Short-Term Field Observations of Nitrous Oxide Saturations in Lake Taihu, China: The Need for High Temporal Resolution Studies

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The incomplete understanding of the processes which control aquatic nitrous oxide (N\textsubscript{2}O) production is partially due to a lack of onsite data with which to describe the temporal resolution of N\textsubscript{2}O production. To help resolve this, we directly measured the N\textsubscript{2}O saturation (relative to atmospheric partial pressure) on an hourly basis over two survey periods (July and September 2003) in Lake Taihu, a large eutrophic lake in eastern China. July N\textsubscript{2}O saturations displayed a distinct diurnal pattern, opposite to those observed by others in subtropical streams, but similar to N\textsubscript{2}O emissions observed from incubated estuarine sediments. Correlative analyses indicate that biogeochemical processes operate as important controls on N\textsubscript{2}O production over very short time scales. Nitrous oxide production processes are not only regulated by O\textsubscript{2} dynamics related to microalgal photosynthesis, but also closely related to organic matter decay at the sediment–water interface. While large-scale changes (~25-fold) in N\textsubscript{2}O fluxes in Lake Taihu are a function of variable N loading, biogeochemical processes concerning O\textsubscript{2} and N transformation at the sediment–water interface have significant (~twofold) impacts on the regulation of N\textsubscript{2}O production over very short time scales. Further, high temporal resolution research focused on developing a comprehensive understanding of lacustrine N\textsubscript{2}O production, including natural and anthropogenic loading and biogeochemical transformation processes, is clearly needed.

Much of the N\textsubscript{2}O emitted from aquatic ecosystems is anthropogenically derived, and given its potency as a greenhouse gas, it is attracting considerable attention (Seitzinger et al., 2000; Wuebbles, 2009; Ravishankara et al., 2009). However, there remains considerable uncertainty in the magnitude of anthropogenic N\textsubscript{2}O emitted from aquatic environments and how N\textsubscript{2}O emissions respond to increasing loads of anthropogenic N and eutrophication in general. This uncertainty is due in part to an incomplete understanding of the processes governing aquatic N\textsubscript{2}O production.

Aquatic N\textsubscript{2}O is an intermediate of dissimilatory NO\textsubscript{3}\textsuperscript{-} reduction (denitrification) in anoxic environments, and a byproduct of NH\textsubscript{4}\textsuperscript{+} oxidation (nitrification) in oxic environments. Anthropogenic inputs of inorganic N (NO\textsubscript{3}\textsuperscript{-} + NH\textsubscript{4}\textsuperscript{+}) can increase the potential for both of these reactions. However, N concentrations are not always the primary factor regulating aquatic N\textsubscript{2}O fluxes (Cole and Caraco, 2001). Eutrophication may lead to significant accumulations of N\textsubscript{2}O by stimulating denitrification due to hypoxia or anoxia in bottom waters (Naqvi et al., 2000; Liikanen and Martikainen, 2003; Cole and Caraco, 2001), whereas decreases in primary productivity and in the supply of organic matter to marine benthos has been observed to decrease denitrification, consequently increasing N fixation in sediment (Fulweiler et al., 2007). A clear understanding of the processes and factors governing aquatic N\textsubscript{2}O production is necessary to develop effective strategies and techniques to reduce future emissions (Seitzinger et al., 2000).

Production of N\textsubscript{2}O in aquatic environments is governed principally by temperature, NO\textsubscript{3}\textsuperscript{-} and organic carbon supply, and the nature of the oxic-anoxic interface, and so therefore commonly exhibits seasonal patterns (Christensen et al., 1990; Mengis et al., 1997; Wang et al., 2006). Diurnal patterns have seldom been observed in the field, so studies focused on short-term changes in aquatic N\textsubscript{2}O production have utilized laboratory experiments. Jensen et al. (1984) found that N\textsubscript{2}O emissions from incubated...
estuarine sediments reached their maximum at night and decreased during the day, conceptually in congruence with the diel cycle of denitrification (Anderson et al., 1984; Christensen et al., 1990; Risgaard-Petersen et al., 1994). Since the diurnal pattern of denitrification is primarily regulated by O₂ production from microalgae photosynthesis (Weathers, 1984; Wang et al., 2006), total denitrification rates would be lower during the day than at night (Anderson et al., 1984; Christensen et al., 1990).

