Isotopic Fractionation of Perchlorate and Nitrate during Biodegradation in an EOS® Biobarrier

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The effectiveness of EOS® edible oil substrate (U.S. Patent #6,398,960) for promoting anaerobic biodegradation of perchlorate, nitrate, and 1,1,1-trichloroethane (1,1,1-TCA) has been evaluated since October 2003 at a rocket manufacturing site in Maryland. This previously installed bio-barrier was used in the current study to evaluate stable isotope fractionation of perchlorate and nitrate during biodegradation within the aquifer.

Untreated groundwater in the shallow aquifer contained elevated concentrations of perchlorate (~7,000 μg/L) and 1,1,1-TCA (~23,000 μg/L) released from a closed lagoon. Nitrate was also present at approximately 5 mg/L. With funding by DoD’s Environmental Security Technology Certification Program (ESTCP), Solutions-IES installed a 60-foot-long permeable reactive biobarrier (PRBB) perpendicular to the direction of groundwater flow. Concentrations of nitrate and perchlorate downgradient of the barrier decreased to < 0.5 mg/L and < 10 μg/L, respectively, within 35 days of installation. The concentration of 1,1,1-TCA downgradient of the PRBB decreased from 5,700 to 240 µg/L (~96%) in 4.5 months.

A push-pull test was performed in 2006 (31 months after the oil injection) to assess the continued effectiveness of the barrier and to quantify the extent of isotopic fractionation of two contaminants of interest, perchlorate and nitrate, during in situ biodegradation. Prior to the tests, field parameters and concentrations of total organic carbon (TOC), 1,1,1-TCA, perchlorate, and nitrate were measured in groundwater from one injection well (IW-3) in the PRBB. Despite decreased dissolved organic carbon from the barrier (TOC = 3 mg/L compared with 418 mg/L 4 days after substrate injection in 2003), the enhanced in situ anaerobic zone stimulated by residual EOS® remained effectively reducing, with an oxidation-reduction potential (ORP) of -80 mV. Perchlorate was 180 µg/L, nitrate was < 0.5 mg/L and 1,1,1-TCA was 100 µg/L. During the push-pull test, approximately 400 L of contaminated groundwater were extracted from an upgradient well, amended with bromide as a tracer, and pumped into IW-3. Groundwater samples were withdrawn from the well during the next 30 h and analyzed for field parameters, perchlorate, nitrate, bromide, and dissolved gases. In addition, samples were collected for measurement of chlorine and oxygen stable isotopes in perchlorate and nitrogen and oxygen stable isotopes in nitrate. Nitrate concentrations decreased from 5.3 to < 0.5 mg/L during...

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the initial 8 hr of the test. The δ^{15}N of the residual nitrate increased by approximately 16 per mil during this period and the δ^{18}O increased by 13 per mil. These increases are consistent with a kinetic isotope effect during nitrate reduction. Perchlorate concentrations decreased from 4,300 μg/L to 500 μg/L during the same 8 hr period, and preliminary data indicate substantial increases in both δ^{37}Cl and δ^{18}O during this time. The push-pull test indicates that the EOS® biobarrier® continues to promote biodegradation of target contaminants nearly three years after installation, and it provides an unusual opportunity to evaluate in situ isotopic fractionation factors for both perchlorate and nitrate undergoing simultaneous biodegradation in the saturated zone.