Impact of oil on groundwater chemical composition

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Abstract. The objective of the paper is to characterize the chemical composition of groundwater samples from the monitoring wells drilled in the petrol station areas within the vicinity of Tomsk. The level of contamination has increased since many macro – and microcomponent concentrations (such as petroleum products, chlorine, sulphates, carbon dioxide and lead, etc.) in groundwater samples of the present study is higher than that in previous period samples.

Introduction
Currently, in the territory of Tomsk there are 119 petrol stations. The intense construction of filling stations, oil refineries, and oil depots within urban areas caused one of the major environmental problem, which is pollution of the geological environment with petroleum products (PP). A great number of works addressed the issue of assessing the degree of groundwater contamination with oil products. However, these studies do not have information on the hydrogeochemical analysis of the contaminated groundwater. In this regard, the assessment of the impact of petroleum products on the chemical composition of the groundwater is topical.

Materials and methods
To clarify the characteristics and the hydrogeochemical state of the groundwater contaminated with oil products, the materials obtained in the course of the present study were analyzed. The author studied chemical composition of the groundwater, sampled from the monitoring wells drilled in the areas of the filling stations in the city of Tomsk.

The background data used for comparison with the present study results are the average values of components contained in the groundwater of the river Tom floodplain, terraces, and watershed, which are represented in the materials by Tomskgeomonitoring [2, 3] and the paper by E.M. Dutova et al. [4].

Results and discussion
The values of major elements concentrations in contaminated groundwater are shown in tables 1 and 2. In the course of the research it was found out that the values of Quaternary horizon waters exceeded the limit values of oil products in all studied samples.

The maximum level of pollution (>7.0 mg/dm³) is characteristic of the oldest petrol station, namely, petrol station 3 and petrol station complex 28, with service life more than 30 years. Moreover, the PP concentration in the groundwater is determined by the lithological composition of the rocks composing the section of the unsaturated zone, as well as by the depth of the groundwater level, which
ensures a certain of protection. According to the method developed by V. M. Goldberg, protection of the groundwater in the areas of filling stations corresponds to categories I–III (from the lowest to medium).

In some samples, the values of lead and sodium exceeded the limit concentrations (table 2).

In case the petrol station and petrol complex were put in line after 2000 (for example, petrol complex 50 works since 2002), the content of lead in the groundwater is less than the maximum contaminant levels, which can be explained by the fact that since 1 July 2003, according to the national law, the production and distribution of leaded petrol are banned in the territory of the Russian Federation.

The results obtained are significantly different from the values characteristic for the groundwater of the river Tom floodplain, terraces, and watershed (beyond the areas of filling stations) (table 1). In the waters contaminated with oil products, pH values decreased in comparison with those in previous research samples, which signifies that the acidity increased. Chloride, sulphate, and free carbon dioxide are the components whose concentrations in the present samples are significantly higher than in the previous research ones.

### Table 1. Groundwater chemical composition.

| Components | Content (minimum – maximum) | Floodplain and river terraces | Watershed |
|------------|-----------------------------|-------------------------------|------------|
|            | Background data (number of samples) | Contamination with PP | Background data (number of samples) | Contamination with PP |
| pH         | mg/dm³ | 7.2 (1262) | 6.68-6.76 | 7.64 (488) | 5.91-6.15 |
| Na⁺        | mg/dm³ | 7.6 (1249) | 4.15-46 | 8.5 (483) | 5.27-40 |
| K⁺         | mg/dm³ | 1.11 (137) | 2.23-5.43 | 0.94 (87) | 2.22-5.1 |
| Ca²⁺       | mg/dm³ | 28.6 (1264) | 60-148 | 44.9 (487) | 18-24.2 |
| Mg²⁺       | mg/dm³ | 7.3 (1240) | 9.76-80.52 | 13.3 (483) | 1.22-3.54 |
| NH₄⁺       | mg/dm³ | 0.65 (1151) | 1.58-5.69 | 0.7 (473) | 0.53-2.44 |
| Cl⁻        | mg/dm³ | 5.3 (1263) | 19.5-101.2 | 3.5 (482) | 19.52-62.5 |
| SO₄²⁻      | mg/dm³ | 4.51 (513) | <2-27.6 | 2.69 (92) | <2-2.04 |
| NO₂⁻       | mg/dm³ | 0.3 (170) | 0.01-0.25 | 0.2 (91) | 0.025-0.112 |
| NO₃⁻       | mg/dm³ | 2.0 (269) | 0.51-2.46 | 1.0 (57) | 0.32-0.37 |
| HCO₃⁻      | mg/dm³ | 158.6 (1265) | 180-810 | 274.6 (487) | 42.7-98 |
| CO₂, as    | mg/dm³ | 17.1 (40) | 132-176 | 19.6 * | 35.2-61.6 |
| Total hardness | mg/EO/dm³ | 3.0 (1256) | 3.8-14 | 4.4 (486) | 1.0-1.5 |
| Mineralization | mg/dm³ | 97.5 (1256) | 303-1191 | 224 (461) | 91-233 |

