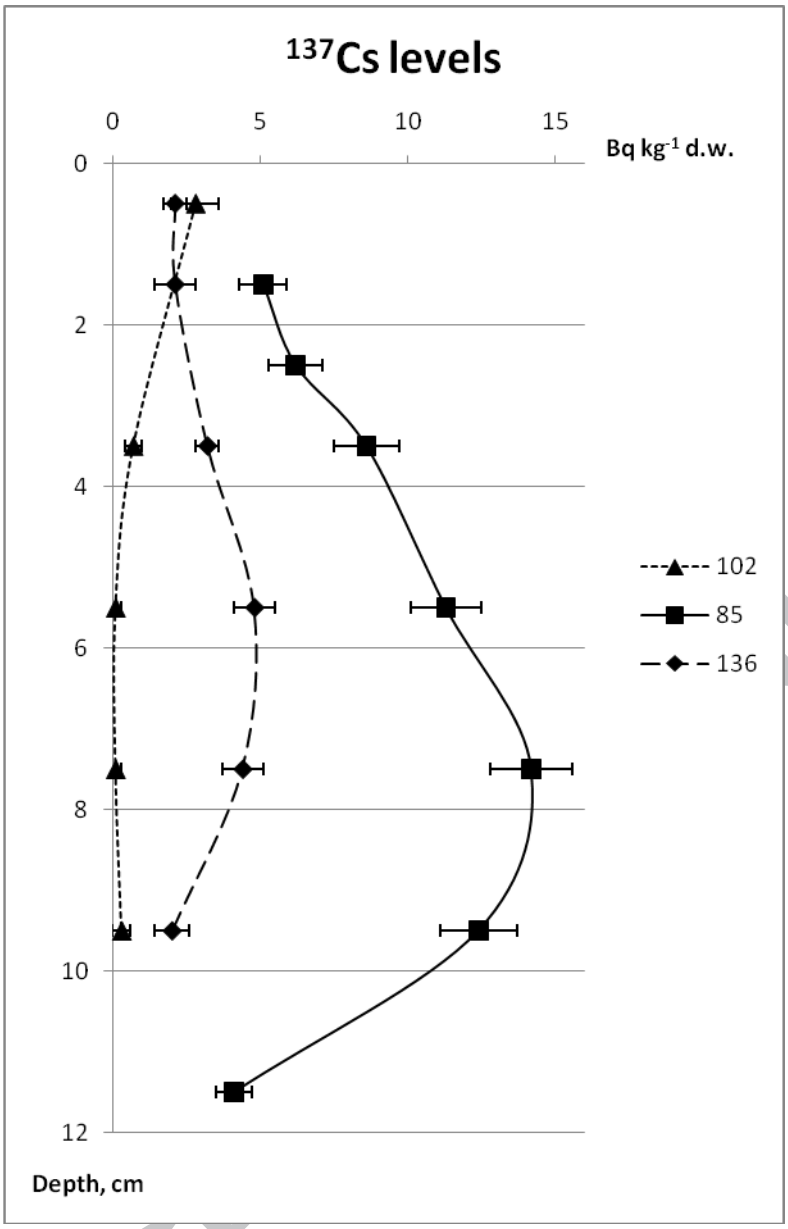

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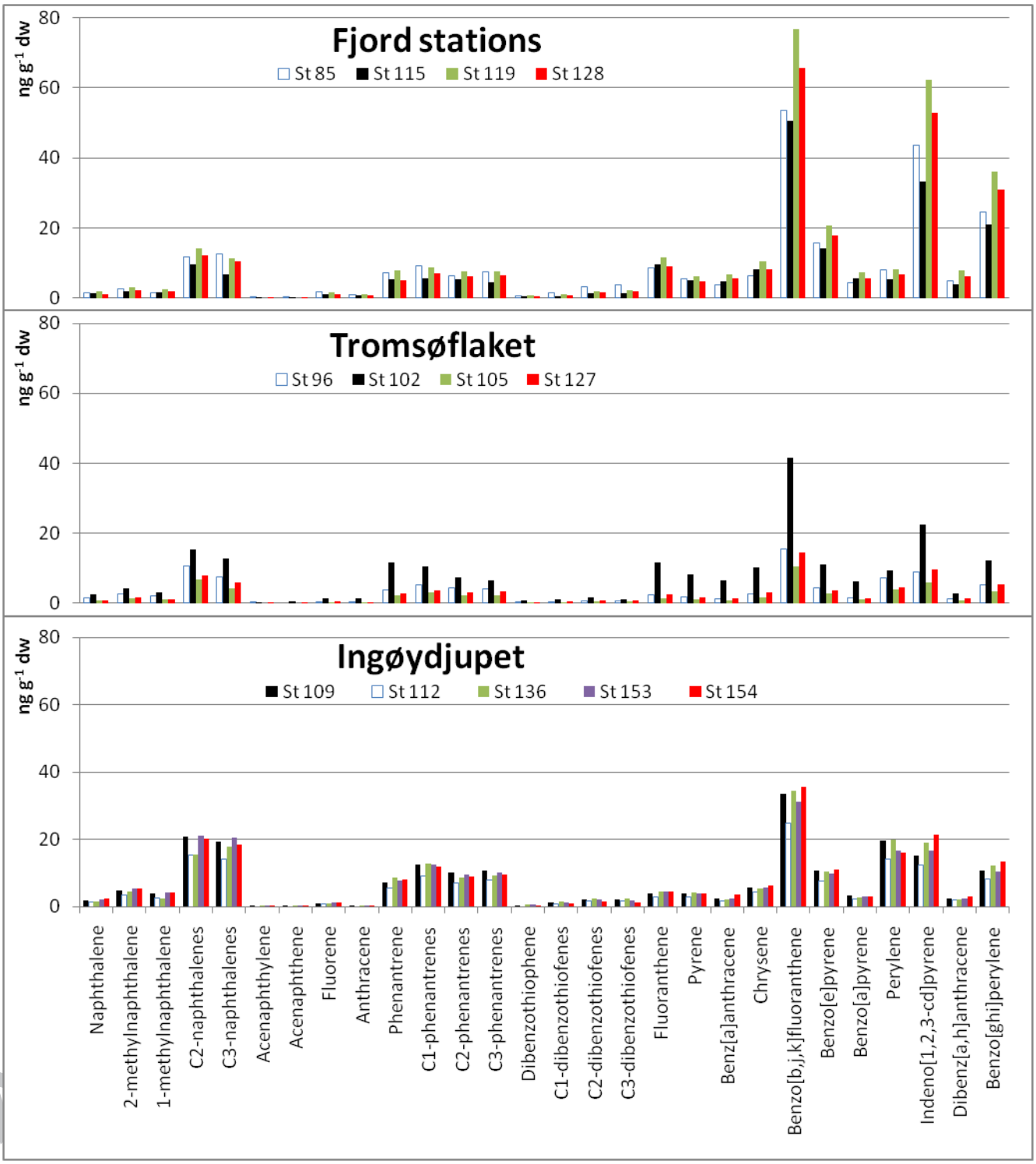

