



Limitations of the isotopic composition of nitrates as a tracer of their origin

Wolfram Kloppmann (1), Neus Otero (2), Bernhard Mayer (3), Mathieu Sebiló (4), Daren C. Gooddy (5), Dan Lapworth (5), Ben Surridge (6), Emmanuelle Petelet (1), Christine Flehoc (1), and Nicole Baran (1)

(1) BRGM, French Geological Survey, Orléans, France (w.kloppmann@brgm.fr), (2) Universitat de Barcelona, Spain, (3) University of Calgary, Canada, (4) Université Pierre et Marie Curie, Paris, France, (5) British Geological Survey, Wallingford, UK, (6) Lancaster University, UK

Nitrogen and oxygen isotopes are traditionally considered and frequently used as tracers of nitrate sources in watersheds used for drinking water production. The enrichment of synthetic nitrate-containing fertilizers in ^{18}O due to the contribution of atmospheric oxygen in the production process confers a specific isotopic fingerprint to mineral fertilizers. In spite of the still widespread use on nitrate-containing synthetic fertilizers, their characteristic N and O isotope signatures are rarely unambiguously observed in nitrate-contaminated groundwater. We postulate, in line with Mengis et al. (2001), that fertilizer-derived nitrate is not directly and rapidly transferred to groundwater but rather retained in the soil-plant system as organic N and then mineralized and re-oxidized (termed the mineralization-immobilization turnover, MIT) thereby re-setting the oxygen isotope composition of nitrate and also changing its N isotope ratios. We show examples from watersheds on diverse alluvial/clastic and carbonate aquifers in eastern and northern France where, in spite of the use of mineral fertilizers, evidenced also through other isotopic tracers (boron isotopes), both N and O-isotope ratios are very homogeneous and compatible with nitrification of ammonium where $2/3$ of oxygen is derived from soil water and $1/3$ from atmospheric O_2 . These field data are corroborated by lysimeter data from Canada. Even if in areas where ammonium is derived from chemical fertilizers, N values still tend to be lower than in areas where ammonium is derived from manure/sewage, this is clearly a limitation to the dual isotope method (N, O) for nitrate source identification, but has important implications for the nitrogen mobility and residence time in soils amended with synthetic fertilizers (Sebiló et al., 2013).