Abdul Shakoor
Kerry Cato *Editors*

IAEG/AEG Annual Meeting Proceedings, San Francisco, California, 2018—Volume 3

Mining, Aggregates, Karst

Springer

Abdul Shakoor • Kerry Cato
Editors

IAEG/AEG Annual Meeting Proceedings, San Francisco, California, 2018—Volume 3

Mining, Aggregates, Karst

Springer

Editors
Abdul Shakoor
Department of Geology
Kent State University
Kent, OH, USA

Kerry Cato
Department of Geological Sciences
California State University
San Bernardino, CA, USA

ISBN 978-3-319-93129-6 ISBN 978-3-319-93130-2 (eBook)
https://doi.org/10.1007/978-3-319-93130-2

Library of Congress Control Number: 2018947486

Cover illustration: Golden Gate Bridge at night. Frederic Prochasson © 123rf.com

This Springer imprint is published by the registered company Springer Nature Switzerland AG
The registered company address is: Gewerbestrasse 11, 6330 Cham, Switzerland

Bacterial Processes in Oil-Polluted Karst Environments in Perm Region (Russian Federation)

Nikolay Maksimovich, Olga Meshcheriakova, and Vadim Khmurchik

Abstract

Rocks and groundwater of karst areas are weakly protected from any pollution. The most common pollutants within them are oil hydrocarbons. Microbial populations of karst rocks and groundwater are able to degrade a large number of contaminants under the existing redox conditions, often used in biotechnological methods of remediation. The authors investigated oil polluted karst territories of the Perm region (Russian Federation) to develop methods of remediation. Two sites of karst rocks and groundwater with different redox conditions and impacted by oil and oil-products were studied. Aerobic hydrocarbon-oxidizing bacterial processes occured in the first site, and this paper describes the complex method of mechanical and microbiological cleaning to achieve complete oil removal. Anaerobic degradation of oil hydrocarbons during sulfate reduction process was detected in the second place. One of the products of this process, hydrogen sulfide, is very toxic to water fauna but readily oxidative in air. The authors recommend constructing special oxidizing and precipitating ponds to improve the environment.

Keywords

Karst rock • Oil pollution • Hydrocarbon-oxidizing bacteria • Bacterial sulfate reduction • Remediation

N. Maksimovich · O. Meshcheriakova (✉) · V. Khmurchik
Institute of Natural Sciences of Perm State, Natural Research University, 15 Bukireva St., Perm, 614990, Russia
e-mail: olgam.psu@gmail.com

N. Maksimovich
e-mail: nmax54@gmail.com

V. Khmurchik
e-mail: khmurchik.vadim@mail.ru

1 Introduction

Karst rocks, such as limestone and gypsum, are well developed on the Earth and occupy its vast territories (approx. 31.5% or 47,000,000 km^2). Rocks and groundwater of karst areas are weakly protected from any pollution, and the remediation of them is difficult and costly. The most common pollutants of groundwater are hydrocarbons and other compounds of oil and oil products. Microbial populations of groundwater are active in situ and able to degrade a large number of contaminants under the existing redox conditions. The presence of sufficient electron acceptors is a principal factor in the degradation of organic contaminants. There are two main biotechnological methods of oil polluted natural habitats remediation: the first one is stimulation of natural microbial hydrocarbon-degrading populations by nutrient supplies (especially N and P), and the second method is introduction of active hydrocarbon-degrading bacteria (and nutrient supplies) into polluted environments in regions of cold and temperate climate, where the warm season is not long (Koronelli 1996). It is known that bacterial populations can utilise oil and oil products both in aerobic and anaerobic conditions. The capability of some bacteria to metabolize hydrocarbons in the absence of molecular oxygen was first recognized about 20 years ago. Since then, the number of hydrocarbon compounds shown to be catabolized anaerobically by bacterial cultures has been steadily increasing. Anaerobic degradation of oil and oil products proceeded during nitrate-reducing (Callaghan et al. 2009), denitrifying (Rabus et al. 2001), iron-reducing (Dawn et al. 2011), sulphate-reducing (Dorota and Borkowski 2007), and methanogenic (Aitken et al. 2013) bacterial processes. So, mentioned bacterial groups could be used to remediate oil polluted natural habitats. However, some products of these bacterial processes are environmentally toxic, i.e. hydrogen sulphide, the product of sulfate reduction process, therefore thorough study of conditions and environmental engineering of additional measures is needed.

