# Accurate quantification of atmospheric nitrate in stream water eluted from a small forested watershed using triple oxygen isotopic composition

*Yusuke Obata[1], Kenta Ando[1], Takuya Ohyama[1], Fumiko Nakagawa[1], Urumu Tsunogai[1], Naoyuki Yamashita[2], Tatsuyoshi Saito[2], Hiroyuki Sase[2]

1.Graduate school of Environmental Studies, Nagoya University, 2.Asia Center for Air Pollution Research

Forest ecosystems are deficient in nitrogen in general. Excess loading of nitrogen, however, often leads to “nitrogen saturation” (Aber et al., 1989) in forest ecosystems from which significant quantify of nitrogen is eluted as nitrate. Enrichment of nitrate often caused environmental problems such as degradation of water quality and eutrophication so that we should clarify the origin and behavior of nitrate in stream water, especially for the mixing ratio of unprocessed atmospheric nitrate within total nitrate. The natural stable isotopic compositions of nitrate ($\delta^{15}N$ and $\delta^{18}O$) have been widely used to determine the origin and behavior of nitrate in stream water (Durka et al., 1994). Besides to these isotopes, the triple oxygen isotopic compositions of nitrate have been available as an additional, more robust tracer for the unprocessed atmospheric nitrate (e.g. Michalski et al., 2004) in recent years, due to the stability during biological processings on nitrate. In this study, we measured stable isotopic compositions of nitrate in a stream eluted from the Kajikawa experimental forest in Niigata Prefecture. Besides, those in soil solutions were determined as well for comparison. The Kajikawa experimental forest have been characterized by high loading rate of atmospheric nitrogen and the stream water had been enriched in nitrate more than 50 μmol $L^{-1}$, so that the forest might be under the nitrogen saturation.
The samples of rainfall, soil solution, and stream water in the study site were collected about once a month since December, 2012 to December,2014. Nitrate concentrations were measured by ion chromatography. The stable isotopic compositions including the triple oxygen isotopic compositions of dissolved nitrate were determined using Continuous-Flow Isotope Ratio Mass Spectrometry (CF-IRMS) system in Nagoya University (Tsunogai et al., 2010).
Although the triple oxygen isotopic compositions of nitrate in soil solutions showed significant seasonal variation from +0‰ to +6‰, these in stream water samples showed small variation. On the other hand, the concentration-weighted mean of the soil solutions (+0.8‰) was consistent with that of stream water samples (+1.3‰). We conducted that the major source of the stream water was groundwater in the forest, in which seasonal variation in soil solutions had been smoothed.
The estimated annual export flux of atmospheric nitrate occupied 9.2±4.4% of the annual deposition flux of atmospheric nitrate in the study site. Previous study showed that the ratio (i.e. direct elution ratio of atmospheric nitrate within total nitrate) increased in proportion to the forest declined (Durka et al., 1994; Tsunogai et al., 2014; Rose et al., 2015). In particular, the ratio obtained in Kajikawa site coincided with those eluted from the nitrogen saturated forest in West Virginia under the Stage 3. We concluded that the ratio likely reflected the turnover time of nitrate with in the forest soil and thus we can apply the ratio in each forest ecosystem. As a result, we conducted that the triple oxygen isotopic composition can be applicable as the indicator of nitrogen saturation.
Stoddard(1994) proposed that the disappearance of seasonality in the nitrate concentrations in stream water as the indication of nitrogen saturation in forest ecosystems. Mitchell et al. (1997), however, reported that the seasonality in stream nitrate concentrations was already lost in those eluted from normal forest in Japan, so that the seasonality was not a reliable index of nitrogen saturation in Japanese forests. Present study implied that the direct elution ratio of atmospheric

 

estimated from the triple oxygen isotopic composition can be an alternative index of nitrogen saturation.

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