

Book of Abstracts

Seventh International Conference of
the CIS IHSS on humic innovative technologies
"Humic substances
and technologies for resilience"
(HIT-2022)

November 18–21, 2022

Sailing Club "Vodnik", Moscow Region, Russia

Non-Commercial Partnership "Center for Biogenic Resources
"Humus Sapiens"" (NP CBR "Humus Sapiens")

<http://www.humus.ru/hit-2022>



Department of Chemistry,
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Molecular signatures of methane seeps unfold in the composition of dissolved organic matter of the Laptev and East-Siberian Seas

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Keywords: dissolved organic matter, methane, molecular composition

<https://doi.org/10.36291/HIT.2022.076>

The Arctic Shelf is a great unique geographical region, including diverse areas with considerable influences of mighty river mainstreams, permafrost and ice wedges. Global warming has caused substantial contribution of a large pool of dissolved organic matter (DOM) and abyssal methane CH₄ from the permafrost thawing into the Arctic Ocean [1]. As a result, surface waters can be systematically oversaturated with CH₄ due to vertical and lateral transport from bottom and littoral sediments.

DOM is a major pool of reduced organic carbon, characterized by varied origin and unique molecular composition within aquatic systems [2]. Determining the chemical constituents of DOM by the complex of analytical methods such as Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT ICR MS), Nuclear Magnetic Resonance (NMR) and Elemental Analysis (CHNS) is supposed to be the ultimate measure for probing the source material, transport and evolution of methane in the Arctic region. The goal of the work was to investigate methane fingerprint on the base of molecular study of DOM.

Solid-phase extraction (SPE) procedure was conducted aboard research vessel Ac. Mstislav Keldysh in October 2020. The SPE was performed for 20 marine water samples from the Laptev and East Siberian Sea. The release of high concentrations of methane was observed for the nine samples from the whole set. Marine water (20–30 L each) was filtrated through GF/F filters, acidified and discharged through Mega Bond Elut PPL cartridges (5 g, 60 mL tube). The cartridges were unloaded in the lab using methanol. Recovery of the cartridges ranged from 80 to 95% for the whole set of samples. The isolates were studied by FT ICR MS (15 T Solarix mass spectrometer located at the Zelinsky Institute of Organic Chemistry of RAS), NMR spectroscopy and elemental analysis. The principal component analysis (PCA) was performed for the sample set on the base of the obtained FT ICR MS and NMR data. The molecular structures of organic matter isolates under methane conditions revealed an abundance of nitrogen, the aliphatic structures and low content of oxygen, whereas the molecular signature of the samples without methane impact were characterized as more saturated with oxygen and aromatic structures.

Acknowledgements. This research was financially supported by the Russian Science Foundation grant no 21-77-30001 (experiment on DOM isolation) and 21-73-20202 (FT ICR MS measurements). Center of Collective Use of Zelinsky Institute is appreciated. This research was conducted in the framework of the scientific educational school of the Lomonosov Moscow State University "Future of the planet and global environmental change".

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