A. Shakoor and K. Cato (eds.), *IAEG/AEG Annual Meeting Proceedings, San Francisco, California, 2018—Volume 3*, https://doi.org/10.1007/978-3-319-93130-2_15

The aim of our study was to research oil polluted karst territories of the Perm region (Russian Federation) and to develop methods of remediation.

We studied two sites of karst rocks and groundwater polluted with oil and oil products and differed in redox conditions.

2 General Characteristics of the Region Karst

Karst rocks such as limestone, gypsum and salt occur within vast areas of the Western Urals (Russian Federation). Modern and ancient karst is widespread there. Three geological structures are presented in this area: the eastern margin of the East European Platform, the CisUrals Foredeep and the Urals' Folded Zone. Sulphate karst and to a lesser extent carbonate karst occur mainly on the Platform. Salt and gypsum karst developed in the CisUrals Foredeep, whereas dolomite and limestone karst, and somewhere marble karst, are registered in the Urals' Folded Zone. Karst rocks are covered by eluvial and deluvial deposits, and overlapped in river valleys by alluvial deposits or non-karstic rocks of a relatively small thickness. Seldom karst rock remains uncovered.

The territory of the Western Urals undergoes strong technogenic impact, which alters significantly the conditions and factors of karst development due to irreversible transformation of relief and rocks, pollution of surface and groundwater, and vegetation degradation.

The Perm region occupies an area of about 160,000 km^2. The karstified rocks, i.e., paleozoic limestones, dolomites, gypsums, anhydrites, and rock salts, are either exposed or lie close to the surface in the area of about 30,000 km^2. The Perm region is one of the areas where oil deposits are development also—oil deposits are distributed in a large part of its territory. A considerable number of oil deposits are located on the catchment area of the Kama River and it tributaries (see Fig. 1). In this area, the groundwater is poorly protected from oil and oil products pollution due to the intense karst development. Karst regions have some features, creating peculiar conditions of oil pollution distribution due to rock 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 chemical 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). Contaminated karst groundwater discharges to rivers which results in pollution of the river and adjacent areas.

3 Aerobic Oxidation of the Oil in Karst Rocks

The first studied site is situated in the Polazninskiy karst area of gypsum and carbonate-gypsum karst in central part of the Perm region. This area encloses the left coastal side of the Kama water reservoir. Karst development in the region was promoted by the formation of the Kama water reservoir in 1954, which induced the water level rise of 20–22 m. 1691 karst forms are found on the area of 28.1 km^2, 97% of them are sinkholes. Other karst forms, such as karrs, karst trenches, hollows, gullies, dry river channels and lakes also occur within this area. The relative average density of karst forms reach 60 per km^2. The existing karst forms are renewed and new ones appear. The bulk of karst cavities occur within the zone of seasonal fluctuation of fractural-karst water, where dissolution of rocks develop most intensely (Milanovic 2000; Pecherkin 1969).

There are oil deposits beneath the banks of the Kama water reservoir. During a 50-year period of oil deposit exploration the oil lens (thickness up to 2–3 m) was formed within karst rocks on the surface of the water table and became a source of pollution of the Kama water reservoir. Investigations revealed 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.

There is a direct connection between the karstic groundwater water table and the Kama water reservoir level: fluctuations of water level in the Kama water reservoir induce the karstic groundwater movement into rock massif and backward in the reservoir, that is favourable to maintain aerobic redox conditions in groundwater. Oxidative weathering and bacterial degradation of lens' hydrocarbons as well as the fluctuation of water table within karst massif led to the formation of bituminous film on the walls of the lens containing cavity, which prevents the direct flow of lens' hydrocarbons to the Kama water reservoir. Water-dissolved oil products discharge as springs to the reservoir freely. The intensity of discharge is controlled by the level of water in the Kama water reservoir (see Fig. 2).

