

## **Long-term Denitrification Processes and Kinetics in a Crystalline Aquifer subject to Pumping from 1991**

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The kinetic of denitrification associated to long-term mixing processes in heterogeneous aquifers is particularly challenging to constrain. Specifically, chemical evolutions related to groundwater exploitation are cases that are poorly known. It remains particularly unclear if long-term pumping whether enhances or slows-down the nitrate reducing processes and what is the source of electron donor sustaining the reaction. The aim of this study is to investigate the dynamic of denitrification processes induced by long-term pumping in the Ploemeur aquifer (Britany, France) which has been operated for water supply since 1991. Several batch experiments have been carried out in order to fully characterize the kinetics of the denitrification reaction involved. Batches consisted in crushed rock: more or less weathered granite and schists, and water sampled from the site. Denitrification always developed except in sterilized batches. Denitrification rate was independent on the rock type but more on the state of the bacterial community. Inorganic dissolved carbon only showed moderate variations while organic carbon remained at low concentrations. Both observations make heterotrophic denitrification unlikely. A silicate dissolution was observed and detailed analysis of the cations quantified a main biotite contribution. The iron produced by biotite dissolution accounts for the denitrification processes observed.

Long term time-series analysis of the conservative elements recorded at the pumped well were used to determine mixing fractions from different compartments of the aquifer based on a Principal Component Analysis approach coupled with an end-member mixing analysis. Discharge fractions were then used to quantify the denitrification kinetic linked to pumping. With increasing concentration of Nitrate entering in the groundwater system since the beginning of the operations, computations confirm that i) autotrophic denitrification processes are dominant and ii) biotite plays a critical role in sustaining the Nitrate reduction processes. Both nitrate reduction and Sulfate production as well as Fluor release ratios support the hypothesis that biotite play a major role of electron donor in this context.

Field-scale pumping experiments in two other crystalline aquifers from Britany also showed similar denitrification reactions without sulfate production in a stoichiometric ratio to nitrate consumption. Metagenomic analysis of these three aquifers showed a highly structured system. Microbial communities are dominated by potential denitrifiers in the upper weathered compartment while the deeper fractured system shows communities dominated by Gallionellaceae group, both groups being potentially involved in the denitrification processes.