



Dual isotope approach for tracing nitrate pollution in a vulnerable zone in La Alcarria (Madrid, 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. In the Madrid Community, according to the nitrate directive (91/676/EU), “La Alcarria” area has been declared by the regional government as a vulnerable zone to nitrate pollution from agricultural sources (Orden 2331/2009). Anthropogenic nitrate is linked to the intensive use of synthetic and organic fertilisers, as well as to septic systems seepage. In order to determine whether the use of synthetic fertilisers during the agricultural activity is the main source of nitrate, a four-monthly monitoring is being carried at the zone. Besides the measurement of physicochemical and microbiological parameters in situ (pH, T, EC, Eh, dissolved O₂ and CO₂) and in the lab (pH, NO₃⁻, NO₂⁻, NH₄⁺, urea, DBO₅, total coliforms and *Streptococcus faecalis*), isotopic analyses of ¹⁵N and ¹⁸O of dissolved nitrate have been performed.

The study zone is located in the Madrid Community and covers an area of 963.4 km². Hydrogeologically, two aquifers, characterised by two lithological facies, can be distinguished. Groundwater temperature ranges between 15 and 19°C, pH is around 7-8, and the conditions are mainly oxic (Eh average value is 160 mV and the dissolved O₂ concentration is around 5.5 mg/L), with a low CO₂ concentration (16 mg/L). The electrical conductivity agrees with the two lithological facies: higher values (2500-6500 μs/cm) for groundwaters flowing through evaporitic materials, and lower values (650-2200 μs/cm) for the carbonated units.

Groundwater samples were collected in successive years: 2006 (May), 2007 (May and November), 2008 (June and December), 2009 (June) and 2010 (September). Nitrate concentrations ranged between 40 and 160 mg/L. Isotope signatures of NO₃⁻ dissolved in groundwater ranged between +1.6‰ and 19.7‰ for δ¹⁵N, and between +0.9‰ and +14.3‰ for δ¹⁸O_{NO3}. Almost half of the samples presented δ¹⁵N values higher than 8‰ indicating that dissolved nitrate is mainly influenced by animal waste applied on the fields (δ¹⁵N_{NH4} between +8 and +15‰) (Vitòria et al., 2005). Nevertheless, a contribution of septic waste cannot be discarded, as well as the presence of nitrate derived from ammonium of synthetic fertilisers, which can undergo volatilisation (before nitrification) and/or denitrification processes (after nitrification). In the case of samples with δ¹⁵N values lower than 8‰ the influence of soil organic nitrate cannot be so important because of the high nitrate concentrations of most of the samples. Therefore, nitrates with δ¹⁵N values < 8‰ are probably coming from synthetic fertilisers ammonium, that can also reach these isotopic values after slight volatilisation. Locally, two samples present δ¹⁵N and δ¹⁸O_{NO3} values nearer to the isotopic composition of fertilisers nitrate (δ¹⁵N ≈ 0‰ and δ¹⁸O_{NO3} ≈ 20‰), indicating a possible influence of this nitrate source depending on the agricultural uses. On the other hand, natural attenuation of nitrate is slightly occurring for all surveys (except on May 2006), since δ¹⁵N and δ¹⁸O_{NO3} showed a coupled increase with a ratio close to 2:1 (Kendall, 2007). Thus, by means of coupling the chemical and isotopic data, the identification of nitrate sources in “La Alcarria” groundwater can be assessed in order to improve the aquifer management.

Kendall, C., Elliott, E.M., and Wankel, S.D., 2007. Tracing anthropogenic inputs of nitrogen to ecosystems, Chapter 12, In: R.H. Michener and K. Lajtha (Eds.), *Stable Isotopes in Ecology and Environmental Science*, 2nd edition, Blackwell Publishing, p. 375-449.

Vitòria, L., Soler, A., Aravena, R., Canals, A. (2005) Multi-isotopic approach (¹⁵N, ¹³C, ³⁴S, ¹⁸O and D) for tracing agriculture contamination in groundwater. In: Lichtfouse, E.; Schwartzbauer, J.; Robert, D. (Eds): *Environmental Chemistry: Green chemistry and pollutants in Ecosystems*. Springer-Verlag, Berlin, 137-147.