Possible sources of pollution by oil products of water body in karst area

S A Buzmakov, D N Andreev, A A Zaytsev, Y V Khotyanovskaya and G A Voronov
Perm State University, 15, Bukireva str., 614990, Perm, Russia
lep@psu.ru

Abstract. This article is devoted to the study of the content of petroleum products in surface and groundwater in the karst area. The hydrological and hydrochemical features of the Yasyl river, the dynamics of oil content in three hydrological phases in the period from 2016 to 2018 are considered. The time and spatial features of the distribution of petroleum products along the length of the water stream are revealed. The hypotheses of the origin of oil products in a water body were put forward.

1. Introduction
One of the most dangerous substances polluting the habitat, due to its properties and scale of use, is oil. Oil products have a negative effect on soil, surface water and geological environment including groundwater [1, 2]. Processes of oil extraction are always associated with the risk of environmental pollution by oil products [3, 4]. The additional risks arise when working in rough geological conditions, for example, in karst areas.

It has been found out that the areas of development of karst formations and their inherent hydrosphere have specific features that contribute to a more intensive spread of pollution [5]. It is proved that in the case of oil pollution, the situation gets complicated due to the changing oil composition during migration, dissolvability and adhesion to rocks [6].

In the Perm region evolution of river bed and karst are among the most common exogenous geodynamic processes [7].

Karst areas are characterized by a significant decrease in the degree of the underground hydrosphere protection and have a number of features that create special environment for the spread of oil pollution [8]. In areas of distribution of karst rocks, where the fracturing and water permeability of rocks are significant, the risk of groundwater pollution increases. In the absence of covering deposits, which play a significant role in preventing pollution of groundwater, precipitation and spillages of oil are easily absorbed by surface karst forms [9].

A prime example is oil production in the river basin of the Iren' river. The Iren'sky karst area is the area of the intensive sulphate karst of the platform type [10].

The aim of the research was to study the oil products content in surface and underground waters of the karst area, as well as to identify the sources of this pollution.
2. Materials and methods
The research was conducted in the southeast of the Perm region in the oil-bearing zone of the Western Urals. The Yasyl river is a right-bank tributary of the Iren' river. Its river basin is 47.6 km² and its length is 11.6 km. There are no permanent gauging stations in the investigated basin [11]. The Yasyl begins with a small seep, disappears from the surface and reappears for several times. Apart from more or less large karst rivers there are small karst brooks. These brooks flow out of the cave, are repeatedly lost and reappear before flowing into the Iren’ river.

In the study area karst funnels, swallow hole, karren, stable holes, caves, karst cracks, blowing holes, underground cavities occur in abundance.

The bottom of the Yasyl valley is characterized by the occurrence of gypsum and anhydrite under sandy-clay deposits below the level of mineralized groundwater. Subsidence on the surface with a diameter up to 5 m also may appear.

On the slopes of the Yasyl valley and blind creek, where karst sulphate rocks are covered by eluvial-deluvial and karst deposits up to 25 m thick, there are conditions for the formation of large underground cavities. The surface may form dips with a diameter of up to 12 m, characterized by a high level of gypsum and anhydrite relative to groundwater and lack of surface formations.

![Figure 1. Location of sampling sites.](image)

According to the water regime, the rivers under consideration belong to the type with a distinct spring flood, summer-autumn rain river floods and a long sustained winter low water period. Snow water takes precedence in feed of water streams. The percentage of melt water in the total flow reaches 70-90%. On average, approximately 20-30% of the annual flow is formed by the underground path [11].

Water samples with signs of oil pollution were taken in order to establish the dynamics of changes in the concentration of water pollution by oil products.
Sampling was carried out during the winter low water period, the flood period and the summer-autumn low water period.

The location of sample areas (SA) is shown in figure 1. A list of SA is presented in table 1.

Quantity measurement and identification of oil products were carried out by infrared spectroscopy (IR spectroscopy) [12].

Laboratory studies also included a reduced analysis of water samples: physical properties, pH, hydrocarbonate and carbonate ions, chlorides, sulphates, calcium, magnesium, sum of sodium and potassium.

Sampling, storage and transportation of water samples were carried out in accordance with state standards.

3. Results and discussions

A chemical analysis of the concentrations of the pollutant components was carried out on selected water samples.

Water in the studied places has a neutral pH (average 7.4). Water salinity is on average 2.2 g/dm$^3$. The change in salinity generally corresponds to a change in the river's feeding regime: the highest values are confined to the winter low-water period, the most fresh water was recorded during the spring flood. The distribution of mineralization over the territory and in time is quite evenly.

