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Abstract

Karst rocks are well developed on the Earth and occupy its vast territories. Groundwater of karst areas is weakly protected from oil pollution, and the remediation of contaminated groundwater is difficult and costly. The main tasks of our study were the development of the strategy of remediation of oil-polluted groundwater at karst region of the Polaznenskoe oil deposit (the Western Urals, Russian Federation), where an oil lens (thickness up to 2–3 m) was formed within karst rocks on the surface of water table and became a source of pollution of the Kama river reservoir. Two-staged strategy of remediation was proposed and used. The first stage included the “mechanical” technique of remediation, the second one – biochemical destruction of water-dissolved oil using oil-degrading bacterial preparation. About 12 m³ of oil-products was pumped out the oil lens, and *approx.* fourfold decrease of n-alkanes within oil layer was achieved after 3 months of the biochemical remediation.

Keywords

Karst • Groundwater • Oil pollution • Water reservoir • Remediation

86.1 Introduction

Karst rocks, such as limes and gypses, are well developed on the Earth and occupy ~31.5 % (47,000,000 km²) of its surface. These rocks are weakly protected from oil pollution (Maksimovich and Bykov 1978). Regions of karst development have some features, creating peculiar conditions of oil pollution distribution—elevated rocks fracturing and permeability of rocks, vertical zonality of water exchange rate. Lithological composition of karst rocks have an indirect impact on oil pollution—it mainly determines the type and

mineralization of groundwater, which in turn both influence on migration capability of oil products and determine the distribution conditions and the scale of pollution (for example, an increase in water salinity decreases the solubility of oil in water). Specific terms of oil pollution are created within the karst coast of water reservoirs, where seasonal fluctuations of water table significantly affect the water hydrodynamics and distribution of pollution, that lead to pollution of surface waters in large parts of water reservoirs (Maksimovich and Meshcheryakova 2009).

Techniques of remediation of oil-polluted surface ecosystems are well developed. The groundwater of highly karstified territory is very susceptible to pollution, and the remediation of contaminated groundwater is difficult and costly. In general, it is considered that polluted groundwater contains acclimated microbial populations capable to transform polluting substances under existing redox conditions (Ghiorse and Wilson 1988; Kaiser and Bollag 1990; Kolbel-Boelke et al. 1988).

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The Perm region (the Western Urals, Russian Federation) is one of the areas of oil deposits development. These deposits occupy vast territories, the third part of them are disposed in karst areas. A considerable number of deposits is located within the drainage area of the Kama river (Gorbunova et al. 1992). The Polaznenskoe oil deposit is an example of such one, and groundwater of this region is weakly protected from oil pollution due to the intense karst development. Early investigations revealed the presence of oil lens on the surface of water table within karst rocks of Kama reservoir coast, and this lens was the permanent source of pollution of reservoir's water with oil (Maksimovich et al. 2005).

The main tasks of our study were the development of the strategy of remediation of oil-polluted groundwater at karst region of the Polaznenskoe oil deposit, and the probation of this strategy in situ.

86.2 The Description of Studied Site

The Perm region (the Western Urals, Russian Federation) occupies an area of about 160,000 km². The karstified rocks, i.e., limestone, dolomite, gypsum, anhydrite, and paleozoic rock salt, are either exposed or lie close to the surface in the area of about 30,000 km². The Perm region is one of the areas of oil deposits development. Oil deposits are distributed on the significant part of its territory. A considerable number of them is located within the drainage area of the Kama river, where the groundwater is weakly protected from pollution due to the intense karst development. Contaminated groundwater discharges to the water reservoir and causes a significant pollution of water reservoir and adjacent environments (Buzmakov and Kostarev 2003; Maksimovich et al. 2005).

