Indirect effects of oil products on the environment

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Abstract. The article is focused on chemical and radioactive contamination of the environment during hydrocarbon production. The objective of the research is to present relatively unknown facts of indirect long-term environmental effects of hydrocarbon production. Traces of radioactive contamination of soils, ground- and surface water were studied, and also in drinking water in the Republic of Bashkortostan. The authors' own field and laboratory studies were used. They were performed as part of the preparation of geochemical base map (GHO-1000) of 1:1000000 scale in the Republic of Bashkortostan and in the Ukhto-Izhemsky oil and gas bearing region. The methods applied for laboratory research were inductively coupled plasma mass spectrometry (ICP-MS) for soil and bottom sediment samples and atomic emission spectrometry (ICP-AMS) for ground- and surface waters. It has been determined that in the areas affected by oil production the chemical pollution aspects include deterioration of the groundwater quality caused by associated water and oil products ingress into aquifers due to violation of the oil and gas well drilling techniques, and soil salination caused by frequent equipment breaks during oil production. Aspects of radiation contamination of the environment during oil production include the intake of radionuclides with associated water, and sometimes with heavy hydrocarbon fractions, as well as the consequences of underground nuclear explosions. It is concluded that the territories of hydrocarbon exploration, production and storage should be classified as areas of potential risk for radioactive contamination and chemical pollution (by inorganic compounds, including heavy metal salts). Uranium concentration in drinking water was determined by the INAA method (instrumental neutron activation analysis).

1 Introduction

Exploration, prospecting and production of hydrocarbons inevitably have a negative impact on the natural environment, and this impact is intricate and not always manifested in situ. For example, oil pollution can be identified visually and immediately. At present, such pollution is monitored even with the help of satellites and through interpretation of aerial and space

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images. In this article, the indirect environmental effects will be addressed, and namely chemical pollution and radioactive contamination of natural environment during oil production. As part of the chemical pollution, only heavy metal pollution will be considered. Impact of this kind cannot be assessed on the spot but it will inevitably be manifested in the future.

The issues of such an impact of oil production on the environment have been and are being studied by many researchers, both domestic and foreign. Among them are Kinzikeev A.R., Gorelov V.S., A.K. Mazitova, G.K. Aminova, Shamraev A.V. and Shorina T.S., Suleymanov R.R., Nazyrova F.I. and many others. This group of scientists was mainly engaged in chemical pollution of environmental components; Abdrakhmanov R.F., Akhmetov P.M., Taraborin D.G., Minigazimov N.S., Arbuzov S.A., Rikhvanov L.P., Belan L.N. and Nikonov V.N. studied the radioactive effects of oil production. Their works analyze the main patterns of radioactive contamination of the oil fields in Bashkortostan and Tatarstan (Akhmetov, Abdrakhmanov, 2005; Minigazimov, 2000). In the works by Zakharchuk S.A., the radiation situation in the oil-producing areas of Azerbaijan and Stavropol is characterized (Zakharchuk, 1998). In the research by Taraborin D.G. (Taraborin, 2003) it has been shown using extensive data that oil and gas production in the Orenburg region is also accompanied by the appearance of radioactive contamination in oil fields with the formation of abnormal fields of increased radiation on the ground surface in relation to the background radioactivity values.

Actually, the increased radioactivity of hydrocarbons and deep-lying formation water has been known for a very long time. It was described in the works by domestic scientists V.I. Vernadsky in 1932 and 1954, A.I. Perelman in 1962, 1965, V.V. Ivanov in 1997 and others, as well as by some foreign researchers. In 1930, M. Herculano de Carvalho, Comptes Rendus Acad reported on the increased radioactivity of associated waters observed during drilling of oil and gas wells. Back in 1926, the Russian oil expert A.A. Cherepennikov discovered the extremely high radioactivity of the formation waters of the Ukhtinskoye oil field. In 1927, L.N. Bogoyavlensky (ibid.) showed that radioactivity is due to an unusually high content of Ra-226, and namely 7.6 x 10-9 g/dm3 (on average), which corresponds to a specific activity of 281 Bq/kg.

In addition, the issue of radioactive contamination of the environment during HC production should be divided into 2 items: one is associated with the natural increased radioactivity of some hydrocarbons and associated waters, and the other is related to the consequences of nuclear explosions in oil fields.

2 Materials and methods

The authors' own field and laboratory studies were used to analyze the indirect impact of oil production on the natural environment. They were performed as part of the preparation of geochemical base map (GHO-1000) on a scale of 1:1000000 in the Republic of Bashkortostan and in the Ukhto-Izhemsky oil and gas bearing region (the Republic of Komi), as well as literary sources, information resources and stock materials.

The methods of laboratory research were as follows|: inductively coupled plasma mass spectrometry (ICP-MS) for soil and bottom sediment samples, and atomic emission spectrometry (ICP-AMS) for ground- and surface waters.