The distribution of sulfate concentrations over the territory of the watershed under consideration is also fairly evenly and gradually decreases to the mouth of the river due to an increase in surface runoff. The concentration dynamics over time is closely related to the seasonal water content and type of water supply of the stream, the maximum values are confined to the winter (on average 1478 mg/L) and summer low-flow periods (average 1310 mg/L), the minimum values to the flood period (on average 1199 mg/L).

The average concentration of the magnesium ion is 27.15 mg/dm$^3$, concentration of the chlorine ion is 15.86 mg/dm$^3$. Moreover, during the flood period the concentration of chlorides increases, which indicates the surface source of origin of this pollutant. The average concentration of sodium ions is 8.7 mg/dm$^3$, of potassium ions – 0.78 mg/dm$^3$.

In general, the water of the studied area is sulphate-calcium-hydrocarbonate which is typical of karst areas.

From the headwaters down to the point of 4 km lower course the concentrations of the main macrocomponents are fairly stable, the formation of the river flow in this section of the channel is due to groundwater. Changes are observed in the water of the dam pond, which accumulates more fresh surface water and the concentration of macro-components is reduced by about 30%.

The distribution of total concentrations of iron in the territory under consideration is rather unbalanced. Maximum concentrations of total iron are confined to the northeastern part of the river basin where are the headwaters of the main brooks forming the Yasyl river. Closer to the middle course the concentration of pollutants is significantly reduced to 0.05 mg/dm$^3$ and remains stable up to the mouth.

The distribution of nitrite concentrations throughout the territory turned out to be uniform. At all sampling points, their concentration ranges from 0.02 to 0.025 mg/dm$^3$.

The overall dynamics of concentrations of oil products by main hydrological seasons for three years is presented in table 1. For the SA 18-27, where samples were not taken in 2016, data for two years are presented. Results highlighted in grey indicate the excess of the Maximum Contaminant Level (MCL) of oil products.

Studies have shown a significant change in the concentration of oil products. Abnormally high concentrations were recorded in 2016 at SA 2 and SA 3, which was not observed in subsequent years. In 2017 a significant decrease in the level of pollution was noted. A significant excess of the MCL in 2017 was noted only on one sample area in the upper reaches of the Yasyl Log (SA 18).

In 2016 elevated concentrations are typical mainly for right-bank tributaries of Yasyl river (SA 3 and SA 5), in 2018 elevated concentrations were recorded in left bank tributaries (SA 10 and SA 18).
In both years (2016 and 2018) the concentration of oil products decreased downstream, as polluted water was diluted with cleaner. In general, migration of the pollution zone from the north-west to south-east can be noted.

### Table 1. Content of oil products in surface and groundwater samples.

| № SA | The name of SA                          | Oil products, mg/dm³       |
|------|----------------------------------------|---------------------------|
|      |                                        | 2016 year | 2017 year | 2018 year |
|      |                                        | March     | April     | July  | March | April | July  | February | April | July  |
| 1    | Seep 1                                  | <0.05     | -         | -     | <0.04 | <0.04 | <0.04 | <0.04     | 0.64  | 0.14  |
| 2    | Seep 2                                  | 5.53      | 1640      | 570   | <0.04 | <0.04 | 0.365 | 0.43       | 0.05  | 4.05  |
| 3    | Seep 3                                  | 3.62      | 2360      | 3200  | 0.09  | <0.04 | 0.08  | 0.29       | <0.04 | 0.47  |
| 4    | Bund, brook 1                           | -         | -         | <0.05 | <0.04 | <0.04 | <0.04 | 0.55       | 0.23  | 4.05  |
| 5    | Seep 5                                  | -         | 16.6      | <0.05 | <0.04 | <0.04 | 0.043 | 0.39       | <0.04 | 4.05  |
| 6    | lake, swallow hole                      | -         | 0.05      | 0.07  | <0.04 | <0.04 | <0.04 | 0.21       | 0.11  | -     |
| 7    | New swallow hole                        | -         | <0.05     | -     | <0.04 | <0.04 | -     | -          | -     | -     |
| 10   | Cave                                    | 3.04      | <0.05     | 0.08  | 0.13  | <0.04 | 36.7 | 37.4       | 8.3   | -     |
| 11   | Seep 7, Arapov klyuch                   | 0.88      | <0.05     | -     | <0.04 | <0.04 | 0.043 | 0.07       | 0.56  | -     |
| 12   | Seep 8, Rock narrow                     | 1.25      | <0.05     | <0.04 | <0.04 | <0.04 | -     | 0.08       | 0.23  | -     |
| 13   | Outfall of the river Yasyl               | -         | <0.05     | <0.05 | 0.04  | 0.04  | 0.192 | 0.34       | 0.56  | -     |
| 18   | Seep 6, Headwater of the Yasyl Log       | -         | -         | -     | 3.9   | 3.9   | <0.04 | 0.80       | 8.5   | 0.27  |
| 19   | Brook 2, below the oil trap              | -         | -         | <0.04 | <0.04 | <0.04 | <0.04 | 0.237      | 0.26  | 0.47  |
| 20   | Brook 3, below the confluence of brook 1 | -         | -         | -     | <0.04 | <0.04 | -     | 0.09       | 0.54  | -     |
| 21   | brook 2                                 | -         | -         | -     | <0.04 | <0.04 | -     | 0.13       | -     | -     |
| 24   | Yasyl, above the confluence of the brook 5| -         | -         | -     | <0.04 | <0.04 | -     | 0.18       | 2.61  | -     |
| 25   | Yasyl, below the confluence of the brook 5| -         | -         | -     | <0.04 | <0.04 | -     | 0.20       | 1.75  | -     |
| 26   | Yasyl, below ponds                       | -         | -         | <0.04 | <0.04 | <0.04 | 0.231 | 5.4        | 0.71  | -     |
| 27   | Yasyl, estuary                          | -         | -         | <0.04 | <0.04 | <0.04 | -     | 0.18       | 0.95  | -     |

