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Natural attenuation of nitrate in some vulnerable areas in Catalonia (NE Spain)

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Nitrate contamination of groundwater resources is a high-priority concern in rural and urban areas in many regions worldwide. The threshold value for drinking water (50 mg/l, Directive 98/83/EC) is usually achieved in regional aquifers in Europe. The European Environmental Agency (EEA) points to agricultural non-point pollution as the primary cause of water quality deterioration (European Environmental Agency, 1999). High nitrate concentration in drinking water poses a health risk as its ingestion, for instance, can cause infant methahemoglobinaemia ("blue baby" syndrome) (Magee and Barnes, 1956). In Catalonia, according to the nitrate directive (91/676/EU), nine areas have been declared by the local government as vulnerable to nitrate pollution from agricultural sources (Decret 283/1998). Anthropogenic nitrate is linked to the intensive use of synthetic and organic fertilisers, as well as to septic systems seepage. Identifying the sources and understanding the processes that control groundwater contamination is an important step for improving the state of the aquifers. It is with this aim that five of these vulnerable areas have been studied applying a multi-isotopic approach (Vitòria et al., 2005) in an ongoing research project. In addition to the classical hydrochemistry data, environmental isotopes (δ^{15} N and δ^{18} O of dissolved nitrate, δ^{34} S and δ^{18} O of dissolved sulphate, δ^{13} C of dissolved inorganic carbon, and δ D and δ^{18} O of water) are used in order to determine the main nitrate source, to quantify to

some extent the degree of denitrification, and to evaluate the controlling factors (organic matter and pyrite oxidation). Apart from distinguishing contaminant sources, isotope data, understood in an appropriate hydrogeological framework, can offer an integrated knowledge of the extent of contamination. This contribution is focused on the study of three of these vulnerable areas: Selva, Garrotxa and Lluçanès.

Groundwater samples were collected in May-06 (Selva), June-06 (Garrotxa) and May-07 (Lluçanès) at 30, 31 and 29 wells, respectively. Nitrate concentrations range from 1.6 to 217.2 mg/L, with the Selva area presenting the highest values. Isotope signatures of groundwater NO₃⁻ range between +2.3%, and 21.1%, for δ^{15} N, and between +1.5%, and +12.6%, for δ^{18} O. Most of the samples present δ^{15} N values higher than 8%, indicating that dissolved nitrate is mainly influenced by pig manure applied on the fields ($\delta^{15}N_{NH4}$ between +8 and +15%), as important contributions of septic waste are not expected in the studied areas. Moreover, around 10% of the sampled wells are also influenced by nitrate from synthetic fertilizers. On the other hand, natural attenuation of nitrate is occurring as the $\delta^{15}N$ and $\delta^{18}O_{NO3}$ show a coupled increase, with a ratio close to 2:1 (Kendall, 1998). The degree of denitrification that the NO_3^- has undergone in each area can be estimated using extreme enrichment factors. In the Garrotxa area, for example, this degree of denitrification appears to be the lowest. Thus, by means of the comparison between chemical and isotopic data, the occurrence of natural attenuation processes and the factors controlling these reactions are assessed for each vulnerable area.

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