The data of field and laboratory studies was processed using Statistica 6.0 and Microsoft Excel programs. The processing of the cartographic material was carried out using the Argis-10.2 software package.

3 Results and discussion

It has been determined that almost all sources are saline in the oil production impact zone within the western part of the Republic of Bashkortostan (Kinzikeev, 2001). This is caused by violation of the oil and gas well drilling techniques. During well boring, it was necessary to strictly isolate all aquifers, but this regulation was not observed. As a result, formation waters with an average mineralization of 20-40 g/l or higher rose through the formed channels of the annulus of wells causing soil salination in the oil production zone.

Another cause of natural water and soil salinization was frequent breaks of conduits returning formation waters to injection wells. According to Gorelov V.S., up to 10 thousand breaks occurred annually in the Republic of Bashkortostan as a whole (Gorelov, 2006). At present, the associated water is mainly used to maintain formation pressure and increase the oil recovery during oil production. This simultaneously solves the problem of their disposal. In some cases, more advanced associated petroleum gas injection technology is also used to increase oil recovery. This new technology literally saves huge territories, because when oil-associated gas was burned, the area of oil production complexes and their impact zone experienced an exorbitant man-made load.

According to the authors (the result of geochemical testing), on sheet N-40 (Ufa), during the compilation of geochemical bases on a scale of 1:1000000, a large number of anomalies of uranium, mercury, zinc, cadmium, molybdenum, nickel and other heavy metals were detected in soils, bottom sediments directly within the contours of oil and gas bearing areas of Bashkortostan.

As part of the 1:1000000 scale compilation, zones with a very high level of contamination of soils and bottom sediments with heavy metals, including uranium, were outlined in the Ukhto-Izhemsky oil and gas bearing region. Figure 1 highlights their linear and areal abnormal geochemical fields (AGF). Linear anomalies are characterized by their proximity to thrust zones. The areal AGF is confined to the oil and gas field localization area. A large Yareg oil field is being developed here (small fields have already been exhausted). The Yareg oil field includes several deposits. The size of a unified (generalized) oil content contour is 37 x 6 km. Naphthenic-aromatic oil belongs to the grade of sulfurous (up to 1.4%), low-paraffin (0.41%), resinous (20%), i.e. heavy oil.

Anomalies of V, Ni, Co, Cu, U, Mn, Zn, i.e. the chemical elements actively concentrated in the soils of oil and gas provinces, are very characteristic of the Ukhto-Izhemsky oil and gas bearing region. The complete association of soil polluting elements in this region is the following: Cd17,1355, Zn8,7323, Sr8.6239, Ni8.5270, V6.0316, U4.0247, Cu3.1217, Th2.9186, Be2.1126, Co2.1114, Mn2.1120, Ag2.0105 (the subscript signifies the accumulation coefficient (Cc), the superscript index is the coefficient of variation (V)).

The association is formed by the chemical elements that are united by the ability to concentrate in oil and, especially, in its heavy fractions. These elements are characterized by a high level of accumulation and a very high differentiation of content in soils and bottom sediments, which indicates their connection with a powerful concentrated source that can be both hydrocarbon deposits themselves and associated waters, as well as hydrocarbon processing facilities.

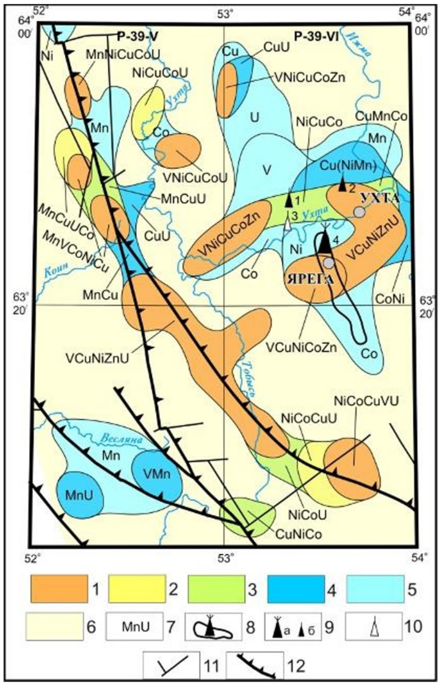

Fig. 1. Map of abnormal geochemical fields of Cu, Ni, V, Co, Zn, U, Mn concentration in the soils of the Ukhto-Izhemsky oil and gas bearing region [13]. 1 – 6. Complexity of geochemical anomalies: 1 – five or more elements, 2 – four elements, 3 – three elements, 5 – two elements, 5 – one element; 6 – background areas; 7 – composition of geochemical associations; 8 – large oil field Yareg (4) and the contour of the deposit; 9 – oil fields: a) large, b) small fields – oil Nizhnechutinskoye (1) and Chibyusskoye (2), 10 – small gas condensate field Vodny Promysel (3); 11 – rupture faults, 12 – large thrust-thrust zones

It is possible that the accumulation of the above elements in groundwater is related to their concentration in oil. Vernadsky V.I. wrote about these unique geochemical conditions in the Ukhta oil and gas bearing region back in 1932.

