5th International In-Situ and On-Site Bioremediation Symposium 5(3) p.463-468
In Situ Bioremediation of Peteroleum Hydrocarbon and Other Organic Compounds
San Diego, USA Battelle Press (1999) Editors Bruce C. Alleman and Andrea Leeson

OXYGEN CONSUMPTION OF NATURAL REDUCTANTS IN AQUIFER SEDIMENT RELATED TO IN SITU BIOREMEDIATION

Jasper Griffioen, Bas van der Grift, Alice Buijs (Netherlands Institute of Applied Geoscience TNO, Delft, The Netherlands)
Niels Hartog (Institute of Earth Sciences, Utrecht University, Utrecht, The Netherlands)

ABSTRACT: Biogeochemical experiments were performed to characterize the reactivity of natural reductants versus that of benzene, toluene, ethylbenzene, and xylenes (BTEX) compounds. Two types of experiments were performed: (1) fluidized-bed experiments in which competition between BEX compounds and natural reductants for incoming oxidants was characterized and (2) microoxymax experiments in which O_2 reduction by natural reductants in sediment was characterized. Oxidation of bulk organic matter (BOM) is distinguished from that of Fe sulfides by the production of CO_2. Oxidation of BEX compounds is generally fast compared to that of BOM or Fe sulfide. However, oxidation of BOM or Fe sulfide is a slow but ongoing process. Natural reductants thus consume oxidants that are introduced naturally or human-induced and need to be considered in planning of in situ bioremediation strategies.

INTRODUCTION

Sandy aquifer sediment may contain natural reductants such as bulk organic matter (BOM) and pyrite (FeS_2). Natural reductants will compete with contaminant reductants, such as petroleum-type hydrocarbons, for the oxidants available. These oxidants may be naturally available (natural attenuation strategy) or introduced by man (stimulated in situ bioremediation strategy). The success or failure of in situ bioremediation strategies is determined partly by the biogeochemical reactivity of the natural reductants present.

The objective of our study was to relate the reactivity of natural reductants to that of BTEX compounds. We have performed two types of experiments: fluidized-bed experiments in which the competition between the two types of reductants can be studied, and microoxymax experiments in which O_2 consumption and CO_2 production of natural reductants is characterized as function of time. Toluene was not studied, because field investigations have shown that toluene was always degraded naturally and is thus of less environmental concern.

MATERIALS AND METHODS

Aquifer sediment was sampled anaerobically using Akkerman sampling tubes. The samples were stored anaerobically in glass jars. The samples were analyzed for carbonate, organic carbon, and total sulfur content by combustion at increasing temperature and infrared (IR) detection using a Stroehlein C-mat 5500 analyzer. Groundwater was sampled with a peristaltic pump and stored in 5- or

10- L glass bottles. The groundwater samples were used immediately in the fluidized-bed experiments, except for one experiment in which artificial groundwater was used.

Fluidized-bed experiments were performed using a 100-cm-long glass tube in which 50 g of sediment was placed (Fig. 1). The glass tube was filled with native groundwater from below. A peristaltic circulation pump was used to fluidize the sediment. A 0.45-µm filter in a stainless steel filter holder was placed following the glass tube to prevent migration of fine particles. Another P-50 Hiload pump injected (treated) groundwater at a flowrate of 30 mL/hr. All materials in contact with sediment and water were made of glass or stainless steel, except a short tube in the peristaltic pump. This was composed of tygon, which is a gastight plastic. The groundwater was flushed with a N_2/CO_2 gas mixture to maintain the anaerobic status and fix the pH. A syringe pump injected a BEX solution at a flowrate of 0.7 mL/hr; Br was added as an inert tracer to calculate the dilution with injected (ground)water. Dilution of the BEX solution with (ground)water resulted in BEX concentrations that are representative for the sites studied. The fluidized-bed tube and the groundwater bottle were cooled at 12°C. Influent and effluent samples were analyzed using routine techniques.

