Assessing nitrate consumption, nitrous oxide and nitrite production during denitrification using push-pull tests in heterogeneous aquifers

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Field quantitative estimation of reaction kinetics is required to enhance our understanding and model biogeo-chemical reactions in aquifers. In this study, we assess kinetics of nitrate consumption and by-products formation (nitrites and nitrous oxide) during autotrophic denitrification using push-pull tracer tests. The interests and origi-nalities of the field experiment are to i) assess autotrophic denitrification by this mean, ii) to conduct push-pull tests in large boreholes in fractured media and iii) to asses nitrous oxide production from denitrification in a field experiment knowing the initial nitrate concentration. Moreover nitrate breakthrough curve in this experiment has been measured thanks to a spectrophotometer specifically adapted for in-situ borehole monitoring.

Experiments were conducted at the hydrogeological observatory of Ploemeur (France) in a crystalline aquifer. The borehole used exhibits a 10 meter extension single fractured zone where the solution is injected. Push-pull tests consists in injecting a well known solution composed of a reactive and a non reactive tracer in a borehole (push phase). After a lag time the solution is pumped (pull phase) from the same borehole to obtain breakthrough curves. Comparison of the breakthrough curves of both tracers gives the consumed mass. The injected solution is composed of nitrate (2 g/L) as a reactive tracer and bromide (1.5 g/L) as a non reactive tracer. Both elements have the similar transport properties. The maximum residence time of the tracer in the medium is 12 hours. Monitoring is done for dissolved oxygen, cations, anions, gases (N_2O, CO_2, N_2), pH, temperature conductivity and for both organic and inorganic carbon.

Comparison of Br^- and NO_3^- breakthrough curves shows that 10 % of the injected nitrate molar mass was transformed during the experiment (2% in NO_2^-, 2% in N_2O and the rest in N_2 and NO). We used the simplified analytical solution developed by Haggerty et al., (1998) to define first order kinetics of nitrate degradation. It leads to a first order coefficient of 0.022 h-1. The kinetic parameters following Michaelis-Menten kinetics are obtained using the method defined in (Istok et al., 2001). Michaelis-Menten parameters Vmax (maximum substrate utilization rate) of $1.4.10-5$ mol/L/h are obtained for the nitrites and nitrous oxide. Michaelis-Menten constants (km) of $1.2.10-3$ mol/L for nitrites and $4.2.10-2$ mol/L for nitrous oxide are estimated. These solutions consider that the physical aquifer parameters do not have influence on the reaction rate. In a second step, we used the kinetic parameters to estimate the influence of the denitrification reaction at the site scale. Results are in good agreement with observed variations of nitrate concentrations at the site scale. Thus, push-pull tracer tests appear a simple and reliable method for characterizing autotrophic denitrification at the field scale.

Cited references
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