



Environmental isotopes (N, S, C, O, D) to evaluate occurrence and temporal variability of natural denitrification processes in a regional system (Osona, NE Spain)

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Nitrate is a widespread contaminant in most European aquifers. The drinking water threshold (50 mg/l, Directive 98/83/EC) is already exceeded in many wells. The main reason for increasing nitrate contents in groundwater is the extensible application of fertilizers in agriculture. Isotope data are a useful tool to evaluate the origin of nitrate contamination and the occurrence of several chemical processes, such as natural attenuation. The Osona area (NE Spain) was classified as vulnerable to nitrate contamination from agricultural sources in 1991 by European Union. High amounts of organic residues are produced by the farming activity and most part of the manure is applied to the field as organic fertilizer, causing a widespread groundwater nitrate contamination. The main goal of this work is to study the temporal variation of nitrate contamination and natural attenuation processes taking place in Osona aquifer. Three sampling surveys were performed in April 2005, October 2005 and May 2006. The isotopic characterization included δD and $\delta^{18}\text{O}\text{-H}_2\text{O}$, $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of dissolved NO_3 , $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of dissolved SO_4 and $\delta^{13}\text{C}$ of DIC.

Isotopic data of the three campaigns confirmed that the most important source of nitrate pollution is the excessive application of pig manure as fertilizer. Results revealed that natural denitrification processes existed in some zones of the study area, and that these processes were related to pyrite oxidation. In most of the studied samples equilibrium between the application of manure and the existence of natural denitrification processes was found, showing slightly changes in the values of $\delta^{15}\text{N-NO}_3$ with time along the studied period. However, in some of the studied samples denitrification processes related to pyrite oxidation predominated, causing $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ increase and $\delta^{34}\text{S-SO}_4$ decrease through time. An estimation of the isotopic enrichment factors associated to denitrification processes was performed using the temporal variations of nitrate and $\delta^{15}\text{N-NO}_3$ of the samples in which denitrification processes predominated. Obtained values of enrichment factors for nitrogen (between -4 and -15 ‰) fall well within the range of values reported for denitrification in groundwater (-4‰, from Pauwels *et al.*, 2000; -5‰, from Mariotti *et al.*, 1988; -10‰, from Spalding and Parrott, 1994; and -16‰, from Bottcher *et al.*, 1990). Further laboratory experiments are required to obtain the real enrichment factors for the aquifer.

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