Note

Marked Variation in Lacustrine N₂O Accumulation Level and Its Mechanism

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Abstract

Compilation of N₂O accumulation data in the low-oxygen zone of Lake Kizaki revealed a marked variation in the maximum N₂O concentrations observed, ranging from 0.17 to 26.5 $\mu\text{g atomN} \cdot \text{l}^{-1}$. The N₂O accumulation level differed noticeably from year to year: from less than 0.6 $\mu\text{g atomN} \cdot \text{l}^{-1}$ in 1983 and 1988, to more than 2.4 $\mu\text{g atomN} \cdot \text{l}^{-1}$ in three other years. The maximum N₂O concentration was correlated with its relative peak position in the low-oxygen zone, with the smaller peak at the "shallower" layer, the larger peak at the "deeper" layer. It was inferred from the N₂O, NO₃⁻ and O₂ profile characteristics that the shift in N₂O production-consumption balance during the denitrification process may be responsible for such a wide variation in N₂O accumulation level and that organic matter availability in the hypolimnion may play a key role in this phenomenon.

Key words: N₂O in lake water, low-oxygen zone, denitrification, organic matter

1. Introduction

Atmospheric N₂O is mostly biogenic: nitrification and denitrification in terrestrial and aquatic environments are considered to be the major agents in global N₂O production (WATSON *et al.*, 1990). N₂O production is due to nitrification in aerobic fertilized soils (BREMNER and BLACKMER, 1981) or in the well-oxygenated zone of a freshwater lake (YOH, 1990). About 0.1 to 0.3% of nitrified N is released as N₂O during this process (BREITENBECK *et al.*, 1981; GOODROAD and KEENEY, 1984; YOH, 1990).

On the other hand, active N₂O production is often reported in soils with higher water contents (BERMNER and BLACKMER, 1981; GOODROAD and KEENEY, 1984; AULAKH *et al.*, 1984) or in oxygen-limited lake hypolimnions (KNOWLES *et al.*, 1981; VINCENT *et al.*, 1981; PRISCU *et al.*, 1986; DOWNES, 1988). Although such N₂O production under oxygen-limited conditions may be of

possible importance, its mechanism and its contribution to the global N₂O source are poorly understood.

During a series of studies in Lake Kizaki and Lake Fukami-ike, large N₂O accumulations have been observed in the low-oxygen zones (YOH *et al.*, 1983; TERAJ *et al.*, 1987; TERAJ, 1987; YOH *et al.*, 1988; YOH *et al.*, 1990). These accumulations are associated with an NO₃⁻ decrease with depth and time, and with denitrification activity, indicating that the main process responsible for N₂O production is denitrification. However, the contribution of nitrification to such an N₂O accumulation is also demonstratable on the basis not only of nitrification activity determination without any substrate enrichments, but also of an NH₄⁺ budget in the low-oxygen zone in Lake Kizaki (YOH *et al.*, 1990). N₂O accumulation is likely under an *in situ* dynamic equilibrium between these productions and further reduction to N₂ (YOH *et al.*, 1990).

The present paper is a further inspection of N_2O cycling under low-oxygen conditions, on the basis of N_2O accumulation data in Lake Kizaki from 1981 to 1988. A marked variability in the maximum N_2O concentration among observations is reported. The mechanism and a possible factor responsible for such a phenomenon are discussed with a focus on the net N_2O production during the denitrification process.

The data sets on the following observations are employed here: 1981 (8 August, 10 October), 1982 (1, 18 August, 4, 24 September, 22 October, 4 December), 1983 (29 October, 2 December), 1984 (30 November) and 1988 (30 September, 29 October). (But the NO_3^- data on 2 December 1983 are lacking.) The results in 1981, 1982 and 1988 have already been described elsewhere (YOH *et al.*, 1983; YOH *et al.*, 1988; YOH *et al.*, 1990).

2. Results and discussion

The N_2O and NO_2^- accumulation levels observed in the low-oxygen zones in Lake Kizaki are plotted in logarithmic scale in Figure 1, in terms of maximum concentrations throughout the water column. The maximum NO_2^- con-

centrations were almost constant at $3.1 \pm 1.7 \mu\text{g atom N} \cdot \text{l}^{-1}$ ($n=12$). These levels are nearly equal to those in oceanic oxygen minimum zones such as the eastern tropical North Pacific Ocean and the Arabian Sea (CLINE and RICHARDS, 1972; DEUSER *et al.*, 1978; ANDERSON *et al.*, 1982). The maximum N_2O concentration, however, showed a marked variation as large as two orders of magnitude, ranging from 0.17 to $26.5 \mu\text{g atom N} \cdot \text{l}^{-1}$. The largest N_2O concentration was obtained in December 1982, when the maximum NO_2^- concentration was also largest (YOH *et al.*, 1988).