Harrison et al. (2005) have argued that laboratory experiments likely do not accurately represent in situ nitrogen cycles. In contrast to the results of some laboratory studies (e.g., Anderson et al., 1984; Christensen et al., 1990; Risgaard-Petersen et al., 1994), Laursen and Seitzinger (2004) documented consistently higher denitrification rates during the day than at night in some rivers draining intensively agricultural lands, and linked the diurnal pattern of denitrification to cyclic patterns of nitrification driven by diurnal variations in water column pH and temperature. Furthermore, Harrison et al. (2005) showed that denitrification ceased at night in a eutrophic subtropical stream as nitrate in the water was depleted, and that N₂O production correspondingly ceased for at least 8 h. By comparison, two completely different diurnal patterns of N₂O were shown in estuarine sediments (Jensen et al., 2004) and in rivers (Laursen and Seitzinger, 2004; Harrison et al., 2005), respectively. Lakes have significantly different environmental settings as compared to either estuaries or rivers. Lacustrine chemistry is sensitive to a range of variables including changes in watershed land uses, nutrient supply, eutrophication, hydrologic variability, and climatic perturbations (e.g., Liikanen and Martikainen, 2003; Whitmore et al., 2006; Martin and Soranno, 2006). Production of N₂O in lakes, including its diurnal variation, can reflect environmental change in the whole watershed area. To the best of our knowledge, no direct field observations of N₂O diurnal cycling in shallow lakes have been performed. We utilized a short temporal sampling interval (1 h) to survey N₂O saturation (relative to atmospheric partial pressure) in Lake Taihu, a shallow and heavily-polluted eutrophic lake. A primary objective was to examine whether diurnal N₂O saturation patterns exist in this lake, as in estuaries and rivers, and if so, to describe the patterns by comparing them to other variables.

Materials and Methods

Study Area

Lake Taihu is the third-largest freshwater lake in China, with a surface area of approximately 2300 km², an average depth of 1.8 m and a residence time of 0.9 yr. It is surrounded by several cities (Fig. 1), all with rapidly growing populations. Municipal and industrial effluents flow into the lake from the surrounding watershed. Additionally, aquacultural feed and runoff from agricultural soils are important sources of nutrients. Consequently, the lake is eutrophied, severely so in Meiliangwan and Wuliuhu bays in the north (McCarthy et al., 2007), where algal blooms resulted in significant ecological and environmental problems in 2007 (Guo, 2007; Yang et al., 2008).

Spatial contrasts in ecology and nutrient levels allow Lake Taihu to be divided into three subareas (Fig. 1): the northern subarea where concentrations of TN and TP are highest, water pollution is greatest, and blooms of cyanobacteria are significant; the southern subarea where water pollution is less severe and vegetation is dominated by submerged and emergent macrophytes; and the central subarea, which is an open transitional zone from algae to macrophytes. Nutrient concentrations decrease with distance from river outflows in the northern subarea due to dilution, consumption and deposition (McCarthy et al., 2007). Spatial distributions of N₂O saturation parallel distributions of nutrients and the degree of eutrophication in the lake (Wang et al., 2009). Saturations of N₂O in the northern subarea are 3 to 7 times higher than those in the middle and southern subareas, with maximum saturation values observed in Wuliuhu Bay (Fig. 1), located between Lake Taihu and the Liangxihe River (Wang et al., 2009).

Wind-driven mixing and shallow water depths prevent stratification in the lake, resulting in sustained oxic conditions in bottom waters (McCarthy et al., 2007). Before sampling, we compared mean N₂O saturations between surface and deeper waters at the Ecological Observational Station (EOS), which were not statistically different (250 ± 40% and 249 ± 14%, respectively) (mean ± SD).

Water Sampling and Measurements

Monitoring of N₂O saturation was conducted at EOS in Meiliangwan Bay (northern subarea; Fig. 1), which has a water depth of ~1 m. Water from 0.5 to 0.7 m depth was assumed to be representative of the entire water column. Most samples were collected hourly, with a few collected at 2-hour intervals over two sampling periods, 19 to 20 July and 22 to 23 Sept. 2003. Samples for dissolved N₂O and CH₄ were collected and separately stored in 70-mL serum bottles and amended with 10 M NaOH and saturated HgCl₂.
respectively. Sample bottles were sealed and returned to the laboratory for immediate analysis.

