Short communication

Littoral zones as the “hotspots” of nitrous oxide (N₂O) emission in a hyper-eutrophic lake in ChinaHongjun Wang^{a,b}, Weidong Wang^{a,*}, Chengqing Yin^a, Yuchun Wang^c, Jinwei Lu^{a,b}^aState Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, CAS, Beijing 100085, China^bGraduate University of the Chinese Academy of Sciences, Beijing 100039, China^cDepartment of Water Environment, China Institute of Water Resources and Hydroelectric Power Research, Beijing 100038, China

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Abstract

N₂O emissions were measured monthly for 1 year using the static chamber method along the littoral and pelagic zones of Meiliang Bay in hyper-eutrophic Taihu Lake. The results indicated that littoral zones were the “hotspots” of N₂O emissions ($-278 \sim 2101 \mu\text{g N}_2\text{O m}^{-2} \text{h}^{-1}$). While the littoral zone accounted for only 5.4% of the area of Meiliang Bay, the N₂O emissions from the littoral zones were about 43.6% of total emissions from the bay. The importance of spatial variation on N₂O emissions was demonstrated by dividing the lake into four unique zones through cluster analysis. The eulittoral zone was the key area of N₂O emissions with an annual 5% trimmed mean $429.5 \mu\text{g N}_2\text{O m}^{-2} \text{h}^{-1}$, following by supralittoral ($138.8 \mu\text{g N}_2\text{O m}^{-2} \text{h}^{-1}$), infralittoral ($98.9 \mu\text{g N}_2\text{O m}^{-2} \text{h}^{-1}$), and pelagic zones ($15.7 \mu\text{g N}_2\text{O m}^{-2} \text{h}^{-1}$). Further, N₂O emissions showed a seasonal trend. Excessive N₂O emissions during algal bloom periods suggested that algae played a significant role in the emission of N₂O.

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1. Introduction

It has been suggested that littoral zones, the transitional boundary between terrestrial and aquatic ecosystems, are potential “hotspots” of nitrous oxide (N₂O) production in the landscape (Groffman et al., 1998, 2000). However, insufficient data exist to support this hypothesis, and the currently recommended methodologies of the Intergovernmental Panel on Climate Change (IPCC) do not account for high N₂O production in these zones

(Houghton et al., 2001). Complicated spatial variation of N₂O emissions in the littoral zone limits accurate assessment. Seitzinger and Kroeze (1998) estimated that China and Southeast Asia accounted for about 50% of the annual N₂O emissions from rivers, estuaries, and continental shelves based on dissolved inorganic nitrogen export by world rivers. However, field measurements of N₂O emissions from freshwater ecosystems are rare in China, with only one study, which might miss some “hotspots” of N₂O emissions, reporting low N₂O emissions from the center of Taihu Lake (Xiong et al., 2002). Global emissions from lakes have not been estimated (Seitzinger et al., 2000), and the measurement of N₂O emissions from the sensitive littoral zones is

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even more deficient. With the increasingly eutrophic conditions of lakes projected to result in increased N_2O emissions (Huttunen et al., 2003a,b), the documentation of these water systems as potential sources of N_2O is urgent. In this preliminary study, we attempted to identify the “hotspots” of N_2O emissions in a hyper-eutrophic lake and investigated how defined zones could improve field investigation methodologies in water systems.

2. Materials and methods

2.1. Site description

Taihu Lake, a shallow eutrophic lake in a zone of northern subtropical monsoonal climate in China, covers a surface area of 2338 km² with average water depth of 1.9 m. The mean annual air temperature is 14.9–16.2 °C, and the growing season spans from March to November. The agricultural area covers about 48% in this catchment and about 39100 t N is input into Taihu Lake annually. The study sites were located in hyper-eutrophic Meiliang Bay (N 31°24′–31°32′, E 120°04′–120°14′) in the north part of Taihu Lake (Fig. 1). The bay has an area of 101 km², encompassed by hills and 55 km of shoreline, of which 35 km was covered with macrophytes. In the bay, the average concentration of total N was 6.7 mg L⁻¹, total P 0.3 mg L⁻¹, nitrate N 1.6 mg L⁻¹, and chlorophyll-a 57 µg L⁻¹ in 2004, and severe algal bloom has been taking place from

1990s. N_2O emissions were measured in two littoral sections (A & B) and two pelagic sites (C1 & C2). In this study, the littoral zone denoted the area between the highest shoreline and the outer limit of floating-leaved vegetation, and the terminology of subzones used follows that of Wetzel (2001) (Fig. 1). Section A was located in a reed-dominated littoral zone, and section B occupied a bare zone without macrophytes and contained only infralittoral zone. Nine sampling sites in section A and three in section B were established along the gradients from open water to shore, marked as A1–A9 (Fig. 1) and B1–B3, respectively. There was few submerged or floating-leaved vegetation in spring from A1 to A3, with A3 at the outer fringe of reed belt. A3–A7 were characterized by *Phragmites australis* with above-ground dry biomass density 3–4 kg m⁻². The dominant species in the supralittoral zone was *Miscanthus saccharifloous*. In section B, the interval was 25 m and all sites were within the infralittoral zone and contained little sediment. Sites C1 and C2 were located in the pelagic zone in the north and south part of Meiliang Bay, and they were more than 500 m away from the shore.

