



Does phosphate enhance the natural attenuation of crude oil in groundwater under defined redox conditions?



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ARTICLE INFO

Article history:

Received 30 October 2013

Received in revised form 11 February 2014

Accepted 9 April 2014

Available online 18 April 2014

Keywords:

La Crau nature reserve

Enhancement

Nutrients

Hydrocarbons

Aquifer

Microcosms

ABSTRACT

After a crude oil spill caused by a broken pipeline in 2009 to a gravel aquifer in southern France, degradation processes under various redox conditions progressively established, but at rates that predict a long life-time of the source under natural attenuation after partial source removal. In this study, we aimed at identifying the rate-limiting factors for each redox condition, with special emphasis on phosphate as limiting nutrient. The study was conducted in laboratory microcosms assembled with material collected on site: sediments, water from monitoring wells, oil and microbial sludge. Redox conditions were promoted by adding electron acceptors (either oxygen, nitrate, limonite (FeO(OH)), cryptomelane (K(Mn⁴⁺, Mn²⁺)₈O₁₆), or sulfate). For each condition, the role of phosphate was studied by repeated additions for up to 290 days. The results showed a very strong stimulation of aerobic and denitrifying rates of oil degradation by phosphate, provided that oxygen and nitrate were repeatedly supplied. Phosphate caused also a marked stimulation of methanogenic degradation, and a relatively small stimulation of metal reduction. These anaerobic processes started only after marked lag phases, and phosphate shortened the lag phase for methanogenic degradation. Degradation of aromatic and aliphatic hydrocarbons with less than 8 carbons, including benzene, was confirmed even under unstimulated conditions. It is concluded that degradation rates at the site are limited by both, availability of electron acceptors and availability of phosphate needed for promoting microbial growth.

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1. Introduction

Ground-water contamination by crude oil, and other petroleum-based liquids, is a widespread problem. Although many remediation techniques exist, residual contamination persists after incomplete or inexistent source removal, and natural attenuation occurs. At monitored sites, researchers have gained a good comprehension of processes that control the fate of spilled crude oil. The crude-oil spill site near Bemidji is one of the best characterized sites of its kind in the world (Essaid et al., 2011). At Bemidji, biogeochemical processes have now been studied for more than 30 years,

and the following major insights were gained: 1) spontaneous evolution of sequenced redox processes evolves, leading to distinct spatial redox zones; 2) the availability of electron acceptors is a major limiting factor for overall oil degradation; and 3) it takes decades for complete oil removal.

On August 7, 2009 five hectares of land surface and shallow subsurface in a nature reserve of restricted access 50 km northwest of Marseille, south of France, was contaminated by 5100 m³ of crude oil (Russian Express) due to the sudden break of a pipeline. Despite immediate cleanup efforts, the most important regional aquifer had been contaminated by gravitational transport of >200 m³ of crude oil through the 10 m thick unsaturated zone. Monitored natural attenuation is currently an option for site treatment after completion of physical remediation by dual-phase extraction, but duration of

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decades is not well accepted. Recently, Barbieri et al. (2011) have shown how each aquifer redox condition can be induced in laboratory microcosms and how then the factors controlling processes can be studied. Therefore, a microcosm study has been initiated to investigate possibilities of enhancement of natural attenuation under defined redox conditions.

In groundwater, nitrate is usually available as a source of nitrogen (N) whereas phosphorus (P) is often a limiting nutrient. Studies have investigated the stimulation potential of N and P, (Dibble and Bartha, 1979) or the consequences of N-limited environment (Allen-King et al., 1994, 1996) on aerobic petroleum hydrocarbon biodegradation. Mills and Frankenberger (1994) evaluated organic and inorganic P sources to promote aerobic bioremediation of diesel fuel. Addition of inorganic P sources can result in precipitation with cations making the P unavailable to the microbes whereas organic P sources need to be mineralized to be available. They showed that diethylphosphate had the higher stimulatory effect compared to potassium phosphate K_2HPO_4 . Bregnard et al. (1996) studied the effect of phosphate on degradation of weathered diesel fuel under aerobic and denitrifying conditions and found that oxygen consumption rates were stimulated by factors of 2–3, and that NO_3^- consumption rate in absence of O_2 was 37% higher when phosphate was added. To the best of our knowledge, no studies investigated whether P can stimulate rates of anaerobic petroleum hydrocarbons biodegradation under other redox conditions.