A headspace equilibrium technique was used to determine concentrations of dissolved gases, expressed by the saturation degree relative to air (Mengis et al., 1997; Wang et al., 2009). Using headspace concentrations, the formula provided by Butler and Elkins (1991) was used to calculate dissolved gas concentrations, with a mean error of ± 4%. Sample water temperature, EC, TDS, and pH were determined in the field using a PIONneer 65 multiparameter instrument (Radiometer Co.); DO was determined using a portable analyzer (HI9145, HANNA Co.); NO$_2^-$ and NO$_3^-$ were determined using a HPLC-1100 liquid chromatograph after samples were filtered (GF/F) onsite; NH$_4^+$, SiO$_2$ and TP were determined using a spectrophotometer (UV-2000, UNICO Co.); and CO$_2$ partial pressure was calculated from HCO$_3^-$, pH, the reaction constant (pKa) between HCO$_3^-$ and CO$_2$(aq) and Henry’s law constant for CO$_2$ (Butler 1982).

Results

Diurnal Pattern of Nitrous Oxide Saturations

A distinct diurnal N$_2$O saturation pattern was observed during 19 to 20 July (Fig. 2). Saturations of N$_2$O decreased during the day, reached a minimum value of 247% before sun set, then increased gradually after nightfall, reaching a maximum of 557% at ∼2 a.m. This pattern is opposite to those reported in the subtropical stream by Harrison et al. (2005), but is consistent with typical diel cycles of N$_2$O emission and denitrification in incubated estuarine sediments regulated by DO (e.g., Jensen et al., 1984; Anderson et al., 1984). Ebulbition contributions from bottom sediments are uncertain, and are not considered here due to the high solubility of N$_2$O. To the best of our knowledge, this is the first documented field observation of a lacustrine diurnal pattern of N$_2$O saturation.

Diurnal Patterns of Other Variables during July

Saturations of CH$_4$ and N$_2$O are nearly identical during this period (Fig. 2, Table 1). The N$_2$O and CH$_4$ peak saturations (∼2 a.m.) correspond to the DO minimum (Fig. 2). The weak inverse relationship with DO and strong positive correlation with CH$_4$ (Table 1) suggests that N$_2$O was produced primarily by denitrification in anaerobic sediments, while CH$_4$ was controlled by diurnal cycling of methane oxidation on 19 to 20 July.

Diel fluctuations of DO, CO$_2$ and pH on 19 to 20 July (Fig. 2) were mainly regulated by metabolic processes in the lake. The TDS concentration is closely related to the release and oxidation of ions from the decomposition of organic matter at the sediment–water interface (Oliva et al., 1999), and showed a diurnal trend coincident with HCO$_3^-$ during this period (Fig. 2). Concentrations of SiO$_2$ showed some diurnal variation, which may be due to periodic activity of some specific algae (e.g., diatoms). The fluctuations of TP concentrations seemed to be episodic and irregular (Fig. 2).

July NH$_4^+$ concentrations also exhibited a strong diurnal pattern (Fig. 2), consistent with those documented by Harrison et al. (2005). Diurnal variation of NH$_4^+$ coincides with that of CO$_2$ partial pressure (Table 1, Fig. 2), reflecting the influence of biotic and abiotic processes on the diel cycle of NH$_4^+$ (microphyte assimilation and O$_2$ controls on nitrification and methane oxidation). Ammonium increased at night, reaching its maximum (∼1.0 mg L$^{-1}$) at sunrise, and decreased during the day, reaching its minimum (<0.1 mg L$^{-1}$) in the afternoon when photosynthesis was most significant and NH$_4^+$ was being assimilated by algae. Diel variation of pH may partially contribute to the diurnal pattern of NH$_4^+$ concentration via ammonia volatilization. Impacts of other microbial geochemical processes (nitrification, dissimilatory nitrate reduction to ammonium, etc.) on the diurnal variation of NH$_4^+$ concentrations are uncertain. During high NH$_4^+$ conditions in the morning, NO$_3^-$ increased (result of enhanced nitrification) with rising temperature, pH, and DO.
Generally, diel variation of N₂O saturation is controlled by O₂ (as in July). The maxima of N₂O saturation, NH₄⁺ related with NO₃⁻ pressure, and HCO₃⁻ concentration in September implies that there may be a sea-sonal pattern in the lake. During the day than at night (Fig. 2), as was also the case during July sampling (Fig. 2). The absence of a diurnal N₂O pattern in September implies that there may be a seasonal effect.

