

Polyaromatic hydrocarbons (PAHs) in the Barents Sea sediment: Small changes over the recent 10 years

S. Dahle¹, V. Savinov¹, J. Klungsøyr², Stepan Boitsov², N. Plotitsyna³, A. Zhilin³, T. Savinova¹ and V. Petrova⁴

¹*Akvaplan-niva, Polar Environmental Centre, N-9296, Tromsø, Norway*

²*Institute of Marine Research (IMR), Bergen, Norway;*

³*Polar Research Institute of Marine Fisheries and Oceanography (PINRO), Murmansk, Russia*

⁴*All-Russia Research Institute for Geology and Mineral Resources of the World Ocean, 1, Angliysky Av., St. Petersburg, 190121, Russia.*

Extended abstract

(Full article included in special issue of Marine Biology Research (vol. 4, 2008), celebrating the 50 years of Norwegian-Russian research cooperation)

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are common environmental contaminants which can be derived from technogenic and natural processes including leakage and erosion of fossil carbon, as well as epigenetic processes such as decaying peat. Occurrence of PAHs in environment is a concern due to their toxicity and carcinogenic effects of certain PAH components.

Studies of PAHs in Barents Sea sediments during the years 1992-1998 demonstrate a wide geographical range of total PAH concentrations as well as strong regional differences (Dahle et al., 2006). Over the recent 10 years, off shore production of oil and gas on the Norwegian shelf has more than doubled, and the transport of oil from Russia through the Barents Sea has increased from zero to 12 million tons per year (2005). Our objectives were to (1) assess whether increased oil and gas activities in the Barents and adjacent seas are observed in increased concentrations or changes in composition of PAHs in Barents Sea sediments and (2) compare PAH levels and composition in Barents Sea sediments from different regions over the recent 10 years in order to reveal possible multi-year variability in the environmental levels of PAHs. The study was initiated by the Arctic Monitoring and Assessment Programme (AMAP) and supported by the Norwegian Council of Ministers.

Material and methods

Surface sediment samples were collected in the Barents Seas during the years 2001-2005 by Akvaplan-niva (Tromsø, Norway), Institute of Marine Research (IMR, Bergen, Norway) and Polar Research Institute of Marine Fisheries and Oceanography (PINRO, Murmansk, Russia). Sediment samples were retrieved using both a 0.1 m² van Veen grab and a gravity corer with a plastic liner.

The chemical analyses were performed at Unilab Analyse AS (Tromsø, Norway), IMR, and PINRO analytical laboratories. The laboratories are accredited for hydrocarbon analyses according to the European standards and have participated successfully in the Quality

Assurance Laboratory Performance Studies for Environmental Measurements in Marine Samples (QUASIMEME).

Following PAH compounds were measured: naphthalenes, phenanthrene/anthracenes dibenzothiophenes, acenaphthylene, acenaphthene, fluorene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b+k]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, perylene, benzo[ghi]perylene, indeno[1,2,3-cd]pyrene and dibenzo[a,h,]anthracene.

The hypothesis of normal distribution was tested using Shapiro-Wilk's W Test. This hypothesis was not rejected for log-transformed data. Cluster analysis (k-means clustering) was used to group the sampling stations by log-transformed PAH compounds in the sediment samples. Standard T-test was used to estimate significant differences ($P < 0.05$) between the geometric means calculated for the two compared periods.

Results and discussions

In the 2000s, total PAH concentration (Σ PAH) in bottom sediments of the Barents Sea varied from 27 up to 6026 ng/g d.w. The highest PAH levels were found in north-western part of the Barents Sea. The PAH levels generally decreased towards south and east. PAH composition and sources of PAHs varied in the different regions.