2.2. N_2O emissions

N_2O emission measurements were taken monthly from Aug. 2003 to Aug. 2004. The closed-chamber technique was applied, with duplicate chambers at

Fig. 1. A schematic of sampling sites in section A.

all sites along sections A and B and triplicate at sites C1 and C2. Samples were collected during 9:00–12:00 at sites of section A and site C, and during 13:00–15:00 at sites of section B. The stainless steel chamber consisted of two parts: pedestal and upper chamber. Its pedestal ($h = 25$ cm, $\varnothing = 40$ cm) had a gutter around the outside in upper rim that could be filled with water to make an airtight seal with upper chambers. When water depth exceeded 25 cm, a height-adjustable buoy with an internal diameter of 40.5 cm kept the pedestal floating on the water surface. The upper chamber ($h = 45$ cm, $\varnothing = 40$ cm) was equipped with two battery-driven (12 V) brushless fans for air-mixing and one temperature probe.

Sampling bridges (60 m long) were installed to avoid disturbing lake sediments in the littoral zone. During the gas-sampling period, the upper chamber was inserted into the water-filled gutter of the pedestal. Four gas samples were taken at 5–15 min intervals from the headspace of the chambers through polytetrafluoroethylene tubes into the 500 mL gas sampling bags (multi-layer polymer with aluminum foil) by the air pump (12 V, 1.8 L min^{-1} , KNF, Germany). N_2O concentration was detected within two days after sampling by gas chromatography (Agilent 4890D) with an electron capture detector. The accuracy of the analyses was maintained by calibrating the gas chromatographs against a standard gas mixture after every 8 samples, which kept the coefficient of variation of the replicated concentration determinations below 1%. N_2O emission rate was calculated from the linear change of its concentrations in the chamber headspace as a function of time, base area, chamber volume, and the molar volume of N_2O at chamber air temperature. Measurements with a $R^2 < 0.9$ in a linear regression of the concentration change over time were considered erroneous and excluded.

On each gas sampling date, dissolved oxygen (DO) and pH were measured in situ in the inundated area by oxygen meter (YSI Model 57) and pH meter (HI 8424 Microcomputer HANNA), respectively, and nitrate concentration in water column was also detected (Wang et al., 2006).

2.3. Statistical analyses

Hierarchical cluster analysis by between group linkage method (Squared Euclidean distance) was used to cluster sites into homogeneous groups according to N_2O emission rates at sites of

section A and to test whether Wetzel's zonation could be applied here. Mann–Whitney U nonparametrical tests were performed to compare the emission rates between the different zones. The alpha value was set to 0.05. All analyses were performed using SPSS statistical package (SPSS Inc., release 11.0.0).

3. Results

N_2O emissions showed large temporal variations, following a seasonal trend in each zone, for example in the eulittoral zone (Fig. 2). Generally the minimum values occurred in winter (Dec. or Jan.), and the maximum appeared at the end of spring, summer or the beginning of autumn. Spatial variation of N_2O emissions for 1 year period in section A (Fig. 3) showed that from open water to lakeshore, N_2O emissions initially increased gradually, with peak values at A5 ($590 \pm 440 \mu\text{g N}_2\text{O m}^{-2} \text{ h}^{-1}$), and then decreased in supralittoral zone. N_2O emissions at A1 occupied only about 1/10 of those at A5. Correlation analysis showed that DO affected N_2O emission significantly ($r = -0.382$, $p < 0.0001$) in the inundated area and nitrate had no effect.

Based on N_2O emissions within 12 months at each site of section A, four zones were divided by cluster analyses (Fig. 3). A1 was one single group, and the other sites just followed Wetzel's zonation. No significant difference of N_2O emissions could be found among sites A1, C1 and C2, thus the pelagic zone included three sites in this study (A1, C1 and C2).

Fig. 2. Temporal variation of nitrous oxide (N_2O) emissions (mean $\pm$ SD) from the eulittoral zone (A5–A7), $n = 5$ –6.

Fig. 3. Spatial variation of nitrous oxide (N_2O) emissions along section A during 1 year period.

