HYDROCARBON MONITORING IN COASTAL SEDIMENTS AND SOILS AROUND THE CITY OF TROMSØ: COMPLEX MOLECULAR GEOCHEMICAL APPROACH

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Coastal sediments are rich in polycyclic aromatic hydrocarbons (PAHs), some of which occur naturally and others that are produced by human activity (e.g. combustion). Any assessment of pollution, however, must consider the various sources and transformation pathways of PAHs. In this study we used the data collected in and around the city of Tromsø (Norway) from the shallow water – land transects during the scientific-research expedition in July, 2018 (RFBR № 18-54-20001, 2018 – 2020; NFR #280724, 2018 – 2020). The main task of the study was to evaluate PAH distribution and sources along environmental gradients (sublittoral – littoral – supralittoral) sampled in the presumably polluted (sites 1, 2) and clean (sites 3, 4) areas around the city using high-precision geochemical analysis (Fig. 1a). The complex approach includes anomalies identification in ‘indicator’ PAHs (EPA 2010) and the basic diagnostic parameters of biomarkers, and their use for the assessment of the vulnerability of biological objects of the environment.

The preliminary study of the group composition of aromatic HCs in the lipid fraction of soil and sedimentary OM was conducted using the method of spectrofluorimetry on «Panorama-02» (Lumex). Significant variations in spectral characteristics of aromatic HCs were identified. The first spectral type with the maximum at 380 nm, that is usually associated with PAHs in the fuel polluted areas, were detected in samples collected near the oil loading terminal (site 1) and in the City center (site 2). The significant increase of the aromatic HCs in the surface sediments of these sites may testify to the input of fresh unoxidized petroleum products (e.g. spent fuels, engine oils etc.). The study of the conditionally unpolluted sites of the Kvaløysletta (site 3) and SW Tromsø beach (site 4), that were expected to have background characteristics of HCs distribution, has shown fluorescence spectra maximum at 280 nm, the second order peak testify to the three- and pentacyclic aromatic HCs input likely associated with both natural and anthropogenic sources. The total content of aromatic HCs here is an order of magnitude lower than in the conditionally polluted areas and is comparable with the recently detected background values of the Barents Sea region.

Analytical procedure included determination of TOC and CaCO₃ and Soxhlet extraction of the dissolved part of dispersed OM with CHCl₃, its chromatographic separation, fractionation and molecular analysis of HCs using GC–MS system Agilent 5973/6850. The average TOC content in samples reaches the upper level of the regional background values of ca. 0.3–2.0% with one exception for the turf sample (4 – supralittoral surface, TOC is up to 4.8%). Distribution of n-C₁₃–C₃₅ alkanes exhibits no uniformity among the studied sites. The maxima of even LMW n-alkanes are detected in both clean and polluted samples (Fig. 1b), but the value of OEP₁₇₋₁₉ is close to 1 only in surface samples of the sites 1 and 2. The content of HMW homologues is high in all samples except those from the City center confirming the lack of vascular plant input to these sediments. Diagenetic hopanes comprise more than 50% of total hopane content in samples from the 1 and 2 sites (C₃₁Si/(S+R) and Ts/(Ts+Tm) ca. 0.5) and a significant input of immature biohopanes is detected in all samples from the 3 and 4 sites (T₁₀/(T₅+T₁₀+T₁₀) ca. 0.7) indicating the input of relatively fresh microbial OM.
Steranes are also present in all samples as a complex mixture ranging from C_{27} to C_{29} for cholestanes and C_{27} to C_{28} for dia- and methyldiacholestanes. The perceptible content of olean-12-ene is detected in sediments of all “clean” sites indicating direct vascular plant input. The cross-plot (Fig. 1e) reflects the difference in thermal maturity of samples according to the steranes isomer ratios. The most dramatic value observed for the sites 1 and 2 is comparable with values that are usually characteristic for oils.

**Figure 1** Schematic map showing location of the studied sites (a); Values of the ratio of LMW to HMW n-alkanes with maximum peaks signed on top (b); Distribution of PAHs of different genesis along the water-land transects of the each site (c); Cross-plots for the genetic (d) and thermal maturity (e) ratios of PAHs and steranes respectively.

Distribution of the main genetic groups of PAH also does not show uniformity in the region (Fig. 1c). Biogenic PAHs (cadalene, retene, tetrahydrocrystene and perylene) are the minor components in all the studied samples, but the input of petrogenic and pyrogenic compounds varies significantly. The highest content of alkylated naphthalene, phenanthrene (Pn), alkyl-Pn and dibenzothiophene is detected in samples of the sites 3 and 4 attesting to the input of diagenetic OM associated with the mineral matrix (MPI ca. 0.3; Pn/(Pn+Alk-Pn) ca. 0.6). The significant increase of the most hazardous compounds, such as benzo[b/j/k]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene (IP) and benzo[ghi]perylene (BgP) in samples of the sites 1, 2 and 4 (turf sample near the road) reflects an additional input of liquid and solid fuel combustion products to the sediments and soils (Fig.1c, d).

Thus, the detailed study of the molecular markers and biomarkers distribution in bottom sediments and soils of the Tromsø coastal zone revealed the significant level of human impact on the environment of the region that requires further attention, study and observation.