Features of bitumoids composition of bottom sediments of the coastal zone of the East Siberian Sea

Yu S Glyaznetsova, I N Zueva, O N Chalaya and S Kh Lifshits
Institute of Oil and Gas Problems, Yakutsk, Russia
E-mail: gchlab@ipng.ysn.ru

Abstract. An anthropogenic influence, in particular, oil contamination on the Arctic ecosystems is studied. For this composition of the chloroform bitumoids extracted from the samples of bottom sediments is explored. The samples were taken near seaport Kolyma River and a coastal zone of the East Siberian Sea. In bottom sediments of the seaport the yield of bitumoid reached 25500 mkg g\(^{-1}\). As appeared, their samples were oil contaminated. Hydrocarbons prevailed significantly over the sum of resinous components in their composition as aliphatic compounds dominated over oxygen groups in chemical structure. N-alkanes make up 28% of the sum of the identified hydrocarbons with a distribution maximum in the area nC\(_{15-16}\). CPI is typical for oil and oil products. The values of ratio of isoprenoids to n-alkanes and the distribution of isoprenoids point to processes of biodegradation of oil hydrocarbons. In the sea samples the yield of bitumoid much less 193-1577 mkg g\(^{-1}\) and oil contamination traces aren’t found. The future of chemical structure and distribution of individual saturated hydrocarbons reveals a strong relationship with terrigenous organic matter of recent deposits. The prevalence of odd hydrocarbons nC\(_{23}\)-nC\(_{35}\) and high concentrations nC\(_{27}\), nC\(_{29}\), nC\(_{31}\) is characteristic for lipids of highest land plants.

1. Introduction
The East Siberian Sea (ESS) is one of the least studied aquatorium of the Russian Federation. Kolyma River is the largest flowing into the ESS, the river flow of which is one of the determining factors of sedimentation in the coastal zone of the ESS [1-3]. Oil and oil products are the most dangerous sources of contamination and are an environmental danger to the Arctic nature environment [3-7]. Along the Kolyma River only in the territory of the Yakutia there are three large oil depots and the Green Cape sea port. As a result of spills during transportation and operation of oil depots there is a contamination of waters and coastal part of land. Oil contamination becomes a source of oil hydrocarbons flow through the river into the sea and its coastal part.

Data on the study of the feature of the geochemical background of hydrocarbons in sediments are given in a number of works performed by various researchers [3, 6, 8-13]. Mainly, the investigations connect with determining of the origin and mechanism of distribution of hydrocarbons in bottom sediments and estimation of level of contamination. In the analysis of the hydrocarbon content in bottom sediments there is a problem of differentiated assessment of the anthropogenic constituent and natural which is due to a natural geochemical background, because often geochemical anomalies associate only with oil hydrocarbons. However, it is known the spread of anthropogenic hydrocarbons occurs on a natural hydrocarbon background, that doesn’t ignore.
The purpose of researches was a determination of content and composition natural and technogenic hydrocarbons in the top layer of bottom sediments of the Green Cape seaport and in coastal zone ESS, on border of the Kolyma River – ESS.

2. Data and Methods
Material of a research were the samples of river superficial (0-5 cm) and bottom sediments of the Green Cape seaport 68°47.32N 161°22.13E and also sea sediments selected in the area 69º40.120N 162º20.38E.

The complex of analytical researches included extraction by chloroform with receiving chloroform bitumoid. For study chemical structure the selected bitumoids we applied IR Fourier spectroscopy (Protege 460 FTIR spectrometer, Nicolet) in the range of 500-4000 cm⁻¹, liquid chromatography and mass spectrometry (GC/MS). The liquid adsorption chromatography method was used to determine the group component composition of the extracts. The method consists in the initial deposition of asphaltenes with petroleum ether followed by the washing out of hydrocarbon fractions and resins with various organic solvents on a sorption column with silica gel [14]. GC/MS studies on the individual composition of saturated hydrocarbon fractions were carried out using a system that includes the Agilent 6890 gas chromatograph which has an interface with the highly efficient mass-selective detector Agilent 5973N. The chromatograph is equipped with a quartz capillary column (30 m long, 0.25 mm in diameter, impregnated with HP-5MS phase). The carrier gas is helium. The flow rate is 1 ml/min. The temperature of the evaporator is 320 °C. The temperature rise was programmed to range from 100 °C to 300 °C at a rate of 6 °C min⁻¹. The ionizing voltage of the source is 70 eV. In more detail techniques of researches are given in work [13, 15-19]. In comparison with the control, the obtained results are statistically reliable.

3. Results and Discussion
The conducted researches have shown that in sample R-1 of the sediments selected in the Kolyma River seaport, content of bitumoid reached 25500 mkg g⁻¹. As appeared, the sample with the maximum bitumoid content is oil contaminated. Hydrocarbons prevailed significantly over the sum of resinous components in their composition (table 1) as well as hydrocarbon groups (CH₂, CH₃) dominate over content of oxygen groups and bonds. The type IR spectrum is characteristic for oil contaminated samples that confirms the appearance of absorption bands of aromatic structures – 750, 810, 880 and 1600 cm⁻¹ (figure 1).