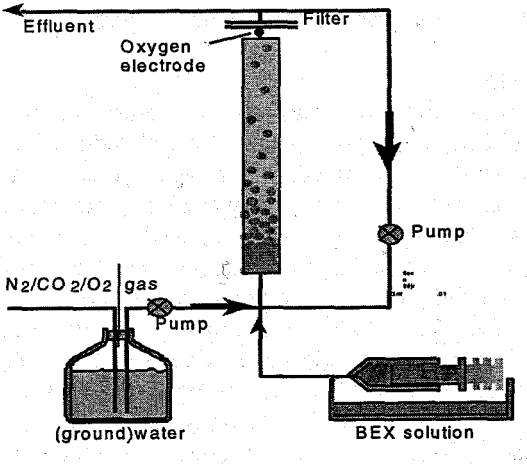

FIGURE 1. Setup of fluidized-bed experiments.

Respiration experiments were performed in duplicate at 22°C using the microoxymax, which is a fully automated respirometer that measures the O_2 consumption and CO_2 production of batch incubations as a function of time. Two experimental series were performed in duplicate. In the first series, 15 grams of sediment was incubated with 50 mL of tapwater in 100-mL glass bottles for 27 days. The supernatant was analyzed afterwards on pH, alkalinity, major cations, and anions using routine techniques. Several sediments were decalcified by extraction with 1.0 M HCl during 16 hours and subsequently repeated flushing with demineralized water.

In the second series, we studied four samples with organic C content ranging from 0.15 to 0.30%. Twenty grams of sediment was incubated in 100-mL glass bottles. A 50-mL solution containing 25 mg/L of trace elements and 0.5 mg/L of vitamins, was added to ensure substrate-limiting conditions. We checked this by running the same experiments with doubled concentrations. Phosphate buffer was added to keep the pH constant at 7.5 to 8.0. The series ended after 107 days.

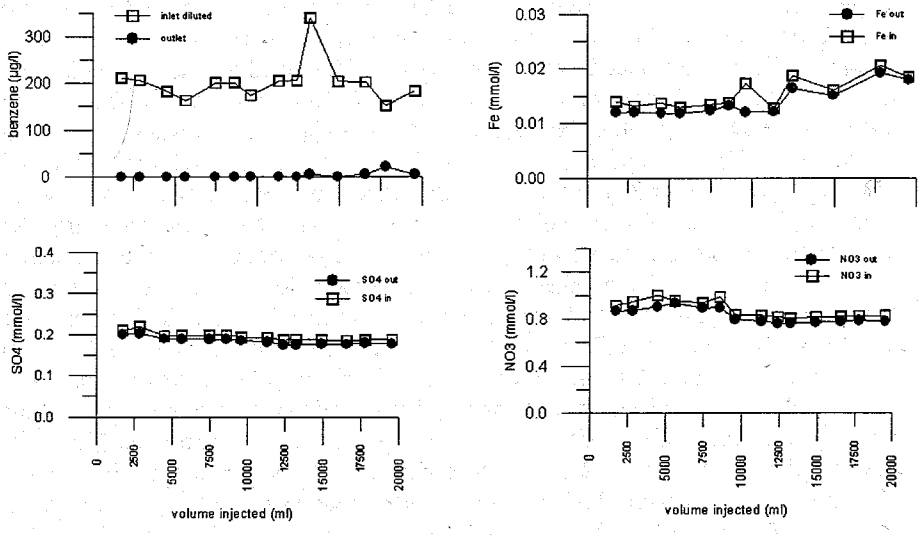

FIGURE 2. Time series of influent and effluent concentration for fluidized-bed experiment with injection of NO_3-enriched tapwater using Flebo sediment.

RESULTS

The research focused on three sites for which the potential for stimulate in situ bioremediation was studied. We will illustrate the results for the Flebo an Slochteren sites. The first has a deep anaerobic status where dissolved H_2S an CH_4 are present above 0.1 mg/L. The Flebo site is contaminated with benzene concentrations of at most 220 µg/L. The Slochteren site is an Fe-anaerobic si contaminated with gas condensate. Figure 2 shows the results of a fluidized-be experiment for Flebo in which tapwater saturated with air and 50 mg NO_3/ added was injected together with a benzene-containing solution. Comparison the influent concentrations with the effluent ones reveals that benzene is degrade during most of the experiment. The oxygen concentration of the effluent w about 0.20 mmol O_2/L, which is significantly below saturation with air at 12°(No significant changes for the redox-sensitive species (NO_3, SO_4, and Fe) we observed. Aerobic degradation of benzene thus occurred. The first-ord degradation constant was minimal at 11.0 day^{-1}, based on the residence time the fluidized bed and the difference between the influent and efflue concentrations. No consumption of natural reductants was observed in the experiments.

