Dissolved Organic Matter of Formation Waters of Oil Deposits in Tomsk Region

I S Ivanova¹, I S Korol¹, D S Korneev¹,²

¹Tomsk Branch of the Trofimuk institute of petroleum geology and geophysics of Siberian branch of Russian academy of sciences, 4, Akademichesky avenue, Tomsk 634055, Russia
²Institute of petroleum chemistry of Siberian branch of Russian academy of sciences, 4, Akademichesky avenue, Tomsk 634021, Russia

E-mail: IvanovaIS@ipgg.sbras.ru

Abstract. Organic matter is an integral part of the chemical composition of natural waters and plays an important role in collection and migration of chemical elements, including pollutants in water bodies. The article presents the chemical and organic composition of layer waters in the Sovetskoe and Vakhskoe oil deposits in the Tomsk region. Underground waters have chloride and sodium, and a high concentration of organic matter (sorg up to 90 mg/l). The goal of the publication is to identify the main patterns in the distribution of diluted organic matter by groups in layer waters in the south of Western Siberia and determine their potential contribution to the migration and collection of micro-elements. On the basis of the collected data on the group composition of diluted organic matter, it has been established that alkanes, naphthalens, alkyl benzenes, cyclohexanes, phenanthrenes are the most common. The results of the analysis of the micro-element composition of the extracted organic matter from the underground waters show that there is no correlation between the micro-elements composition of the water organic matter and various groups of compounds in it. We have made a suggestion that the key role in the migration and accumulation of micro-elements in water belongs to high-molecular components of organic matter that is characterised by its diverse composition and complex insufficiently studied structure.

1. Introduction

In recent years researchers have focused a lot on diluted organic matter (DOM) in natural waters [1-12]. For example, in Arctic due to climate warming, thawing permafrost draws organic matter from frozen soil into newly formed frost-thaw lakes. In the regions with well-developed oil and gas industry, diluted organic matter is an indicator for pollution of natural habitats, including water ones. Organic matter is an intrinsic and least studied compound in the chemical composition of underground waters in the Western Siberian Basin. Organic compounds play an important part in the migration of chemical elements. By forming organic and mineral complexes, they facilitate the accumulation and migration of many metals in the water, including toxic ones [13-17].

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2. Materials and methods

In 2017 in the territory of the Tomsk and Tyumen regions 10 samples of salty underground waters were collected from oil extraction wells (Figure 1) for the purposes of studying structural and group composition of diluted organic matter. The depth of sample collection varies from 1750 to 2450 meters.

![Map of the sample collection points](image_url)

**Figure 1.** Map of the sample collection points in the area of the Strezevoy town: 1 – border of the Western-Siberian hydro-geological region; 2 – border of the Tomsk region; 3 – sample collection point for deep-seated underground salty water.

The chemical composition of waters was studied using the traditional methods in the Problem Scientific and Research Hydro-chemical laboratory (Tomsk Polytechnic University, Tomsk). Diluted organic matter was studied in the Institute of oil chemistry of the Siberian Department of the Russian Academy of Science (Tomsk) using the method of three-stage extraction with different pH levels [18] that was based on the production of chloroformic concentrates. This method was selected due to the fact that it allows to extract fulvic acids (FA) and humic acids (HA) [19]. This method extracts chloroformic concentrates (CC) with the organic matter in the amount of 8-62 mg/l from water samples filtered to eliminate mechanical impurities. The analysis of organic compounds in water CCs was conducted using the method of chromatography-mass spectrometry and a mass-spectrometer Finnigan DSQ-EI/250 (Thermo Scientific, USA). Moreover, the Tomsk branch of the Institute of oil and gas geology and geophysics managed to establish the element composition of the isolated organic concentrates from layer waters employing one of the modern spectroscopic research methods, namely, an X-ray fluorescence analysis (XFA). Arl Perform’X Thermo Scientific.

3. Results and discussion

Underground waters collected from oil wells are attributed to the Neocomian water bearing complex and are chloride sodium salt ($\Sigma = 18–23 \text{ g/l}$), slightly acidic waters (pH = 6.3–6.7). The waters do not have sulphates and have a low level of carbonates. Deeper underground waters from the Jurassic water bearing complex are salty waters and weak brines ($\Sigma = 20–37 \text{ g/l}$) with chloride and sodium composition with pH varying from 6.4 to 7.2. The deeper the samples are taken, the more the concentration of such micro-elements as Li, P, Sr, Ba.
On the basis of the collected data on the DOM group composition, it has been established that in oil layer waters the most common elements are hydrocarbons (HC), such as alkanes (up to 85%), naphthalenes (up to 20%), phenanthrenes (up to 3%), alkylbenzenes (up to 11%), cyclohexanes (up to 9%) (Table 1, Figure 2). Also, hetero-organic compounds were found (alkyl phenols and dibenzothiophene, oxygen and sulfur-containing compounds respectively) in the concentration up to 3%. The DOM distribution by groups in the Neocomian and Jurassic water bearing complexes are shown in Figure 2.