In addition, the N_2O accumulation level differed distinctively from year to year (Fig. 1). As distinguished by closed and opened symbols in the figure, all the maximum N_2O concentrations were less than $0.6 \mu\text{g atom N} \cdot \text{l}^{-1}$ in 1983 and 1988 (twice in each year), but exceeded $2.4 \mu\text{g atom N} \cdot \text{l}^{-1}$ in other years (1981, 1982 and 1984). In 1983 and 1988, the maximum N_2O concentrations were approximately one order of magnitude lower than the maximum NO_2^- concentrations.

In Figure 2, the maximum N_2O concentrations are plotted as a function of the relative

Fig. 1. Maximum concentrations of NO_2^- and N_2O on each observation in Lake Kizaki. Note that abscissa is logarithmic scale.
1981, (Δ); 1982, ($\circ$); 1983, ($\blacktriangle$); 1984, ($\square$); 1988, ($\bullet$)

Fig. 2. Relationship between maximum N₂O concentration on each observation and its relative position in low-oxygen zone. Relative peak position (Z) estimated as:

$$Z = (\text{NO}_3^-_{\text{max}} - \text{NO}_3^-_{\text{N}_2\text{O}}) / \text{NO}_3^-_{\text{max}}$$

where $\text{NO}_3^-_{\text{max}}$ and $\text{NO}_3^-_{\text{N}_2\text{O}}$ are maximum NO_3^- concentration, and NO_3^- concentration at N₂O peak, respectively. Abscissa values, 0 and 1, imply N₂O peak occurrences in uppermost and lowermost low-oxygen zones, respectively.

N₂O peak position (Z) in the low-oxygen zone ($0 < \text{O}_2 < 0.4 \text{ ml} \cdot \text{l}^{-1}$). The Z value ranges between 0 and 1, which implies that the N₂O peak is formed at the uppermost layer and the lowermost layer of this zone, respectively. This parameter is estimated in terms of the NO_3^- decrement at the N₂O maximum from the maximum NO_3^- concentration of the year;

$$Z = (\text{NO}_3^-_{\text{max}} - \text{NO}_3^-_{\text{N}_2\text{O}}) / \text{NO}_3^-_{\text{max}}$$

where $\text{NO}_3^-_{\text{max}}$ and $\text{NO}_3^-_{\text{N}_2\text{O}}$ are the maximum NO_3^- concentration of the year, and the NO_3^- concentration at the N₂O maximum, respectively. (Only the data of peak-forming N₂O accumulation are employed here. Since N₂O and NO_3^- concentrations were determined from the same water samples, this parameter may serve

as a precise index of the relative N₂O peak position.)

The N₂O peak position in the low-oxygen zone also varied widely, ranging from $Z=0.1$ to 0.8 (Fig. 2). The datum in parentheses may be erroneous, since the oxygen concentration, $0.26 \text{ ml} \cdot \text{l}^{-1}$, was exceptionally high in comparison with the usual oxygen concentrations at the N₂O peak of less than $0.13 \text{ ml} \cdot \text{l}^{-1}$ (e.g., YOH *et al.*, 1988). If this datum could be excluded, a correlation would be seen between both parameters, showing that the maximum N₂O concentration increases progressively along with an increase of relative depth in low-oxygen zones. Indeed, the lowest concentration of the N₂O maximum was found associated with the "shallowest" peak (October 1988; YOH *et al.*, 1990), while the highest concentration with the "deepest" peak (December 1982; YOH *et al.*, 1988) (Fig. 2). Such a relationship among the data suggests that the widely varying N₂O level is not arbitrary but under the control of a certain mechanism.

A typical N₂O vertical distribution of the low N₂O accumulation is shown in Figure 3. At this time (October 1983), the N₂O maximum at 21 m depth was associated with low-oxygen content ($0.07 \text{ ml} \cdot \text{l}^{-1}$), in agreement with previous observations in this lake. However, the maximum N₂O concentration was only $0.41 \mu\text{g atom N} \cdot \text{l}^{-1}$. With the small N₂O maximum coinciding with a small O₂ minimum at 14 m depth, the N₂O profile was inversely correlated with the oxygen profile down to N₂O maximum. This is typically indicative of N₂O formation by nitrification (YOSHINARI, 1976; YOH, 1990). In addition, it is worth noting that the maximum N₂O concentration was not very different from the N₂O concentration at the NO_3^- maximum (20 m), down to which aerobic nitrification likely prevails. These N₂O profile characteristics suggest that the principal N₂O source throughout the water column is nitrification, and hence denitrification probably contributes little to N₂O production even under low-oxygen conditions.

This view is consistent with the result of the ¹⁵N abundance determination of dissolved N₂O

Fig. 3. Vertical distributions of water temperature (●), oxygen (○), N_2O (■), NO_3^- (□) and NO_2^- (▲) in Lake Kizaki on 29 October 1983.

by WADA *et al.* (in press) on this occasion. The $\delta^{15}\text{N}$ value of N_2O at the N_2O maximum layer (21 m) was found to be -6.0‰ , considerably lower than that of available NO_3^- (or NH_4^+) in the water column of this lake, namely 0.2‰ , presented by YOSHIOKA *et al.* (1988). Based on such ^{15}N depletion in N_2O , WADA *et al.* (in press) suggested that nitrification may be responsible for N_2O production.

