

# Quantifying nitrate spiraling rate in streams by using the triple oxygen isotopes as tracers

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Nitrate is a key nutrient in aquatic environments, so that its concentration in stream water affects the primary production in the downstream aquatic ecosystems, such as lakes, estuaries, and coastal oceans. It is not always straightforward to regulate nitrate concentration in stream water because it is controlled by several processes, such as direct nitrate loads from external sources, internal supply of remineralized nitrate via microbial nitrification, nitrate assimilation by plants and microorganisms, and nitrate removal through denitrification.

Recent progress in the stable isotope analysis of dissolved nitrate have enabled us to use it as tracer to determine the origin of nitrate in stream water. The  $^{17}\text{O}$ -excess, which is stable during assimilation and denitrification processes, could be a robust and accurate tracer to quantify contribution ratios of atmospheric nitrate in stream water dissolved nitrate. Absolute concentration of atmospheric nitrate in the stream water sample could be calculated by multiplying total nitrate concentration by  $^{17}\text{O}$ -excess of nitrate in the sample.

In this study, we determined the absolute concentration of atmospheric nitrate together with total nitrate concentration in stream water as natural tracers to quantify both removal rates of dissolved nitrate via assimilation and/or denitrification and gross supply rate of remineralized nitrate via nitrification. Our study was carried out at Yasu river which is one of the major inflows of Lake Biwa, the largest freshwater lake in Japan. Water samples were collected using a bucket at 15 stations distributed along the river and analyzed both concentration and stable isotopic compositions of dissolved nitrate in the samples. In addition, incubation experiments were conducted by adding artificial isotope tracers into both stream water samples and riverbed sediments to verify the accuracy in the estimation of both removal and supply rates of nitrate in stream water using the natural tracer proposed in this study. The estimated rates using natural  $^{17}\text{O}$ -excess tracer coincide well with the rates determined from the incubation experiments. Our newly proposed  $^{17}\text{O}$ -excess tracer method could be an alternative standard method to quantify nitrate dynamics in stream water.

Keywords: atmospheric nitrate, triple oxygen isotopes, streams, nitrate dynamics