K-means-clustering of the 2001-2005 datasets groups the hundred sampling stations into five distinct geographical areas based upon levels and compositions of PAHs. The five areas are Svalbard offshore, Bear Island Trough, SW Barents Sea, NE Barents Sea and SE Barents Sea. The highest PAH levels were found in sediments from Svalbard offshore area. The fine-grained fraction of the sediments was dominating; pelites made up 80% on average. Total PAHs concentrations (Σ PAH=sum of 27 PAH analytes) in sediments from this area varied from 2698 ng/g to 6026 ng/g d.w, with a geometric mean 4383 ng/g d.w. Alkyl-substituted homologues of naphthalene and phenanthrene prevailed in the PAH composition. High values of Fossil Fuel Pollution Index (FFPI) (54-79%) suggest a predominance of petrogenic PAHs. Comparative analysis of PAH patterns in bottom sediments from Svalbard offshore area and in Spitsbergen's coal samples show compositional similarities (Dahle et al., 2006). This suggests natural erosion and weathering of coal-bearing formations on Svalbard archipelago to be a main source of PAHs in sediments from this area.

The Bear Island Trough is 400-500 m deep and dominated by Atlantic water. Total sediment PAH concentrations ranged from 893 ng/g to 2206 ng/g dw. Sediments from Svalbard offshore and Bear Island Trough areas exhibit similar PAH patterns, with a predominance of two- three-ring PAH compounds. However, the two areas differ in their relative content of pyrogenic PAHs (Σ PyrPAH = sum of four- to six-ring PAHs perylene excluded).

In addition, we observe higher PAH ratios ($ANT/178 = \text{anthracene}/(\text{anthracene} + \text{phenanthrene})$, and $IND/276 = \text{indeno}[1,2,3\text{-cd}]\text{pyrene}/(\text{indeno}[1,2,3\text{-cd}]\text{pyrene} + \text{benzo}[\text{ghi}]\text{perylene})$) for Bear Island Trough compared to Svalbard offshore area indicating a relatively high content of combustion PAHs. This may be due to stronger inflows of Atlantic water.

NE Barents Sea includes the eastern part of the Great Bank and Central Trench areas. Total PAH concentrations ranged from 406 to 1136 ng/g dw. Perylene and benzofluoranthenes were the most abundant PAH compounds. Geometric mean PAH concentration was similar to those

measured during the 1990s. The limited temporal variability in PAH concentrations in this area was supported by our data on down core PAH distribution.

The range of Σ PAH concentrations found in sediments from SE Barents Sea was 137-860 ng/g d.w with a prevalence of pyrogenic PAHs. Benzofluoranthenes and indeno[1,2,3-cd]perylene were the most abundant. Mean Σ PAH and Σ PyrPAH concentrations found in the 2000s and 1990s did not differ significantly. However, the levels of Σ NPD (sum of naphthalene, phenanthrene, dibenzothiophene and their alkylated homologues) and FFPI in samples from 2000s were significantly higher than in the 1990s. At the same time, the ANT/178 ratio found in the 2000s was significantly lower than in the 1990s, and at a level which indicates a dominance of petroleum sources (Yunker et al., 2002)

In SE Barents Sea, the range of total PAH concentrations was 137-860 ng/g d.w. Pyrogenic compounds dominated in the PAH composition; indeno[1,2,3-cd]pyrene, benzofluoranthenes and benzo[ghi]perylene are the most abundant compounds. Concentrations of Σ PyrPAH and Σ NPD from this area in the 2000s were significantly higher than in the 1990s. However, in contrast to the SW Barents Sea area, an increase of Σ NPD was not accompanied by an increase of FFPI, but by a significant increase of FLT/202 (fluoranthene/fluoranthene+pyrene) and IND/276 ratios. It is suggested that the increase of PAH concentrations in SEBS sediments reflects higher input of combustion or/and anthropogenic PAHs.

References

- Dahle S, Savinov V, Petrova V, Klungsøyr J, Savinova T, Batova G, Kursheva A. 2006. Polycyclic aromatic hydrocarbons (PAHs) in Norwegian and Russian Arctic marine sediments: concentrations, geographical distribution and sources. *Norwegian Journal of Geology*, 86:41-50.
- Yunker MB, Macdonald RW, Vingarzan R, Mitchell RH, Goyette D, Sylvestre S. 2002. PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Organic Geochemistry* 33: 489-515.