Oil Pollution of River Bottom Sediments

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Abstract. The impact of oil products on river bottom sediments and their wettability is considered on the example of the small Kurcha-Murcha River. The wettability of bottom sediments (pollution up to 18000 mg/kg) was determined by the contact angle of wetting of the solid phase (method of static drop). It is shown that the contact angle of wetting can be used to assess the pollution level of the river bottom sediments.

1. Introduction

Oil pollution is one of the most important environmental problems not only in the areas of its production and transport, but also in processing. This requires the improvement of methods for assessing the content of oil and petroleum products and the pollution level by them of individual components of ecosystems: soils, surface and groundwater, and river bottom sediments. Bottom sediments (BS) are the final stage of migration of all pollutants coming from adjacent land and from the atmosphere, and can serve as integral indicators of the pollution of the territory with oil and petroleum products. Their concentration in BS, pore waters and bottom water layer is much higher than in the water column.

The surface of the solid phase of BS has a great influence on the sorption/desorption, transport and spatial distribution of petroleum products [1] and availability of nutrients for microbiota. Note that biochemical processes of self-purification in BS are extremely slowly. Many of the processes occurring in BS depend on the wettability of the solid phase, which is numerically characterized by the contact angle of wetting (CAW).

The main factor in the formation of hydrophobic-hydrophilic properties of sediments is organic matter [2, 3]. Organic matter of humus nature, coming from the catchment area, has an amphiphilic character (the presence in the molecules of hydrophilic groups and hydrophobic zones) and affects the sediment wettability. In turn, oil and petroleum products, when exceeding a certain concentration, lead to a change in the nature of wettability (change of hydrophilicity to hydrophobicity). In this case, CAW becomes greater than 90°, and the sample loses its ability to absorb and retain moisture. The latter circumstance allows us to assume that the value of the CAW can characterize the pollution level
2. Objects and methods
The research was carried out in the Kirov administrative district of Khabarovsk (Russian Federation). The site is located in a periodically flooded coastal zone of the Amur River at the confluence of a small Kurcha-Murcha River. The surface is planned bulk fillings. The thickness of bulk soils is 3.4–3.6 m, represented to a depth of 1.9–2.2 m with gravel soils with sand and sandy fillings. The vegetation on the considered site is completely absent, the reason for which are frequent and prolonged flooding during high water levels in the Amur River, as well as backfilling with coarse elastic material. The river flows into the Amur River at the oil terminal. Its length is 2.5 km; the catchment area is 2.7 km². The mouth part of the river is enclosed in an underground sewer, into which all water from its catchment is collected. There are large industrial enterprises on the territory of the Kurcha-Murcha catchment area: NNK-Khabarovsk Oil Refinery (with oil sludge tank), NNK-Khabarovsknefteprodukt (both of them have underground storage tanks for petroleum products), cargo river port, etc.

BS sampling was carried out during the low water period (May 25 – June 13, 2018). Soil grounds were selected to characterize the territory. Their general characteristics of physicochemical properties and the content of petroleum products were determined earlier [4].

The measurement of CAW was performed by the static drop method using the DSA 100 drop shape analysis system (KRÜSS, GmbH, Germany). The DSA 100 system consists of three units: a sample table with three mobile axes, a video camera and a dosing system, which is controlled by a special program. The device allows us to measure CAW by static and dynamic drop methods. A special needle is used in the static drop method; a drop of a certain volume is brought into contact with the measured surface. Then the needle rises, and the drop remains on the sample surface. The process is recorded by a video camera in macro mode. The shape of the drop is analysed using software and the CAW is calculated. The volume of a drop of distilled deaerated water is 1.5 μl, its rate of flow is 75–100 μl/min. The magnitude of the CAW depends on the method of sample preparation for analysis. Therefore, it is necessary to dwell on the preparation of the sample for analysis. The sample was separated from the plant residues and stones, sieved through a sieve <0.5 mm. Sifted sample was placed for 24 hours in an oven at a temperature of 45-50°C. Pieces of double-sided adhesive tape (0.5 x 0.5 cm in size) were glued to the slides. The prepared sample was applied on the adhesive layer of the tape in a smooth layer and gently pressed down with another slide with a load of 300 mg for 1 minute. To obtain the smoothest layer, the procedure was repeated several times.

The main research method was supplemented with the analysis of particle size and gross composition and sample analysis with methods of scanning electron microscopy (SEM analysis). To obtain comparable data, as in the case of determining the CAW, the fraction <0.5 mm was analyzed. The particle size distribution was determined by laser diffraction (volume distribution) on a particle size analyzer (Mastersizer 3000, United Kingdom). The gross composition of air-dry samples was determined by the X-ray fluorescence method (Pioneer S4, Bruker AXS, Germany) by the silicate method. SEM analysis was performed using VEGA 3 LMH (TESCAN, Czech Republic). Samples were prepared by spraying – Pt, magnification – up to 20000x. X-max 80 energy dispersive spectrometer (Oxford Instruments, United Kingdom) was used for the analysis of the elemental composition of the most representative sites.

3. Results and discussion
The adsorption of oil and petroleum products depends on the granulometric and chemical composition of the sediments. BS of the Kurcha-Murcha and the Amur Rivers and soil grounds of the study area are characterized by a close gross composition (Table 1). Since the territory of the site is
geomorphologically related to the channel of the Amur River, it is flooded during the floods and is under water for quite a long time.