![Figure 1. IR-spectra of extracts of sediment samples: (a) R-1; (b) S-1.](image-url)
Presence of oil hydrocarbons shows features of composition and distribution of saturated hydrocarbons (figure 2). N-alkanes make up 28% of the sum of the identified hydrocarbons and are characterized by prevalence of relatively low-molecular n-alkanes ($\sum_{b.b.t.} nC_{20}/\sum nC_{21}$) with a distribution maximum in the area $nC_{15.16}$. The relation of the sum of even alkanes to odd (CPI) is typical for oil and oil products [20, 21]. High content of the isoprenoids prevailing over n-alkanes is detected (table 1). Pristane (Pr) and phytane (Ph) dominate in isoprenoids composition and prevail over a near eluated n-heptadecane ($nC_{17}$) and n-octadecane ($nC_{18}$). The latest is characteristic in distribution of the saturated hydrocarbons which underwent influence of processes of biodegradation. According to the received results, as well literate data, the biodegradation processes caused transformation oil hydrocarbons proceed in the Arctic conditions at low temperatures [22, 23].

Studying of the sea sediments samples S-1, S-2 and S-3 from a coastal zone ESS has shown that yield of bitumoid changes in abroad limits from traces to values 193 - 1577 mg g$^{-1}$ (table 1). The composition of their samples is close to sample R-2, which is characteristic for natural background of the river [24]. In group composition of bitumoids resines components dominate over hydrocarbons and asphaltenes. According literate data and own results a character of IR-spectra of bitumoids is typical for terrigenous organic matter of recent deposits. Compounds with long methylene chains dominate as bitumoids as their fraction (hydrocarbons, resins and asphaltene) in chemical structure (figure 1). As rule absorption of doublet band in the field of 720-730 cm$^{-1}$ prevails in spectra as absorption bands of aromatic rings practically are absent. Presence in spectra absorption band of high intensity in the field of 1700-1740 cm$^{-1}$ is equal absorption of methylene chains 1465 cm$^{-1}$. In this case it indicates a prevalence resinous components over hydrocarbons.

Saturated hydrocarbons are presented generally by alkanes of a normal structure, high-molecular homologs prevail in their composition (table 1, figure 1). A distribution maximum is on $nC_{27.29}$. N-alkanes are characterized by prevalence of homologs with odd number of atoms of carbon in a molecule, CPI values are rather high. The content of isoprenoids is very low it shows the ratio isoprenoids/n-alkanes. Pr and Ph are prevailing in isoprenoids composition.

### Table 1. Geochemical characteristic of bottom sediments.

| Parameter                  | R-1    | R-2    | S-1    | S-2    | S-3    |
|----------------------------|--------|--------|--------|--------|--------|
| Yield bitumoid, mg g$^{-1}$| 25500  | 710    | 1577   | 318    | 193    |
| Group component composition|        |        |        |        |        |
| Hydrocarbons               | 75.60  | 11.50  | 14.7   | 22.2   | 21.9   |
| Benzol resins              | 6.40   | 9.30   | 40.3   | 18.3   | 17.5   |
| Alcohol-benzol resins      | 16.10  | 31.70  | 28.5   | 45.4   | 46.4   |
| Asphaltenes                | 22.50  | 71.1   | 68.8   | 63.7   | 63.9   |
| Individual composition of  |        |        |        |        |        |
| saturated hydrocarbons:    |        |        |        |        |        |
| $\sum_{b.b.t.} nC_{20}/\sum nC_{21}$ | 2.58   | 0.21   | 0.04   | 0.06   | 0.08   |
| Maximum n-alkanes          | $nC_{15.16}$ | $nC_{27.29}$ | $nC_{27.29}$ | $nC_{27.29}$ | $nC_{27.29}$ |
| Isoprenoids/n-alkanes      | 1.67   | 0.11   | 0.01   | 0.03   | 0.04   |
| CPI                        | 0.70   | 3.44   | 4.77   | 4.59   | 4.47   |
| Pr/$nC_{17}$               | 61.00  | 0.74   | 0.67   | 1.12   | 0.83   |
| Ph/$nC_{18}$               | 3.41   | 0.89   | 1.25   | 1.37   | 1.18   |
| Pr+Ph/$nC_{17}+nC_{18}$    | 8.25   | 0.83   | 0.86   | 1.25   | 0.92   |

*a* b.b.t. temperature of beginning boiling; e.b.t. temperature of end boiling.
Figure 2. GS/MS (TIC) chromatograms of saturated hydrocarbons in the samples of sediments: (a) R-1 and (b) S-1.