Similar profiles can be seen in other cases of low N_2O accumulations in 1983 and 1988. In December 1983, the distribution of N_2O was also inversely correlated with that of oxygen down to the N_2O maximum (data not shown). In addition, such a shallower N_2O peak position than the NO_2^- peak shown in Figure 3 has never been encountered in the cases of larger N_2O accumulations (YOH *et al.*, 1983; YOH *et al.*, 1988), but was observed in October 1988, when the smallest maximum N_2O concentration ($0.17\text{ }\mu\text{g atom N}\cdot\text{l}^{-1}$) was recorded (YOH *et al.*, 1990). Hence, it seems likely that these low N_2O accumulations may be characteristically arisen from insignificant N_2O productions

through denitrification.

One explanation for the decreased contribution of denitrification to N_2O production is that denitrification may be inactive during these years, since there is a correlation between denitrification activities and *in situ* N_2O concentrations for samples from the water column (TERAI, 1987). In an attempt to find the difference in levels of denitrification activity, the NO_3^- distribution for the same season (September or October) are compared among the years in Figure 4. The NO_3^- -decreasing layers were considerably shallower (2–4 m) in 1983 and 1988 than those in other years, indicating that denitrification was rather active in both years despite the low N_2O accumulations. Therefore, the low N_2O accumulations in 1983 and 1988 cannot be attributed to denitrification activity per se.

Accumulated N_2O in the low-oxygen zone appears to undergo a rapid turnover via N_2O production and N_2O reduction to N_2 , in view of N_2O concentration and the denitrification rate (TERAI, 1987; YOH *et al.*, 1990). Therefore, the

Fig. 4. Difference in NO_3^- profile in hypolimnion of Lake Kizaki in autumn (September and October) in different years.

size of the N_2O pool in water can be subtly influenced by the production-reduction balance of N_2O . Thus, low N_2O accumulation despite active denitrification in both 1983 and 1988 is considered to be due to a decrease in the net N_2O production during the denitrification process. This could account for the observation that nitrification is the principal process responsible for N_2O production when N_2O accumulations are low (Fig. 3), and for the remarkably wide variation in N_2O accumulation levels associated with peak formation depth (Figs. 1 and 2).

It is of great interest to know the environmental factor(s) causing such variations in N_2O accumulation. Oxygen tension, pH, NO_3^- concentration, and NO_2^- concentration are experimentally known to be the factors affecting gaseous composition during denitrification (WIJLER and DELWICHE, 1954; FOCHT, 1974; BLACKMER and BREMNER, 1978; FIRESTONE *et al.*, 1979). However, there is no discernible differ-

ence with respect to these parameters in the hypolimnion of Lake Kizaki.

The supply of reductant (organic matter) seems to be a crucial factor in the denitrification process itself, since dissolved organic carbon concentration in this hypolimnetic water is as low as $0.5\text{--}1.0 \text{ mgC}\cdot\text{l}^{-1}$ (KATO and SAKAMOTO, 1981; TERAI, pers. comm.). It is thought that increased organic matter availability may decrease the proportion of N_2O during denitrification (FOCHT and VERSTRAETE, 1977; FIRESTONE and DAVIDSON, 1989). HANAKI (pers. comm.) recently observed that the $\text{N}_2\text{O} : (\text{N}_2\text{O} + \text{N}_2)$ ratio decreased with an increase in the $\text{COD} : \text{NO}_3^-$ ratio in continuous culture systems of denitrifying activated sludge.

The hypolimnetic oxygen consumptions were more advanced in both 1983 and 1988 than in other years based on a comparison of dissolved oxygen profiles among the years (data not shown). This fact suggests that there were comparatively abundant supplies of decompos-

ble organic matter in both years of low N_2O accumulations. Thus, there is a possibility that organic matter availability may have played a key role in the N_2O accumulation level in this lake.

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摘 要

湖沼における N_2O 蓄積レベルの 著しい変動とそのメカニズム

本崎湖低酸素条件下における N_2O 蓄積量をこれまで得られたデータについて比較したところ、 $0.17\text{--}26.5\ \mu\text{g atom N}\cdot\text{l}^{-1}$ にわたるきわめて大きな変動が見出された。さらに、1983 年、1988 年にはいずれも $0.6\ \mu\text{g atom N}\cdot\text{l}^{-1}$ 以下、他の年では $2.4\ \mu\text{g atom N}\cdot\text{l}^{-1}$ 以上と、年によって著しい違いを示した。 N_2O 蓄積量の変動はピークの低酸素層中の出現深度と関連しており、小さなピークほどその上部に、大きなピークほどその下部に出現する一連の関係が認められた。 N_2O 、 NO_3^- 、 O_2 濃度の各年の分布特性から、このような N_2O 蓄積量の変動は脱窒過程における N_2O 生成・消費間のバランスの変化によってもたらされたものであり、深水層への易分解性有機物の供給状態がその重要な要因であると考えられた。

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