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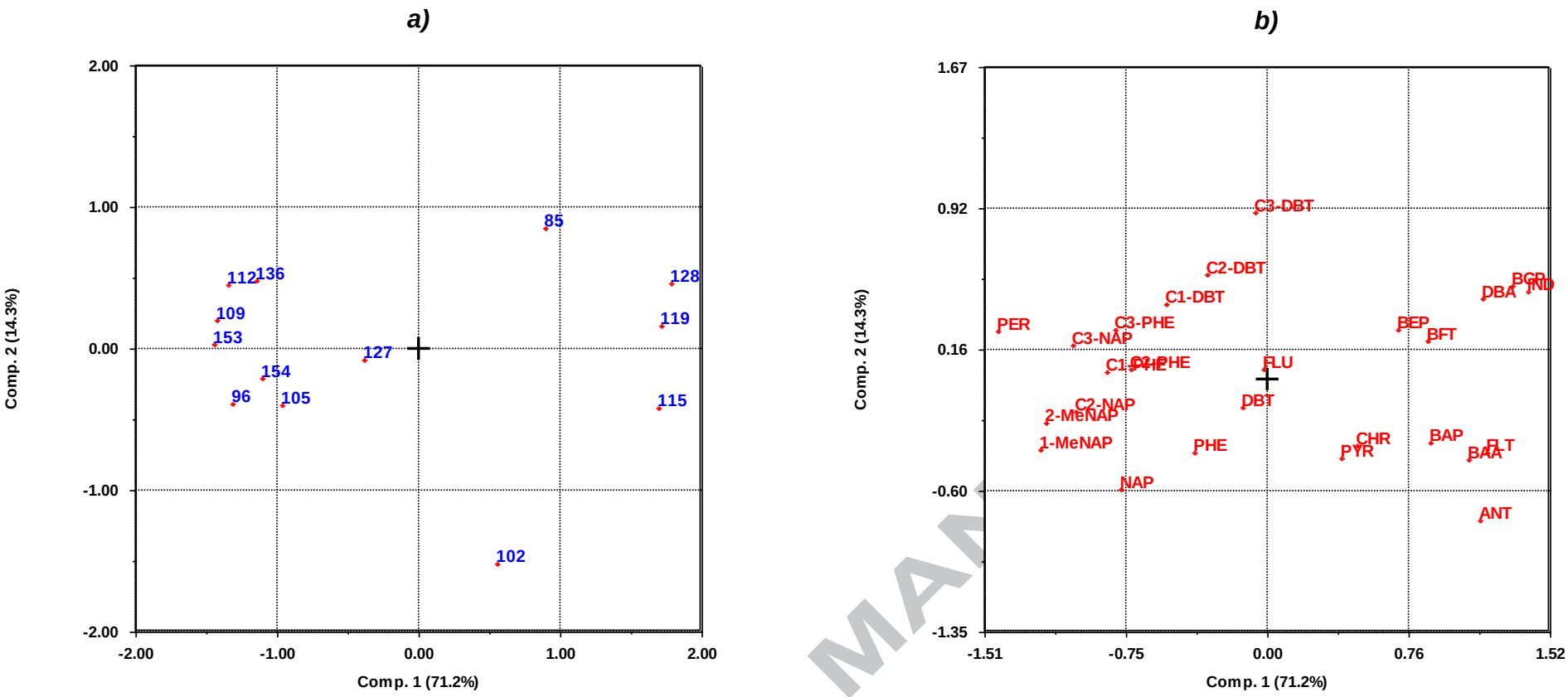

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