Elevated concentrations of oil products vary by year. If in 2016 elevated concentrations are representative of right-bank tributaries of the Yasyl (sampling points SA3 and SA5), then in 2018 increased concentrations were recorded in left-bank tributaries (selection points SA10 and SA18). Accordingly, in 2016 and in 2018 the concentration of oil products decreased downstream as polluted water was diluted with cleaner. In general, migration of the pollution zone from the north-west to south-east can be noted.

During the period from April 2016 to July 2018 a significant excess of the concentrations of oil products at SA10 was detected, and in July the concentration of oil products at this point dropped significantly (to 8.3 mg/L), but still remained quite high.

### 4. Conclusion

The chemical composition of Yasyl river water is typical for rivers of karst territory. Concentrations of chlorides, potassium, nitrates are within the MCL. High concentrations of oil products are recorded in the upper reaches of the water stream (in the outlets of groundwater) and, probably, are associated with technogenic activities. Additional pollution is contributed from the use of fertilizers in the river basin, however, it does not have a strong influence.
Based on the results of chemical analyses and the distribution of concentrations of oil products several hypotheses of their origin can be advanced:

1) squeezing the reservoir oil-containing water into the near-surface karst cavities and further entering the surface water bodies. This hypothesis is opposed by the pulsating nature of the pollution inflow (at the point of the SA 10, the concentrations of oil products varied from 0.04 mg/L to 36.7 mg/L in less than 6 months) with a stable water content level during the seasons, which is not typical of such types of pollution;

2) emergencies on pipelines. A sufficiently large amount of oil products entering the water body proves wrong of this hypothesis. This version can explain the pulsating nature of the pollution, however, all emergencies should be recorded and it is quite difficult to hide these accidents, thus, this version is unlikely.

3) opened old karst cavities filled with certain organic residues (peat, etc.), which are determined in the analysis exactly as oil products. This version cannot be completely excluded, but rather high concentrations of oil products speak against it. Pollution migration can be referred to this version, i.e. there may be several karst craters filled with organic waste, which are gradually opened in different parts of the catchment area the Yasyl river, providing periodic sharp bursts of concentrations of oil products.

4) the version is similar to version №3, but instead of organic residues, it is possible to assume the presence of technogenic pollution. When performing works on arranging the group of wells, scheduled pipeline repairs or other works, the subsoil contaminated with oil products could be buried in the nearest large karst funnels, covering all this with a layer of clay as the aquiclude. Over time it was eroded, the water began to seep into the karst cavities and continue to enter surface water bodies with oil products. This version is possible because of the wandering nature of pollution sources (pollution funnels are opened gradually) and rather high concentrations of oil products in water.

Thus, oil pollution in karst areas is specific. High concentrations of oil products were recorded several times at different points in the catchment. The source of their income was not reliably established. The establishment of the genesis of technogenic indications is a rather complex geoecological problem. Systematic integrated hydrogeological and ecosystem studies are needed in order to find a solution to it.

To assess the most likely scenario for the flow of oil products in the water of the Yasyl River, it is necessary to continue monitoring the chemical composition of water and supplement the work with a survey of the area of localization of maximum concentrations of oil products.

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