### Conclusion

The results of the present study show that the groundwater in the areas of filling stations is contaminated with oil products due to poor environmental protection.

The concentrations of many components (such as petroleum products, chlorine, sulfates, free carbon dioxide and lead, etc.) in the present samples are significantly higher than those in the previous research samples.

Today, the monitoring wells are in the areas of 21 petrol stations and complexes, out of total 119 located in Tomsk. It is recommended that monitoring wells should be drilled in the areas of all Tomsk filling stations for groundwater sampling no less than twice per year.
**Table 2.** Chemical composition of groundwater contaminated with petroleum products (present study data).

| Components                      | Petrol station №28 | Petrol station №37 | Petrol station complex №64, well H-1 | Petrol station complex №64, well №9 | Petrol station complex №64, well №6 | Petrol station №60 | Petrol station complex №64, well №3 | Petrol station complex №64, well №50 | Petrol station №4 | Maximum contaminant level (in compliance with Sanitary rules and regulations 2.1.4.1074-01) |
|---------------------------------|--------------------|--------------------|---------------------------------------|--------------------------------------|--------------------------------------|-------------------|-------------------------------------|--------------------------------------|------------------|------------------------------------------------------------------------------------------|
|                                 | $Q_{\text{m}}$     | $Q_{\text{cd}}$    | $Q_{\text{m}}$                         | $Q_{\text{m}}$                        | $Q_{\text{cd}}$                      | $Q_{\text{m}}$    | $Q_{\text{cd}}$                      | $Q_{\text{m}}$                                      | $Q_{\text{cd}}$ |                                                                               |
| pH                              | 6.68               | 6.27               | 6.48                                  | 7.57                                 | 7.59                                 | 7.81              | 6.76                                | 5.91                                 | 6.15             | 8.67                                                                                      |
| Electrical conductivity, mS/cm  | 0.42               | 0.128              | 0.338                                 | 0.244                                |                                      |                   |                                     |                                      | 0.301            | 0.1                                                                                      |
| Bicarbonate – ion, mg/dm$^3$     | 180                | 61                 | 165                                   | 166                                  | 315                                  | 335               | 810                                 | 98                                  | 42.7             | 480                                                                                      |
| Carbonate ion, mg/dm$^3$         | <3                 | <3                 | <3                                    | <3                                   | <3                                   | <3                | <3                                  | <3                                   | 36               |                                                                           |
| Carbon dioxide, mg/dm$^3$        | 176                | 35.2               | 48.4                                  | 3.52                                 |                                      |                   |                                     |                                      | 37.84            | <3                                                                                     |
| Ammonium ion, mg/dm$^3$          | 5.69               | 0.1                | 0.33                                  | 0.066                                | 0.57                                 | 0.04              | 1.58                                | 2.44                                 | 0.53             | 0.41                                                                                     |
| Nitrite ion, mg/dm$^3$           | <0.01              | 0.037              | <0.01                                 | 0.25                                 | 0.19                                 | 2.43              | 0.025                               | 0.025                                | 0.112            | 0.09                                                                                     |
| Nitrate ion, mg/dm$^3$           | 2.46               | 0.25               | 0.14                                  | 0.59                                 | 9.2                                  | 4.04              | 0.51                                | 0.37                                 | 0.32             | 1.41                                                                                     |
| Sulfate ion, mg/dm$^3$           | 27.6               | 2.23               | <2                                    | <2                                   | 90                                   | 27.6              | <2                                  | <2                                   | 2.04             | <2                                                                                       |
| Chloride ion, mg/dm$^3$          | 19.5               | 19.5               | 64                                    | 23.1                                 | 510                                  | 49                | 101.2                               | 62.5                                 | 19.52            | 254                                                                                      |
| Phosphate ion, mg/dm$^3$         | 0.03               | <0.01              | <0.01                                 | 0.001                                | 0.003                                | 0.005             | 0.014                               | <0.01                                | <0.01            | 0.01                                                                                     |