Table 1

Nitrous oxide emissions: 5% trimmed mean, median, range, and total emissions in the different zones of Meiliang Bay

Location	<i>n</i>	5% trimmed mean	Median ($\mu\text{g N}_2\text{O m}^{-2} \text{h}^{-1}$)	Range	Width (m)	Length (km)	Area (km^2)	Total emissions ($\text{g N}_2\text{O h}^{-1}$)
Infralittoral zone	71	98.9	75.2	−265.1–2101.4	50	55	2.7	267
Eulittoral zone	36	429.5	364.5	71.0–1641.1	20	35	1.8	773
Supralittoral zone	24	138.8	138.5	−278.0–437.0	30	35	1.1	153
Pelagic zone	37	15.7	19.0	−177.6–163.1			98.3	1543

There was also no statistical difference among sites in section B, although the emissions increased gradually from B1 to B3. Therefore, all sites in section B are within infralittoral zone. Significant difference was detected between the infralittoral zones of sections A and B ($p = 0.021$). The N_2O emission data in August were extremely high at the infralittoral zone of section A, resulting in that the median was $87 \mu\text{g N}_2\text{O m}^{-2} \text{h}^{-1}$ and the maximum reached $2101 \mu\text{g N}_2\text{O m}^{-2} \text{h}^{-1}$. If the data in August were not taken into account for nonparametric test, no statistical difference of N_2O emissions was found between the infralittoral zones of sections A and B.

According to the above analysis, four groups representing different zones in the lake could be confirmed by the N_2O emissions (Table 1). The strength of N_2O emissions was as follows: eulittoral zone > supralittoral zone > infralittoral zone > pelagic zone. The 5% trimmed means of N_2O emissions in the sublittoral zones, which includes eulittoral,

supralittoral, and infralittoral areas, were 6–27 times higher than those from the pelagic zones.

Based on the length of shoreline with and without macrophytes, the width of each zone and the 5% trimmed mean of N_2O emissions, conservative estimations for average N_2O emission from Meiliang Bay are given in Table 1. Results showed that the littoral zone accounted for only 5.4% of the area of Meiliang Bay, and the N_2O emissions from the littoral zones ($1193 \text{ g N}_2\text{O h}^{-1}$) were about 43.6% of total emissions from the bay.

4. Discussion

4.1. N_2O emissions in water systems

Aquatic systems are suggested to contribute one third of global anthropogenic N_2O emission, however, few measured field data resulted in considerable uncertainties in N_2O emission estimates

(Seitzinger et al., 2000). Lakes are the sink of regional N and consequently should have effects on N₂O emissions, especially in areas where a large amount of N fertilizer is applied. The field data are even more limited and global emissions from lakes have not been estimated (Seitzinger et al., 2000). Based on few reported N₂O emissions from lakes with different trophic state in Finland and Switzerland (Mengis et al., 1997; Huttunen et al., 2003a, b), there is an increasing trend of N₂O emissions from oligotrophic to eutrophic lakes.

Our results indicated that the pelagic zones of eutrophic lakes were important N₂O sources. Littoral zones with relatively small dimensions, however, may play a disproportionately large role in N₂O production in water systems. In the littoral zone of Meiliang Bay, extraordinarily high levels of N₂O were emitted with annual 5% trimmed mean $429.5 \mu\text{g N}_2\text{O m}^{-2} \text{h}^{-1}$ in the eulittoral zone, and the emission rates evidently exceeded the field data in natural aquatic systems (Mengis et al., 1997; Hashimoto et al., 1999; Huttunen et al., 2003a, b) and even corresponded to or exceeded the emissions from wetlands treating waste water (Freeman et al., 1997; Johansson et al., 2003). The littoral zones were the “hotspots” of N₂O emissions in these aquatic systems. Eutrophication may play an essential role in increasing N₂O emission in aquatic systems. In our study, there was no land source pollution discharging to the littoral zone and the nutrient sources were mainly from the eutrophic open water in forms of suspended sediment and algae. Algae in eutrophic water body may be an important contributor by producing N₂O directly (Weathers, 1984), as suggested by our finding of highest N₂O emissions during summer in the reeded infralittoral zone when algae blooms occurred.

4.2. Zonations for N₂O investigation in water systems

Traditionally, studies of N₂O emissions from natural system have been based on a limited number of widely spaced sampling points, with an assumption that measured ratios were representative of the larger area (Reay et al., 2003). However, coarse-scale measurements, which ignore large spatial variation, may miss some “hotspots” of N₂O emissions and result in an underestimation. Numerous studies found significant spatial variation about N₂O emissions within the riparian or littoral zones (e.g. Groffman et al., 1998; Huttunen et al.,

2003a, b), however, there are no recommended approaches for investigation in water systems in which the littoral zone may account for a large portion of greenhouse gas emission (Groffman et al., 1998). Our investigation displayed four N₂O emission zones by cluster analysis, and they correspond well with classical limnological zonation method by Wetzel (2001). Although an accurate estimation of N₂O flux from Taihu Lake could not be made based on our limited data, the conservative estimation of N₂O flux from Meiliang Bay showed that littoral zones played an important role in N₂O emission from the whole bay. The littoral zone must be taken into account in investigations of water system N₂O emissions. If it is possible, even fine sublittoral zones (infralittoral, eulittoral, and supralittoral zones) should be considered.

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