To improve the ecological situation the technology of mechanical and microbiological cleaning of polluted waters was utilized, consisting of the pumping oil out of the lens using a special technique and the biochemical destruction of oil using the natural biodegradation based on activation of

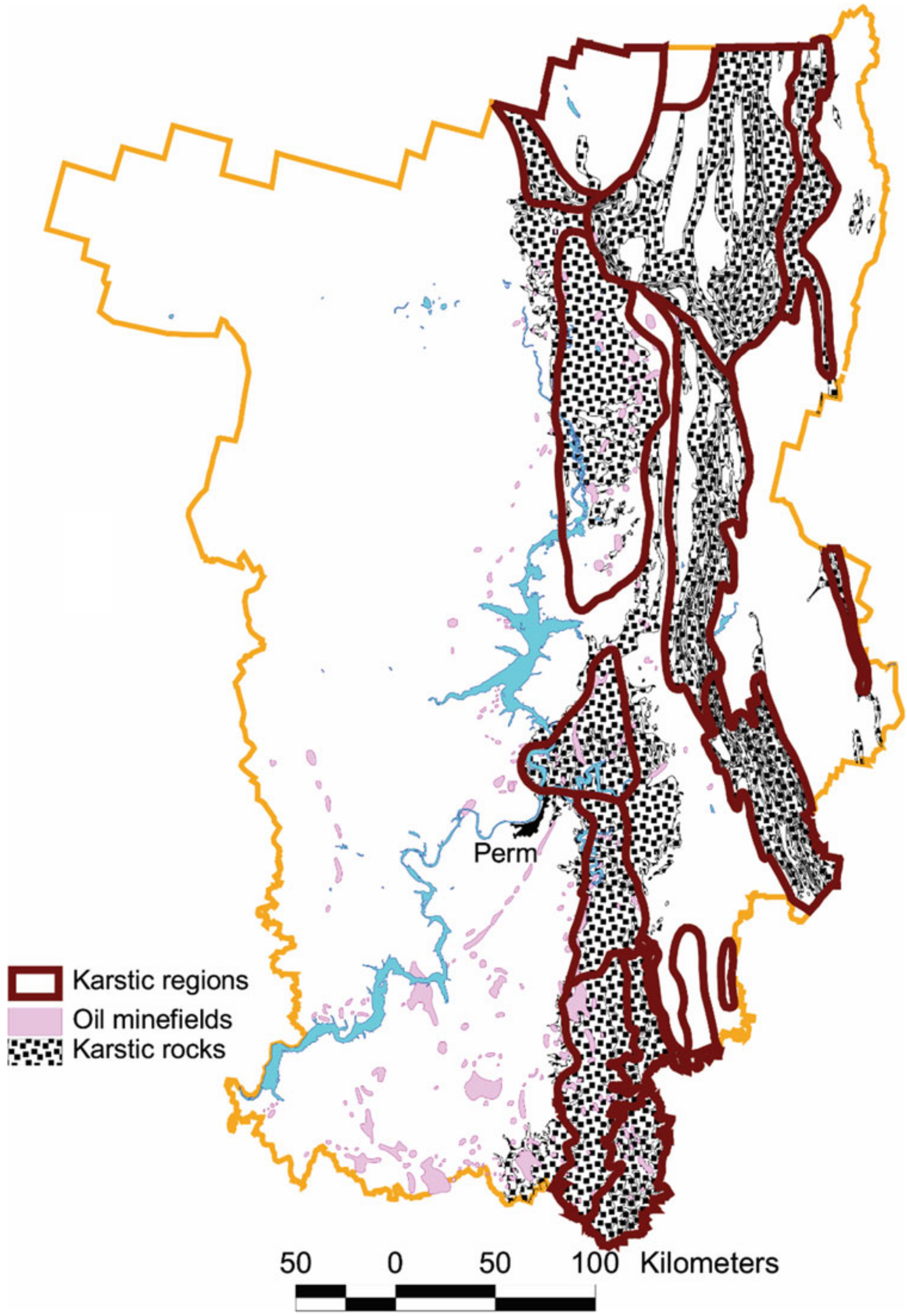

Fig. 1 Karst territories in Perm Region

aerobic oil-degrading bacteria in groundwater. The work consisted of several stages: the isolation of active hydrocarbon-oxidizing bacteria from karstic groundwater and the study of their oil degrading capability; the development of bacterial preparation based on isolated hydrocarbon-oxidizing bacteria; the stimulation of groundwater hydrocarbon-oxidizing microflora with inorganic nutrients supplies; and the introduction of developed bacterial preparation into groundwater to achieve complete oil removal (Maximovich and Khmurchik 2009).