Figure 3 shows the results of the microoxymax experiments for Flebo. A experiment with untreated sediment and another with decalcified sediment we performed. Degradation of BOM was the major process for the untreate sediment. This is indicated by the consumption of O_2 together with the productic of CO_2. The molar ratio of CO_2 produced to O_2 consumed was equal to 1. degrading BOM can thus be represented by CH_2O. The results show th oxidation of BOM occurred at a rate of 1.3 µmol O_2/g_{sed}.day initially and 0 µmol O_2/g_{sed}.day after 27 days. For the decalcified sediment, O_2 was consumed a much higher rate of 4.2 µmol/g_{sed}.day initially and 2.9 µmol/g_{sed}.day after 2 days. No CO_2 production was observed after 2 days, which means that anoth redox process must have taken place. CO_2 production in the initial stage attributed to degassing. Analyses of the supernatant after the incubations ga SO_4 concentrations of 28.7 and 30.3 mmol/L and Fe concentrations of 12.6 a 14.7 mmol/L. Sulfides thus were oxidized in the second experiment. T extraction by HCl had removed a coating that prevented oxidation of pyrite. Th coating was most likely either Ca carbonate or Fe oxyhydroxide. The p decreased to 2.15 and to 2.17 in these experiments, whereas the pHs for t untreated sediment were 7.57 and 7.90 (and for tapwater 8.0). Pyrite oxidati causes strong acidification and may change the oxidation mechanism (Evangel & Zhang, 1995). We have not further investigated this.

The fluidized-bed experiments for Flebo indicate that benzene is mo reactive than naturally present reductants. An experiment with sediment fro Slochteren, in which artificial suboxic NO_3-containing water was injected, sho the following. Initial Fe sulfide oxidation by pyrite was observed together wi degradation of ethylbenzene and the three xylenes, but little or no degradation benzene. The small increase in SO_4 concentration (except for one initial and

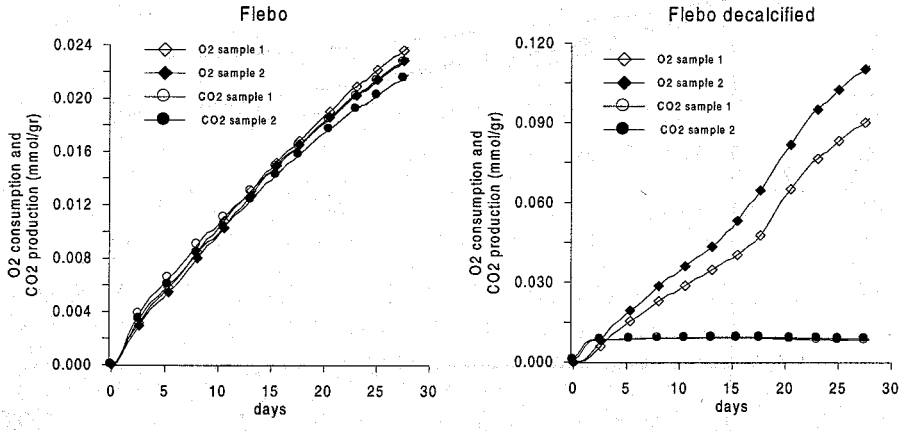

FIGURE 3. Cumulative O_2 consumption and CO_2 production for microoxymax experiment with untreated and decalcified Flebo sediment.

another measurement) for the first 7000 ml was less than the decrease in NO_3 concentration, when corrected for reaction stoichiometry. Additional reduction of NO_3 thus happens. Dissolved Fe was below the detection limit of 1.0 µmol/L and the pH remained near-neutral, which means that complete Fe sulfide oxidation to Fe oxyhydroxide had occurred. The amount of SO_4 produced corresponds to a S content of the sediment of 190 ppm, which is an order of magnitude smaller than the total elemental S content of 0.4%. The microoxymax experiments for the Slochteren sediment also indicate Fe sulfide oxidation for both the untreated and decalcified sediment (not shown here). The total O_2 consumption rate varied from 0.6 to 2.1 $\mu mol/g_{sed}.day$ for the untreated sediment, and it was two times lower for the decalcified sediment. Little BOM oxidation was observed despite an organic C content of 0.8%.