Mineralized waters of the Upper Proterozoic metamorphic complex have increased radioactivity, with the concentration of radium salts 3×10-10 – 7.6×10-8 mg/dm3. It should be noted that they are used for the extraction of rare and radioactive elements. The water is slightly alkaline. The water contains J in up to 25 mg/l concentration (on average 10 mg/l), Br up to 230 mg/l (on average 100-130 mg/l), therefore it is also used for medicinal purposes.

Similar groundwater is localized in the Middle Devonian aquifer complex and contains (mg/l): Br – 30-230, Cl – 8-25, Ba – 10-60, J – 8-20, Ra – 1-9×10-10 (according to the Explanatory Note to the State Geological Map of the Russian Federation – a new series, scale 1:1000 000, sheet P-38,39 (Syktyvkar). VSEGEI, 1999). The involvement of groundwater enriched with rare and radioactive elements in the technological process of oil production apparently leads to radioactive and chemical pollution of the oil production areas. In addition, heavy oil usually has an increased level of radioactivity.

As shown above, during oil production, the so-called associated water (also known as formation water) is involved in the technological cycle and it enhances the natural upward migration of radionuclides and heavy metals. According to some data, radium and radon emissions from oil and natural gas production exceed those from coal combustion and nuclear power. The Table compares the emission levels of these uranium decay derivatives [9].

Table 1. Relative emission levels of some radionuclides converted to ionizing energy flux (J/s).

Radionuclides	Nuclear power and ore mining *	Coal combustion *	Oil and natural gas production *	Global natural emissions
Rn	53000	3000	75000	120 000 000
Ra	0.22	10	20	1100

Migration and deposition of uranium, radium and other alkaline earth metals are largely determined by their chemical properties. Radium deposition, for example, is facilitated by sulfate barriers in the oxidation zone [4]. Hydrogen sulfide radium-containing water rising from beneath in the oxidation zone become sulphate, leach and decompose scattered metals from the host strata. As a result, radium is deposited together with BaSO4, and sometimes with CaSO4, where it becomes an almost insoluble permanent source of radon emanation.

Reducing geochemical barriers are needed to accumulate uranium. On them, the extremely mobile in aqueous solutions U^{6+} passes into $U^{4+.}$ During drilling, the following seems to happen: differences in Eh values in the zones of influence of hydrocarbon contacts create contrasting geochemical barriers on which dissolved uranium in a hexavalent form is restored to a sedentary tetravalent state and [1] is sorbed on drilling equipment, in various sludge accumulators, oil sludge barns. Radioactive thorium salts, potassium isotopes and strontium are also accumulated causing gamma radiation doses to rise up to several thousand μR/h.

Since the 1980s, the facts of deposition of radioactive metal salts on process equipment have been known at the Romashkinsky (Tatarstan) and Shkapovsky (Bashkortostan) hydrocarbon deposits. Within the mining claims of these deposits, the gamma dose rate in the equipment clean-up places, according to V.N. Nikonov [8], reached 3000 μR/h. Minigazimov N.S. noted that radioactive contamination was also recorded in the areas of numerous ruptures of oil pipelines and water conduits [7].

A.I. Perelman (Perelman, 1962, 1965) noted that increased radioactivity is characteristic of the heaviest fractions of hydrocarbons. It is assumed that the radioactivity carriers in oil are organometallic complexes, higher aromatic hydrocarbons and sulfur compounds (Figure 2).

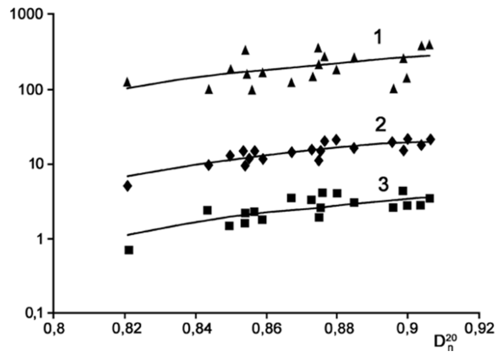

Fig. 2. Correlation of oil density with its various characteristics. 1 – radioactivity of oil (counts per minute), 2 – the sum of resins and asphaltenes (%), 3 – sulfur content (%)

As follows from the above graph [6], the trend of radioactivity of oil is coherent with the trend of sulfur compounds in its composition, as well as the sum of resins and asphaltenes.