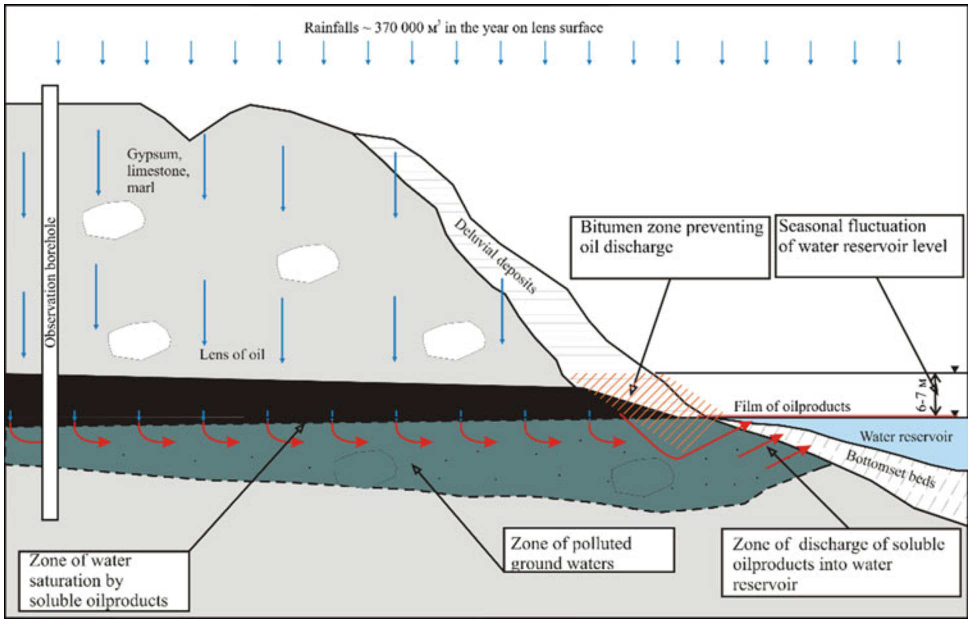

Fig. 2 Mechanism of pollution of the Kama water reservoir by oil products in the Polazninskiy karst area

4 Anaerobic Oxidation of the Oil in Karst Rocks

The second studied site is situated in the Irensky karst district in the south part of the Perm region. Forms of karst in the district are diverse. Karst depressions concentrate surface runoff and feed karst groundwater, which in turn discharges to rivers. Karst rivers are typical to the Irensky karst district, most of them are tributaries of the Iren river. Effluents of these rivers are represented by the karst springs arising at the foot of the gypsum rocks (Gorbunova et al. 1992). The Turaevka and the Kamenka karst rivers flow on the territory of the Irensky karst district. Part of the riverbeds are underground and discharge as karst springs. The Kokuyskoye oil deposit occupies part of the territory of the Irensky karst district, its oil-producing wells are located in the catchment area of the Turaevka and the Kamenka rivers.

Until the 1990s the water in the rivers was clean and used as potable. Numerous accidental spills of oil and technical fluids on the surface and leaks of oil through broken sides of oil-producing wells led to pollution of karstified rocks with oil and oil products. Now water of the Turaevka and the Kamenka rivers contains saturated and unsaturated hydrocarbons, hydrocarbon acids, ethers, alcohols, and halogenated derivatives. The bottom of the rivers are covered with a thin layer of dark brown oil tar for tens of meters downstream from their discharges from the rocks, and subaqual springs in the riverbeds periodically discharge. A strong smell of hydrogen sulfide comes from the water of these rivers, as well as the deposition of elemental sulfur covers the underwater part of the river plants.

In our opinion, these features indicate the development of bacterial sulfate-reducing process where oil hydrocarbons serve as carbon and energy sources to bacteria. So, there is natural bioremediation process developed under anaerobic environmental conditions. These conditions established in the underground part of riverbeds after the depletion of water-dissolved oxygen in oxidative processes. The product of bacterial sulfate-reducing process, hydrogen sulphide, is very toxic to river fauna, but readily oxidizable on air. The product of hydrogen sulphide oxidation is elementary sulphur undissolved in water. Therefore we recommended construction of oxidizing and precipitating ponds downstream of the rivers' discharges from the rocks to improve the environment.

