

Measurement of dissolved dinitrogen / argon ratio by Membrane Inlet Mass Spectrometry

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Quantification of denitrification is quite important in the study of nitrogen (N) biogeochemistry in the lake ecosystems. The precise measurement of denitrification, however, is still difficult partly because the denitrogen, the product of denitrification, is always abundant in lake water. Precise measurements of denitrogen production (excess N_2) are quite labor-intensive and time-consuming. Thus indirect methods of denitrification such as C_2H_2 blockage methods and ^{15}N -tracer methods have been applied to quantify the denitrification. Although these methods can allow us to obtain quantitative results, the additions of substrates or inhibitors can possibly alter the N cycles in the samples to some extent. There is a need, therefore, to develop and validate the more non-invasive technique to enable accurate determination of dinitrogen production.

Measurement of N_2 / Ar ratio is one of the promising, non-invasive techniques. Ar is non-reactive gas and dissolved Ar concentration depends on the equilibrium with ratio of N_2 / Ar . The purpose of this research is to measure N_2 / Ar ratio in a lake ecosystems and to quantify the denitrification. Membrane Inlet Mass Spectrometry (MIMS) was used (Kana *et al.* 1994), which introduces the water sample gases. The stripped gases are detected using a quadrupole mass spectrometer after passing through a liquid nitrogen trap to remove water vapor and CO_2 . Compared to other methods such as IRMS and GC, MIMS is easy to operate with less analytical time.

The study site is Lake Kizaki in Omachi city at Nagano prefecture, central part of Japan. Lake Kizaki forms stratification in summer and winter, and has circulation periods in spring and autumn. Due to this thermal condition, dissolved oxygen is depleted in the deeper hypolimnion from late summer to late autumn (Yoh *et al.* 1988). At previous research in Lake Kizaki, after Koyama *et al.* (1967) and Terai (1979) measured N_2 concentration, and since then there is no attempt to measure N_2 / Ar . When the stratification is formed in summer, dissolved oxygen is consumed nitrate is used by denitrification in the deep hypolimnion. Yoh *et al.* (1988) reported a large accumulation of N_2O in suboxic layer in hypolimnion, but the contribution of nitrification and denitrification in N_2O production has not understood. So, quantification of the seasonal change of denitrification in Lake Kizaki can provide important information on nitrate balance of production and consumption, and N_2O emission processes.

We measured N_2 / Ar ratio profile in October when anaerobic environment completely formed at the hypolimnion in Lake Kizaki. N_2 / Ar ratio increased from the 21.25 m depth to the bottom where dissolved oxygen decreased to zero. So denitrification occurred in this suboxic layer. In addition, dinitrogen concentration by calculated N_2 / Ar ratio was $665 \sim 687$ micro molar and excess N_2 production was $23 \sim 47$ micro molar. By the previous research, maximum concentration of nitrate was about 20 micro molar. Maximum concentration of nitrate was about 20 micro molar in water column in Lake Kizaki (Y. Sasaki, unpublished). Thus, dinitrogen production measured here ($23 \sim 47$ micro molar) is much larger than expected from the concentration of nitrate in the water column. It is thus suggested that other processes, such as nitrification-denitrification coupling, denitrification in the sediment contribute the dinitrogen production in hypolimnion. In the presentation, we discuss the seasonal change of denitrification and the possible factors of denitrification in Lake Kizaki.

(Yoh *et al.* 1988, *Arch. Hydrobiol*, 113, 2, 273-294)

(Koyama *et al.* 1967, *Geochemical Journal*, 1, 109-124)

(Terai 1979, *Jap. J. Limnol.* 40, 2, 81-92)

(Kana *et al.* 1994, *Analytical Chemistry*, 66, 23, 4166-4170)