But, as mentioned above, the problem of radioactive contamination of the environment is associated not only with the increased natural radiation of some hydrocarbons and associated water, but also with the consequences of nuclear explosions in oil fields. The latter were carried out in the second half of the last century in the oil and gas regions of the USSR and the USA. The goals of these explosions were twofold: increasing oil recovery and creating storage facilities for the disposal of toxic industrial waste. At that time it was believed that such explosions were safe for the environment and only in the 1990s some facts became evident about complicated radiation situation in the explosion-affected areas with the ensuing consequences.

Using of the Republic of Bashkortostan as an example, one can trace the consequences of underground nuclear explosions in oil fields. According to [10], from 1965 to 1984 several such explosions were carried out in the territory of Bashkortostan: two explosions in the vicinity of Sterlitamak in order to create underground reservoirs for the disposal of industrial waste, as well as five explosions to the west of Meleuz to intensify oil and gas production. In 2004, the maximum value of the background radiation in the affected area reached 250 μR/h [5].

Figure 3 shows a map of the spatial distribution of uranium in drinking water deposits in the territory of the Republic of Bashkortostan. Analyzing this cartographic material, we see that the most contrasting anomalies of uranium are confined to the sites of underground explosions, the maximum of which is located in the Meleuzsky district of Bashkortostan. Anomalies of almost the same intensity (27.0 – 45.7 mg/kg) occur in the territory of oil production where it has been going on for more than 60 years. These are the Belebeysky, Tuymazinsky and partly Davlekanovsky districts

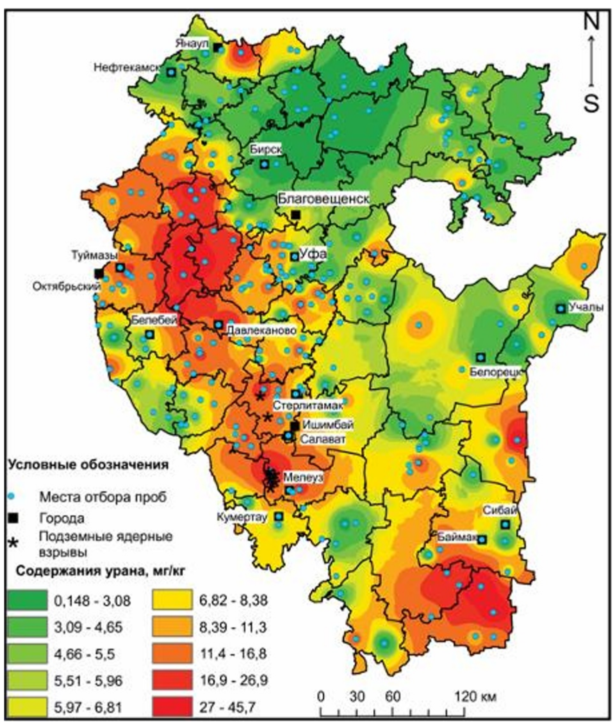

Fig. 3. Uranium content in drinking water deposits [10]

Smaller in area, but of the same intensity, anomalies are noted in the mining areas near the towns of Uchaly, Buribai and Baymak.

However, it should be noted that on the territory of the Republic of Bashkortostan there are areas where the background radiation level, according to the gamma survey data, approaches the maximum permissible values, and sometimes exceeds it [8]. This is due to the natural manifestations of uranium and thorium mineralization. This phenomenon explains a group of anomalies in the Beloretsky and Burzyansky districts. Although the intensity of these anomalies is less (6.8 – 11.3 mg/l), their area is more extensive.

In addition, it should be noted that the excess of uranium content in salt accumulations of drinking waters in the settlements of Meleuz, Salavat and Sterlitamak is consistent with data on the increased content of this element in the soils of these areas (Asylbayev, 2016). However, unambiguous evidence of the effect of underground nuclear explosions on elevated uranium concentrations in drinking waters requires further study.

4 Conclusion

So, among the indirect effects of oil production on the natural environment, some aspects of the pollution with heavy metals and radiation contamination have been considered. Chemical pollution is caused by the following:

- by ingress of associated water into the aquifers due to violations of oil and gas well drilling techniques;
- deterioration of the ground- and surface water quality, as well as soil salinization, caused by frequent equipment failures during oil production.
- Radioactive contamination causes are as follows:
- enhancement of natural upward migration of radionuclides by associated water during drilling of oil and gas wells;
- heavy hydrocarbon fractions and industrial waste during their extraction often have an increased radioactive background which leads to radioactive contamination of the oil production area;
- the consequences of underground nuclear explosions in oil fields, as a result of which the territory in the zone of their impact in places exceeds radiation safety standards. In the same territories, intense anomalies of uranium content are recorded in the sediments of drinking water and, according to soil survey data, in the soils.

Taking into consideration the above mentioned facts, oil production areas should be classified as areas of potential radioactive and chemical contamination and actions should be implemented to remediate them.

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