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Multi-Isotopic Analysis Applied to Asses the Efficacy of Induced Denitrification: Laboratory and Field Scale Assays

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Denitrification, the microbial transformation of NO_3^- to N_2, is the most important reaction that attenuates nitrate pollution in groundwater. This process, that takes place in anaerobic environments, can be induced by the presence of organic matter and/or sulphide minerals. The study of induced attenuation of nitrate pollution has been performed at laboratory and field scale, using pyrite and organic matter as electron donors. A multi-isotopic approach (δ^{15}N and δ^{18}O of NO_3^-, δ^{34}S and δ^{18}O of SO_4^{2-}, δ^{13}C of DIC) was performed in order to provide a tool to quantify the efficacy of induced attenuation.

Batch experiments using pyrite as electron donor were conducted. Contaminant destruction ranged from 67% to 82% after 94 days. Comparable denitrification efficiency was obtained in similar experiments but using pure culture of the denitrifying bacterium *Thiobacillus denitrificans*. The isotopic composition of dissolved nitrate (δ^{15}N, δ^{18}O) showed an inverse linear relationship with the ln [NO_3^-], allowing to calculate the enrichment factors. In both type of experiments, the εN ranged from -15.0 to -27.6‰ and the εO from -13.5 to -21.3‰ in the range of published data for groundwater and in vitro experiments (Lehmann et al. 2003). In a δ^{15}N vs. δ^{18}O diagram samples followed a denitrification trend with a ratio εN/εO between 1.13 and 1.30, slightly lower than the literature values (Fukada et al 2003, Böttcher et al., 1990). Regarding organic matter oxidation experiments, contaminant consumption was complete after 4 days. The enrichment factors obtained were similar to those obtained in the sulphide oxidation experiments, being the εN = -26.4‰ the εO = -23.5‰ and an εN/εO = 1.15.

Induced attenuation experiments using organic matter as the electron donor were also performed at field scale. The pilot test ran for 7 months in groundwater natural gradient conditions, and by regular addition of carbon source and phosphate. After an initial period of system set-up, nitrate levels were reduced to below detection levels. The calculated enrichment factors were εN = -8.8‰ and εO = -4.8‰ with a ratio εN/εO = 1.86. Although further research is needed, especially at field scale, enhanced and/or induced denitrification should be taken into account as a good alternative for groundwater remediation. The isotopic composition provides an excellent tool to monitor the efficacy of induced attenuation.

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