| Total hardness, mg-EQ/dm$^3$     | 3.8                | 1.1                | 3.7                                   | 1.4                                  | 6.6                                  | 2.44              | 14                                  | 1.5                                  | 1.0              | 8.3                                                                                      |
| Calcium, mg/dm$^3$               | 60                 | 20                 | 44                                    | 24                                   | 95                                   | 39                | 148                                 | 242                                  | 18               | 80                                                                                       |
| Magnesium, mg/dm$^3$             | 9.76               | 1.22               | 18.3                                  | 2.44                                 | 22.73                                | 7.83              | 80.52                               | 3.54                                 | 1.22             | 52.46                                                                                   |
| Sodium, mg/dm$^3$                | 4.15               | 10.3               | 17.1                                  | 4.0                                  | 330                                  | 111               | 46                                  | 40                                  | 5.27             | 197                                                                                      |
| Potassium, mg/dm$^3$             | 2.23               | 1.33               | 2.5                                   | 9                                    | 19                                   | 7.34              | 5.43                                | 5.1                                  | 2.22             | 4.1                                                                                      |
| Iron, total, mg/dm$^3$           | 681                | 124.5              | 69.1                                  | 31.65                                | 18.87                                | 257.7             | 137.7                               | 55.86                                | 27.2             | 46.55                                                                                   |
| Mineralization on the amount of  |                    |                    |                                       |                                      |                                      |                   |                                     |                                      |                  |                                                                               |
| salts, mg/dm$^3$                 | 303                | 116                | 311                                   | 264                                  | 1382                                 | 574               | 1191                                | 233                                 | 91               | 1104                                                                                     |
| Oil, emulsion, mg/dm$^3$         | 2250               | 1.75               | 0.54                                  | 0.298                                | 0.601                                | 0.915             | 0.833                               | 7.41                                 | 4.8              | 27.5                                                                                     |
| Oil, vol %                      | 7.98               |                    |                                       |                                      |                                      |                   |                                     |                                      |                  |                                                                               |
| Lithium, mg/dm$^3$               | 0.003              | 0.002              | 0.007                                 | 0.001                                | 0.0012                               | 0.0009            | 0.005                               | 0.005                                |                  | 0.03                                                                                     |
| Zinc, mg/dm$^3$                  | 0.22               | 0.05               | 0.5                                   | 0.22                                 | 0.11                                 | 0.58              | 0.36                                | 0.089                                | 0.068            | 0.26                                                                                     |
| Cadmium, mg/dm$^3$               | <0.0002            | <0.0002            | <0.0002                               | <0.0002                               | <0.0002                               | 0.00056           | <0.0002                             | <0.0002                             | 0.0009           | 0.0001                                                                                   |
| Lead, mg/dm$^3$                  | 0.21               | 0.018              | 0.05                                  | 0.038                                | 0.0045                                | 0.029             | 0.076                                | 0.0045                               | 0.0059           | 0.0092                                                                                   |
| Copper, mg/dm$^3$                | 0.52               | 0.029              | 0.11                                  | 0.06                                 | 0.022                                 | 0.19              | 0.056                                | 0.2                                 | 0.024             | 0.57                                                                                     |
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