



Using nitrate N and O stable isotopic signatures to identify the source of nitrate in chalk groundwater

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Intensification of agriculture in the 20th century has resulted in increased concentrations of nitrate in groundwater, including that in chalk aquifers. The dual porosity nature of chalk, arising from interaction between fractures and less permeable matrix, makes identification of land-management strategies to limit and reduce nitrate contamination complex. The aim of this project is to assess the origins of nitrate in chalk groundwater using dual stable isotope analysis. Work focusses on the Kilham subcatchment in the Northern Province Cretaceous Chalk aquifer, Yorkshire, UK, which has been the site of detailed groundwater quality investigations by the Environment Agency of England and Wales.

In order to implement dual stable isotope analysis, a nitrate extraction method exploiting the varying solubility of ions in acetone, originally developed for surface water samples, has been adapted for high-carbonate chalk groundwater. Initial stable isotopic results show two discreet signatures of nitrate contamination. One signature most likely represents nitrate from manure (9-11‰ $\delta^{15}\text{N}$, 4-8‰ $\delta^{18}\text{O}$). A second signature (3-6‰ $\delta^{15}\text{N}$, 4-8‰ $\delta^{18}\text{O}$) may represent nitrate produced by mineralisation of ammonium fertilisers or soil nitrogen. However, and surprisingly, no nitrate with heavy-oxygen (18-25‰ $\delta^{18}\text{O}$) signatures characteristic of nitrate fertiliser produced by the Haber Bosch process (the process responsible for most inorganic fertiliser production) was detected. The absence of such a signature may indicate that fertiliser is essentially fully utilised by biomass, and nitrogen originating from this source only made available for leaching as nitrate when it is partially returned to the soil by mineralisation of nitrogen from biomass after harvest. Such transformations would severely limit the applicability of nitrate fingerprinting for nitrate source identification in aquifers with long residence times.