Several studies conducted at Bemidji revealed that phosphate- and iron-bearing minerals were attacked by microorganisms. Hiebert and Bennett (1992) performed an in situ microcosm study of the influence of surface-adhering bacteria on quartz and feldspar diagenesis. They showed that minerals were colonized by indigenous bacteria and chemically weathered at a rate faster than theoretically predicted. Another in situ microcosm study revealed that native organisms preferentially colonized feldspars that contain trace P as apatite inclusions (Bennett et al., 2000). These feldspars weathered rapidly, whereas nearby feldspars without trace P were uncolonized and unweathered. Rogers and Bennett (2004) addressed the question of whether the microbial community benefits from release of minerals during weathering. Their study showed that in microcosms containing silicates and glasses with trace phosphate mineral inclusions microbial biomass increased, indicating that the microbial community can use silicate-bound phosphate inclusions. They proposed that microorganisms may use organic ligands to dissolve the silicate matrix and access these otherwise limiting nutrients. Bekins et al. (2005) studied local differences in n-alkane degradation and found that recharge-facilitated transport of phosphate and nitrate were the most-likely factors for explaining variances in degradation rates.

Like P, bioavailable Fe and Mn can be scarce in groundwater because of the low solubility of iron and manganese oxyhydroxides at neutral pH. At Bemidji temporal changes related to limited availability of iron and manganese have been observed (Baedecker et al., 1993; Cozzarelli et al., 2001). Mn^{2+} increased, peaking 8 years after the spill, and then decreased, suggesting that the manganese available for reduction was being depleted. Fe^{2+} concentration began to increase following the drop in Mn^{2+} and peaked 11 years after the spill (Essaid et al., 1995). Tuccillo et al. (1999) did a

quantitative examination of the Fe geochemistry in Bemidji using several extraction techniques on sediments (Heron et al., 1994; Ryan and Gschwend, 1991). They showed that prolonged Fe(III) reduction had caused measurable changes in the sediment Fe geochemistry.

In order to understand the limiting factors for crude oil degradation at the La Crau site, the objectives of this study were (1) to simulate each redox condition observable on site and to study its limitation by electron acceptor availability, (2) to assess whether phosphate could shorten the lag phase of processes which appeared slowly at the field site (iron-reduction or methanogenesis) and (3) to study the impact of phosphate on degradation rates and types of kinetics of electron acceptor consumption.

2. Material and methods

2.1. Site description

The site is in the “La Crau” alluvial plain formed by the former river Durance (Naudet et al., 2004). These deposits are made of coarse gravel with fine gravel and sand in the interstices, cemented near the surface in the form of Puddingstone with fractures. These layers overlay silt or sandy-silt deposits of low permeability (unpublished classified report). The “La Crau” reserve is a steppe grazed by low numbers of sheep, and the underlying aquifer shows low concentrations of nitrate (5–10 mg/L) and phosphate (<0.2 mg/L).

The remediation of the surface soils by replacement and off-site disposal of contaminated top soils has been completed. The remediation of aquifer contamination is still ongoing in 2013 and consists in plume management by hydraulic groundwater barriers with re-injection of activated charcoal-treated waters, and dual-phase oil extraction in the source zone. So far, the oil extraction permitted the recovery of 31 m^3 of oil in 3.5 years.

Several wells in the plume were sampled in April 2010 in order to investigate redox conditions nearly one year after the spill. This field study showed that a wide range of redox processes from aerobic respiration to sulfate reduction was observable in the plume. Microbiological investigations suggested that the majority of cultivable microorganisms were sulfate-reducing strains (unpublished classified report). Methane has been detected 2 years after the spill and dissolved CH_4 concentrations doubled every six months since then.

2.2. Water, sediments and crude oil sampled on site

Uncontaminated sediments were collected from 8 to 9 m depth in a quarry located a few hundred meters away from the spill site at La Crau. The coarse fraction >4 mm and the fine fraction <0.124 mm were removed by wet sieving. Sediments were treated repeatedly with H_2O_2 (30%) to remove organic matter.

Water used in experiments was collected from 2 different monitoring wells on site. Pz 39 is upstream of the source where water contained dissolved oxygen up to 8 mg/L, 5 mg/L nitrate and 60 mg/L sulfate. Pz 23 is in the source zone where water was free of oxidants. Both wells were purged prior to sampling, and samples were stored at 4 °C before microcosm assembling.

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