Determination of $\delta^{15}N$ and $\delta^{18}O$ in nitrate: a method comparison

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Nitrogen ($\delta^{15}N$) and oxygen ($\delta^{18}O$) isotope ratios of NO_3^- are often used to trace dominant NO_3^- pollution sources in water. Three methods are currently employed: (i) the silver nitrate ($AgNO_3$) method, (ii) the bacterial denitrification method and (iii) the cadmium reduction method. The $AgNO_3$ method is only applicable for fresh-water samples with 100–200 mmol of NO_3^-, because it requires NO_3^- purification by anion-exchange and subsequent precipitation as $AgNO_3$, for analysis by elemental analyser-isotope ratio mass spectrometry (EA-IRMS). The existence of large blanks from dissolved organic matter can also be an issue in the application of this method. The bacterial denitrification method uses bacteria to convert NO_3^- into N_2O[1] and the cadmium method produces N_2O by chemical reduction of NO_3^- to NO_2^- with a subsequent reaction with azide [2]. Since the formation of N_2O eliminates any interferences and is amenable to gas chromatography-IRMS, the N_2O methods have a detection limit below 1μmol and can also be used for seawater samples. Despite these advantages, the N_2O methods are not yet universally adapted and a reliable method comparison is still missing. Here we present a first systematic comparison of all three methods using river-, ground- and contaminated water samples having a wide range of $\delta^{15}N$- and $\delta^{18}O$-NO_3^- values and NO_3^- concentrations.

[1] Sigman *et al* (2001) *Anal. Chem.* **73**, 4145-4153 [2] Ryabenko *et al* (2009) *L&O-Methods* **7**, 545-552