The reactivity of BOM was studied in more detail in series 2 for a set of aquifer sediments from 't Klooster, Hengelo. The sediments contained less than 0.1% Fe sulfides. The low SO_4 concentrations in solution (< 0.8 mmol/l) at the end of the experiment indicate that no significant Fe sulfide oxidation had occurred. The results of the duplicate experiment are comparable, and the identical rates for both low and high nutritional conditions confirmed C_{org}-limiting conditions. In all samples the molar production of CO_2 equalled the molar O_2 consumption and thus indicated the degradation of BOM. The remaining amount of initial BOM ranged from 91% to 80% at the end of the experiment (Fig. 4). The decreasing degradation rates during the experiment suggest that a significant fraction of BOM will be relatively stable under the oxidizing conditions applied. The first-order rate constants ranging from 0.0008 yr^{-1} to 0.002 yr^{-1} are, however, intermediate to high rates in marine sediments in the broad range of oxic degradation rates (Henrichs, 1993).

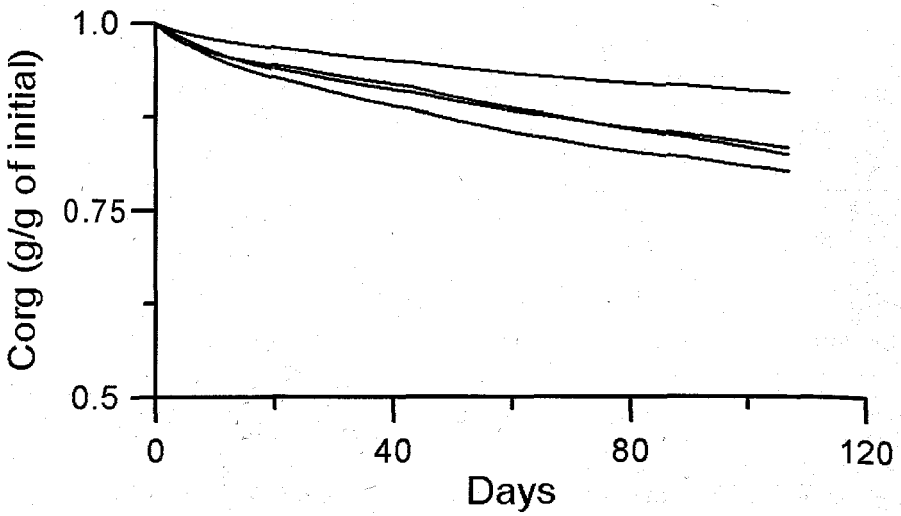

FIGURE 4. Calculated fraction of bulk organic matter remaining during microoxymax incubation with sandy sediments from 't Klooster, Hengelo.

DISCUSSION AND CONCLUSIONS

The general results show that natural reductants are an important sink for either natural or human-induced oxidants. Although the reactive amount is in general low for sandy sediments, it is sufficient to contribute significantly to the reduction capacity of sediments. The slow kinetics sets a limit to stimulated bioremediation of, for example, petroleum-type hydrocarbons by means of injecting oxidants such as oxygen or nitrate. The time period during which the natural reductant reacts will be on the order of several weeks to months. A significant loss of oxidants introduced will occur if sufficient reaction time is available.

ACKNOWLEDGMENTS

We would like to thank Hugo van Buijssen for his assistance in the microoxymax experiments.

REFERENCES

Evangelou, V.P., and Y.L. Zhang. 1995. "Pyrite oxidation mechanisms and acid mine drainage prevention." *Crit. Rev. Env. Sci. & Technol. 25*: 141-199.

Henrichs, S. M. 1993. "Early diagenesis of organic matter: The dynamics (rates) of cycling of organic compounds." In M.H. Engel and S.A. Macko (Eds.), *Organic Geochemistry,* pp. 101-117. Plenum, New York.