The studied area is situated in the central part of Perm region within the Polaznenskiy site of Polaznenskiy karst region (gypsum and carbonate-gypsum karst developed predominantly). This area encloses the left coastal side of the Kama water reservoir (Fig. 86.1). Karst development in the region was promoted by the formation of Kama water reservoir in 1954, which induced the water level rise in 20–22 m. 1691 karst forms were mapped within the area of 281 km² in 2010 year, 97 % of them were sinkholes. Other surface karst forms, such as karrs, karst trenches, hollows, gullies, dry river channels and lakes were also registered. The existing karst forms are renewed and new ones appear. The bulk of karst cavities occurs within the zone of seasonal fluctuation of fractural-karst water, where dissolution of rocks developed most intensely.

The studied site is specified by a number of peculiar features caused by karst development, which favor the contamination of the groundwater with oil products. Above all, the surface runoff is virtually absent. Atmospheric

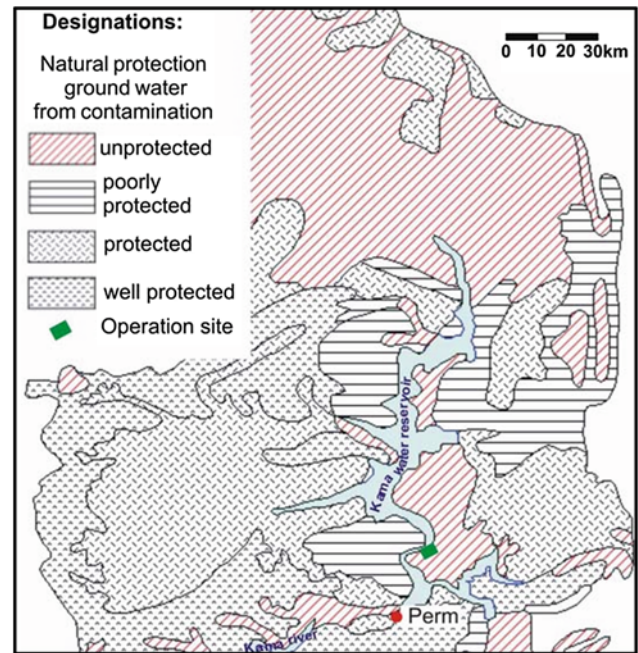


Fig. 86.1 Scheme of natural protection of ground water from pollution (Maksimovich et al. 2005), and location of studied area

precipitations as well as oil spills are freely absorbed by rock fractures, funnels, depressions, and other karst forms to feed aquifer soon. This is a specific feature of the given oil deposit area. At other oil deposit areas, where the environmental conditions are different, the oil spills firstly contaminate the surface water, soil, and rocks in the aeration zone, and groundwater last. Under significant oil spills fractured zones and cavities can turn to reservoirs of oil and contribute to formation of technogenic deposits (Gorbunova and Maksimovich 1991). So, during 50-years period of Polaznenskoe oil deposit exploitation the oil lens (thickness up to 2–3 m) was formed within karst rocks on the surface of water table and became a source of pollution of the Kama river reservoir. The investigation reveals that the most probable and basic source of formed oil lens were spills and discharges of oil on the ground surface during initial stages of deposit exploitation (Maksimovich et al. 2005). Numerous attempts to remediate oil polluted karst rocks in this site during last 35 years had no success (Buzmakov and Kostarev 2003).

86.3 The Strategy of Remediation

Taking into accounts complicated geological and environmental conditions at studied site, two-staged strategy of pollution control was proposed and used. The first stage included the “mechanical” technique of remediation: the pumping oil

out the lens using specially constructed device. The second stage included the biochemical destruction of water-dissolved oil and oil film on water table using oil-degrading bacterial preparation and activation of indigenous oil-degrading bacteria in groundwater. The second stage, in turn, consists of several phases: the isolation of indigenous active hydrocarbon-degrading bacteria from karstic groundwater and the study of their degrading capability; the development of bacterial preparation, based on isolated hydrocarbon-degrading bacteria; the stimulation of groundwater hydrocarbon-degrading microflora by inorganic nutrients supplements; and the introduction of developed bacterial preparation into groundwater to achieve more significant (if not complete) oil removal. It must be noted that the introduction of actively metabolizing hydrocarbon-degrading bacteria into polluted environments seems to be essentially actual in regions of cold and temperate climate, where warm season is not long.