The same structure and features of distribution of individual saturated hydrocarbons for all studied samples of sea bottom sediments find strong relationship with the terrigenous organic matter derived from high land plants [20, 21]. The prevalence of odd hydrocarbons in the range nC<sub>23</sub>-nC<sub>35</sub> and high concentrations nC<sub>27</sub>, nC<sub>29</sub>, nC<sub>31</sub> is characteristic for lipids of organic matter of this type.

4. Conclusion
Thus, the conducted researches of sea and river bottom sediments have shown the differences in their genesis established on a complex of geochemical indicators, including on composition of molecules biomarkers.

It is interesting to note that composition and features of chemical structure of bitumoids of bottom sediments of a coastal sea zone, didn't reveal close connection with aquagene organic matter.
Moreover, a genetic relationship with terrigenous organic matter is detected as on a composition of relic hydrocarbons and the character of their distribution, as features of chemical structure of bitumoids. Thus, sea bottom sediments from a coastal zone were formed, mainly, as a result of a drift of organic matter of the highest land plants by river flow. In the studied samples oil contamination traces aren’t found.

On the contrary in the river bottom sediments of seaport a presence of oil hydrocarbons is established. Typical for oil contaminated samples very high values of the yield of bitumoids, their chemical composition and other geochemical indicators indicate oil contamination of river bottom sediments.

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References
[1] McClelland J W, Dery S J, Peterson B J, Holmes R M and Wood E F 2006 Geophysical Research Letters 33 L06715
[2] Dachs J, Bayona J M, Fillaux J and Albaiges J 1999 Marine Chemistry 65 195–210
[3] Nemirovskaya I A 2004 Hydrocarbons in the Ocean (Moscow: Scientific World) p 328
[4] Safronov A F 2015 Economy of the East of Russia 2(004) 21-5
[5] Patin S A 2017 Oil and Continental Shelf Ecology Vol 1 (Moscow: Vnireo publishing) p 326
[6] AMAP (Arctic Monitoring and Assessment Programme) 2004 (Oslo: AMAP) p 310
[7] Filler D M, Snape I and Barnes D L 2008 Bioremediation of Petroleum Hydrocarbons in Cold Regions (Cambridge University Press) p 273
[8] Petrova V I, Batova G I, Kursheva A V, Litvinenko I V, Savinov V M and Savinova T N 2008 Oceanology 48 196-203
[9] Vetrov A A, Semiletov I P, Dudarev O V, Peresypkin V I and Charkin A N 2008 Geochemistry International 46 156-67
[10] Pugach S P and Pipko I I 2012 Proc. of the Russian Academy of Sciences 47 671-74
[11] Karlsson E S, Bruchert V, Tesi T, Charkin A, Dudarev O, Semiletov I and Gustafsson O 2015 Marine Chemistry 170 11–22
[12] Boitsov S, Petrova V, Jensen H K B, Kursheva A, Litvinenko I, Chen Y and Klungsoyr J 2011 Marine Environmental Research 71 357-68
[13] Yunker M B, Macdonald R W, Snowdon L R and Fowler B R 2011 Organic Geochemistry 42 1109-46
[14] Uspensky V A, Radchenko O A, Gorskaya A I and Shishkova A P 1975 Methods of Bituminological Studies (Leningrad: Nedra) p 123
[15] Kashirtsev V A 2003 Organic Geochemistry of the Naphtides of the East of Siberian Platform (Yakutsk: Publisher of the SB RAS) p 160
[16] Jovančičević B, Pavlović I, Vrvić M, Beškoski V, Antić M, Kronimus A and Schwarzbauer J 2008 Water Air Soil Pollution 190 299-307
[17] Brakstad O G, Nonstad I, Faksness L G and Brandvik J 2008 Microbial Ecology 55 540-52
[18] Dahle S, Savinov V, Petrova V, Klungsoyr J, Savinova T, Batova G and Kursheva A 2006 Norwegian Journal of Geology 86 41–50
[19] Wang Z, Fingas M and Page D S 1999 Journal of Chromatography A 843 369-411
[20] Kashirtev V A, Gaydak V V, Chalaya O N and Zueva I N 2012 Geology and Geophysics 53 1027-39
[21] Zueva I N, Chalaya O N, Kashirtev V A, Gaydak V V and Safronov A F 2014 Proc. Cretaceous System of Russia and Neighboring Countries. Problems of a Stratigraphy and Paleogeography (Velevostok: Dalnauka) 127-30
[22] Filler D M, Snape I and David L 2008 Barnes *Bioremediation of Petroleum Hydrocarbons in Cold Regions* (Cambridge University Press) p 273

[23] Glyaznetsova Yu S, Zueva I N, Chalaya O N and Lifshits S Kh 2012 *Arktika and North* 5 97-108

[24] Glyaznetsova Yu S, Zueva I N, Lifshits S Kh and Chalaya O N 2018 *Proc. Conf. Geology and Mineral Resources of the Northeast of Russia* vol 1 (Yakutsk: Publisher Permafrost Institute) pp 279-82