5 Conclusion

Karst territories occupy approximately one third of the Earth surface. Karst rocks and water are weakly protected from any pollution, including from the surface. The remediation of karst territories is often technically difficult and expensive.

Karst rocks and water contain natural bacterial populations, which could degrade a great number of various pollutants. The most common pollutants of karst rocks and water are hydrocarbons and other compounds of oil especially in oil industry regions.

As natural bacterial populations can degrade oil and oil products both in aerobic and anaerobic conditions, environment oil pollution of any origin—natural, man-made or both—could cause the activation of aerobic or anaerobic microflora of water and rocks. So, this capability of natural bacteria could be used in bioremediation technologies. However, some products of these bacterial processes could be environmentally toxic, therefore thorough study of environment conditions and engineering of additional measures could be needed.

Authors studied two sites of oil polluted karst territories of the Perm region (the Western Urals, Russian Federation). Aerobic bacterial degradation of oil products occurred at the first studied site and anaerobic one at the second site. The complex method of mechanical and biotechnological remediation of the first site was elaborated: a bulk of oil was eliminated with pumping; natural hydrocarbon-oxidizing bacterial populations were stimulated with inorganic nutrients supplies; hydrocarbon-oxidizing bacteria were isolated and bacterial preparation was made and applied to achieve complete oil removal. Recommendations on engineering of additional constructions were made to improve the environment at the second studied site.

Acknowledgements Work was financially supported by the RFBR (project 16-35-00104 mol_a).

References

Aitken, C.M., Jones, D.M., Maguire, M.J., Gray, N.D., Sherry, A., Bowler, B.F.J., Ditchfield, A.K., Larter, S.R., Head, I.M.: Evidence that crude oil alkane activation proceeds by different mechanisms under sulfate-reducing and methanogenic conditions. Geochim. Cosmochim. Acta **109**, 162–174 (2013)

Callaghan, Amy V., Tierney, M., Phelps, C.D., Young, L.Y.: Anaerobic biodegradation of n-hexadecane by a nitrate-reducing consortium. Appl. Environ. Microbiol. **75**(5), 1339–1344 (2009)

Dawn, H.E., Risso, C., Smith, J.A., Lovley, D.R.: Anaerobic Oxidation of Benzene by the hyperthermophilic archaeon *Ferroglobus placidus*. Appl. Environ. Microbiol. **77**(17), 5926–5933 (2011)

Dorota, W., Borkowski, A.: The geomicrobiological role of sulphate-reducing bacteria in environments contaminated by petroleum products. Geomicrobiol. J. **24**(7–8), 599–607 (2007)

Gorbunova, K.A., Andreichuk, V.N., Kostarev, V.P., Maximovich, N. G.: Karst and caves in Perm region. Perm University Publishing House, Perm, 200 p. (1992) (in Russian)

Koronelli, T.V.: The principles and methods of intensification of biological degradation of hydrocarbons in environment (review). Appl. Biochem. Microbiol. **32**(6), 579–585 (1996) (in Russian)

Maximovich, N.G., Khmurchik, V.T.: Groundwaters clarification experience from oil pollution by biological methods. Ind. Saf. Ecol. **4**(37), 34–36 (2009)

Milanovic, P.T.: Geological in Karst: dams, reservoirs, grouting, groundwater protection, water tapping, tunneling. Zebra, Belgrad, 347 p. (2000)

Pecherkin, I.A.: Geodynamics of the coasts of the Kamsky reservoirs, vol. 2. Geological processes, Perm, 308 p. (1969) (in Russian)

Rabus, R., Wilkes, H., Behrends, A., Armstroff, A., Fischer, T., Pierik, A.J., Widdel, F.: Anaerobic initial reaction of n-alkanes in a denitrifying bacterium: Evidence for (1-methylpentyl) succinate as initial product and for improvement of an organic radical in n-hexane metabolism. J. Bacteriol. **183**(5), 1707–1715 (2001)