86.4 The Results of Remediation

The special device to pumping oil out the oil lens was constructed (Patent RU 81522) and applied at studied site. Detectors of oil lens' depth and thickness, mounted on the device, allowed to decrease the lens thickness to *approx.* 0.1 m after pumping out. About 12 m³ of oil-products was pumped out at this stage.

Microbiological investigation of karstic groundwater revealed the presence of active hydrocarbon-degrading bacteria, which were used for bacterial preparation (Patent RU 2312719). We introduced bacterial preparation and mineral supplements in groundwater every week during summer months. To monitor the remediation processes the special sampler was constructed (Patent RU 54398), and the samples of groundwater and oil were retrieved on infra-red spectroscopic (IRS) and gas-liquid chromatographic (GLC) analyses before and after the biochemical stage of the remediation.

IRS and GLC analyses revealed a decrease in total n-alkanes concentration ($\Sigma n - C_{12} - 34$) within oil layer on water table. The changes in n-alkanes ratios ($\Sigma n - C_{15} - 18 / \Sigma n - C_{19} - 22$, $\Sigma n - C_{17} - 23 / \Sigma n - C_{24} - 30$, $\Sigma n - C_{<21} / \Sigma n - C_{>20}$) showed that bacteria metabolized oil hydrocarbons of small and medium molecular weight without any preference of "even" or "odd" n-alkanes.

As a whole, *approx.* fourfold decrease of n-alkanes within oil layer was achieved after 3 months of the biochemical remediation.

86.5 Conclusions

Mechanism of contamination of the water reservoir with oil became quite complicated in the presence of karst rocks and requires a special strategy for the implementation of environmental protection measures.

The combination of mechanical and biochemical methods accelerates the remediation of contaminated groundwater in karst rocks.

We assume that the special effects from the use of proposed remediation strategy could be expected in solving of more difficult task—the remediation of karst rocks of reservoir's coast in the zone of seasonal fluctuations of water table from the sorbed oil.

This work was financially supported by the Russian Foundation for Basic Research (project "Ural-2004" no. 04-05-96039).

References

- Buzmakov SA, Kostarev SM (2003) Human-induced changes in environmental components in oil-producing regions of Perm region. Perm State University, Perm, p 171 (in Russian)
- Ghiorse WC, Wilson JT (1988) Microbial ecology of the terrestrial subsurface. *Adv Appl Microbiol* 33:107–172
- Gorbunova KA, Maksimovich NG (1991) Technogenic influence on karst territories of Perm region. *Geogr Nat Resour* 3:42–46 (in Russian)
- Gorbunova KA, Andreychuk VN, Kostarev VP, Maksimovich NG (1992) Karst and caves of Perm region. Perm State University, Perm, p 200 (in Russian)
- Kaiser J-P, Bollag J-M (1990) Microbial activity in the terrestrial subsurface. *Experientia* 46:797–806
- Kolbel-Boelke J, Anders E-M, Nehrkorn A (1988) Microbial communities in the saturated groundwater environment. II: diversity of bacterial communities in a pleistocene sand aquifer and their in vitro activities. *Microbiol Ecol* 16:31–48
- Maksimovich GA, Bykov VN (1978) Karst of carbonate oil- and gas-bearing massifs. Perm State University, Perm, p 96 (in Russian)
- Maksimovich NG, Meshcheryakova OYu (2009) Methods of dealing with oil pollution of the karst coast of water reservoirs. *Ecol Urban Territ* 4:55–58 (in Russian)
- Maximovich NG, Kazakevich SV, Hmurchik VT (2005) Development of methods protection of the Kama reservoir from oil pollution. In: Quality and management of water resources: Proceedings of the 3rd Symposium. St. Petersburg, pp 362–369