Table 1. The composition of diluted organic matter in underground waters, % per fraction.

| Groups of components      | \( K_1 \) (Sovetskoe deposit) | \( J \) (Vakhskoe oil deposit) |
|---------------------------|--------------------------------|--------------------------------|
| Enriched HC               | 63,3-91,7 (80,4)               | 65,1-92,1 (78,9)               |
| Aromatic compounds        | 10,5-36,9 (19,2)               | 5,7-26,7 (17,1)                |

Note: The Table shows minimum and maximum values and in medium values are given in brackets.

Figure 2. The DOM group composition in the waters of the Sovetskoe (a) and Vakhskoe (b) oil deposits.

The carbon component is presented mostly by aliphatic structures, e.g. n-paraffins and isoualkanes. The Neocomian water complex (the Sovetskoe oil deposit) has the concentration of n-paraffins of 59-85%, while in the waters of Jurassic deposits it is 61-83%. Alkanes are used as geochemical markers for the genesis of the organic matter, as the prevalence of some homologues of n-paraffins reflects the contribution of individual biological agents into the formation of the DOM composition. It has been established that in all deep-seated underground waters, n-paraffins have both homologues in the \( C_{11} \)-\( C_{23} \) line that are typical for oil and long-chain structures starting from \( C_{26} \) and higher that are common for vegetation.

All natural waters in the region have high concentrations of Fe, Mn, Sr. The concentration of iron reduces as it gets deeper, by about 5 or 6 times [20]. This can be explained by the fact that the concentration of organic matter reduces in the deep water that form with Fe and other micro-elements complex compounds and help to preserve them in the solution. However, the underground waters from Jurassic deposits again have bigger concentrations of Fe, up to 45 mg/l that achieve the maximum in the cross-section (16 mg/l on average), which is possibly associated with oil as an additional source of organic matter. In order to establish the roles of individual groups of organic matter in the migration and accumulation of micro-elements in water, an X-ray fluorescence analysis of extracted organic concentrates from the layer waters was conducted. It has been established that, in addition to C,H,N, the organic matter contains such elements as Ca, Mg, Na, Cl, Ba, Si, Fe. The issue of the interconnection between micro-elements and diluted organic matter, which can be present in waters in the form of various hydrocarbons and hetero-organic compounds, is essential. New relevant data can help to establish the role of organic matter in the migration and accumulation of micro-elements in water. The results of the analysis of the micro-element composition of the extracted organic matter from the underground waters show that there is no correlation between the micro-elements.
composition of the water organic matter and various groups of compounds in it. First, the explored organic matter has relatively low-molecular hydrocarbons and a small amount of sulphur- and oxygen-containing compounds without covalent-bonded micro-elements in their structure. Therefore, their transfer by organic matter through covalent bonds is impossible. Second, non-polar enriched hydrocarbons (alkanes and cyclohexanes) account for the majority of the organic matter in water, and they are not likely to form various intermolecular bonds with ions. Whereas, the share of polar hetero-organic compounds and aromatic components with the developed π-conjugation system that can form non-covalent bonds, is small. So, we can say that the key role in the migration and accumulation of micro-elements in water belongs to high-molecular components of organic matter that is characterised by its diverse composition and complex insufficiently studied structure. The chemical properties and structural organization of highly-molecular components of organic matter in water can determine their characteristic qualities in terms of transport of micro-elements through various mechanisms.

4. Conclusion
The conducted research showed that layer waters of the studied oil deposits are chloride, sodium, salty, slightly acidic waters. The concentration of Li, P, Sr, Ba grows with the depth. On the basis of the collected data on the group composition of diluted organic matter, it has been established that hydrocarbons are the most common in layer waters, in particular these are alkanes, naphthalens, alkyl benzenes, cyclohexanes, phenanthrenes. The concentration of hetero-organic compounds is not high, and they are represented by alkyl phenols and dibenzothiophenes. The results of the analysis of the micro-element composition of the extracted organic matter from the underground waters show that there is no correlation between the micro-elements composition of the water organic matter and various groups of compounds in it. We have a made suggestion that the key role in the migration and accumulation of micro-elements in water belongs to high-molecular components of organic matter that is characterised by its diverse composition and complex insufficiently studied structure.

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