For the same reason, the granulometric composition of the fine-grained sediments is close: the main fraction (250–500 μm) is 46–49% (Table 2). The exception is BS1 and BS3, which is associated with the hydrological features of the location of these points.

| Sample | SiO₂ | TiO₂ | Al₂O₃ | Fe₂O₃ | MnO | CaO | MgO | Na₂O | K₂O | P₂O₅ | S   |
|--------|------|------|-------|-------|-----|-----|-----|------|-----|------|-----|
| BS1    | 78.32| 0.32 | 9.95  | 5.53  | 0.10| 1.45| 0.75| 2.48  | 2.67| 0.33 | 0.15|
| BS2    | 89.17| 0.26 | 10.14 | 3.65  | 0.06| 0.88| 0.56| 2.36  | 2.91| 0.08 | 0.05|
| BS3    | 85.04| 0.39 | 11.84 | 3.04  | 0.06| 0.99| 0.66| 2.94  | 3.03| 0.08 | 0.02|
| BS4    | 84.19| 0.32 | 11.41 | 3.71  | 0.07| 1.30| 0.92| 2.82  | 3.17| 0.09 | 0.03|
| S1     | 87.73| 0.24 | 10.03 | 3.71  | 0.08| 1.06| 0.54| 2.37  | 2.90| 0.10 | 0.11|
| S2     | 90.77| 0.23 | 10.07 | 3.11  | 0.07| 0.97| 0.49| 2.34  | 2.92| 0.08 | 0.08|

Table 2. Particle size distribution of sediments, fraction <0.5 mm, %.

| Sample | Fraction size, μm | <1 | 1–5 | 5–10 | 10–50 | 50–250 | 250–500 | 500–1000 |
|--------|------------------|----|-----|------|-------|--------|---------|----------|
| BS1    |                  | 2.10| 10.61| 7.93 | 21.32 | 20.67 | 20.67  | 10.70    |
| BS2    |                  | 0.75| 4.38 | 2.82 | 6.32  | 20.69 | 47.31  | 17.72    |
| BS3    |                  | 1.80| 8.57 | 4.66 | 11.64 | 38.21 | 30.24  | 4.88     |
| BS4    |                  | 0.66| 3.94 | 2.43 | 4.31  | 30.00 | 43.27  | 13.20    |
| S1     |                  | 1.26| 6.55 | 3.80 | 9.36  | 19.11 | 45.53  | 10.30    |
| S2     |                  | 0.85| 4.31 | 2.43 | 4.31  | 27.79 | 48.51  | 10.16    |

The analysis of the CAW showed that oil and petroleum products at a concentration above 1000 mg/kg lead to a change in the wettability character of BS and ground soils: the CAW becomes much more than 90°. There is a significant change in the quality of the surface of the solid phase: from hydrophilic it turns into hydrophobic (hydrophilicity changes to hydrophobicity). The CAW practically does not change, remaining within 116–130°, with the considered contents of oil 2100–17600 mg/kg (Table 3). Note that the accuracy of determining the CAW by this method is 5°. Bottom sediments remain hydrophilic with oil content up to 1180 mg/kg (the CAW 63°). This value, up to the analysis, coincides with the recommended permissible level of oil content for soils of land.

| Sample | Oil products (mg/kg) | Level of pollution (Pikovsky, 1993) | CAW (degree) |
|--------|----------------------|-----------------------------------|--------------|
| BS1    | 17640                | dangerous                         | 130          |
| BS2    | 7590                 | dangerous                         | 121          |
| BS3    | 1180                 | moderate                          | 63           |
| BS4    | 3560                 | strong                            | 115          |
| S1     | 4560                 | strong                            | 128          |
| S2     | 2120                 | strong                            | 116          |

It is 1000 mg/kg in accordance with the document “Procedure for determining the extent of damage from land pollution by chemical substances” (approved by Roskomzem on November 10, 1993, and the Ministry of Natural Resources on November 18, 1993). Currently, in the Russian Federation there is no regulatory document that defines the MPC of pollutants in BS. According to the classification of Pikovsky [5], the content of oil products in the soil up to 100 mg/kg corresponds to “background”
concentration, 100–500 mg/kg – “increased background”, 500–1000 mg/kg – “moderate level” of pollution, 1000–2000 mg/kg – “moderately hazardous”, 2000–5000 mg/kg – “strong” and more than 5000 mg/kg – “dangerous” pollution. According to the data obtained, it can be argued with a high degree of confidence that for BS the permissible level of oil content is a value of 1000 mg/kg as for soils and ground soils.

According to the SEM data, at a given concentration, films of oil products are not fixed on the grains of primary minerals and filling the pores with oil products, as with high levels of pollution. In addition, at high levels of oil pollution, a significant increase in the content of Fe and Mn on the surface of oil films is diagnosed. As in polluted soils [6], ferruginous microaggregates and Fe-Mn nodules with high carbon up to 70 at.% content are formed. That is why BS1 is characterized by a high content of Fe₂O₃ and MnO.

4. Conclusion
The CAW (the contact angle of wetting) of river bottom sediments depends on the level of pollution with oil and petroleum products. A permissible level of oil content for bottom sediments is a value of 1000 mg/kg, as for soils and ground soils. The surface of the sediments remains hydrophilic – CAW is less than 90°. With a strong and dangerous level of pollution according to Pikovsky, the surface becomes substantially hydrophobic: the CAW increases to 110–120° and more.

5. References
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