Significant differences in several parameters were observed between samples collected in July vs. September (Fig. 3), which are most likely due to seasonal variations in biogeochemical cycles in the lake. Maximum DO values were much lower in September than in July, reflecting less photosynthetic activity due to relatively lower temperatures and reduced solar radiation. High dissolved Si and TDS concentrations (Fig. 3) in September likely resulted from relatively lower consumption and assimilation. September CO₂ partial pressures and HCO₃⁻ concentrations are rather low, and pH values are slightly higher than those in July. These data suggest lower metabolic rates in September, which is in agreement with Hu and Pu (2000), who showed a reduced supply of total organic matter and a consequent depletion of labile organic matter in September. Also, concentrations of regenerated NH₄⁺ from organic matter decay, and its oxidation product, NO₃⁻, are approximately one order of magnitude lower in September than July, under conditions of low assimilation.

In comparison, inorganic nitrogen concentrations were less variable in September. Ammonium displayed a trend similar to those of TDS and CO₂ partial pressure (Fig. 3), indicating that NH₄⁺ was mainly derived from organic matter decomposition (as in July). The maxima of N₂O saturation, NH₄⁺, NO₃⁻, and HCO₃⁻ occur at 15:00 (Fig. 2) when photosynthesis was most significant (highest DO, lowest CO₂ partial pressure, and HCO₃⁻). Saturations of N₂O were positively correlated with NO₃⁻ concentration (Table 1). The most significant correlations of N₂O saturation were with CH₄ (r = 0.85, p < 0.01) and NO₃⁻ (r = 0.54, p < 0.01) in July, and with NO₃⁻ (r = 0.59, p = 0.01), TDS (r = 0.52, p = 0.01) and temperature (r = 0.43, p = 0.05) in September (Table 1).

Rapid redox fluctuation, from oxidation to complete reduction, has been observed in a subtropical stream by Harrison et al. (2005). The same process may be occurring in Lake Taihu, resulting in rapid changes in the controlling mechanisms and rate of N₂O production. Therefore, we separated the data series obtained on 19 and 20 July for correlation analysis (Table 1), then compared variations in the correlations over the short term.

For data obtained on 19 July, N₂O saturations were strongly correlated with CH₄, but were not with DO. It is noteworthy that N₂O saturations were significantly positively correlated with HCO₃⁻, TDS, and NH₄⁺, all of which originate mainly from organic matter decomposition. Saturations of N₂O were also significantly positively correlated with NO₃⁻, though N₂O is thought to be mainly produced via denitrification of NO₃⁻. In comparison, N₂O saturations on 20 July were positively correlated with CH₄, CO₂ and NO₃⁻ and negatively with DO. This is in congruence with the hypothesis that N₂O was produced by denitrification of NO₃⁻ in the water, and that DO was controlling the penetration depth of NO₃⁻ into anaerobic sediments (Christensen et al., 1999), where NO₃⁻ is reduced to N₂O (then to N₂). Temperature can promote photosynthesis, thus increasing DO concentrations in the water and the depth of the oxic layer in sediments; temperature was negatively correlated with N₂O saturations. The negative correlation of N₂O saturations with TDS (r = -0.90, p < 0.01, Table 1) is likely related to microbial processes occurring at the sediment–water interface.

**Discussion and Conclusions**

The occurrence of diel variation in N₂O saturations shows that high temporal resolution sampling, or high-frequency, continuous observations are needed to survey N₂O production in lakes. High temporal resolution observations indicate that diurnal patterns of N₂O saturation in aquatic environments vary considerably (e.g., Harrison et al., 2005; Fig. 2 herein), and these contrasts likely represent important information concerning N₂O production. In aquatic environments, rapid redox transformations of N species, particularly at the sediment–water interface, can occur in just a few hours (Harrison et al., 2004). Here, DO is not the most correlative parameter to N₂O saturations in July (r = -0.19, p = 0.36) or September (r = 0.37, p = 0.10) (Table 1). The most significant correlations of N₂O saturation were with CH₄ (r = 0.85, p < 0.01) and NO₃⁻ (r = 0.54, p < 0.01) in July, and with NO₃⁻ (r = 0.59, p = 0.01), TDS (r = 0.52, p = 0.01) and temperature (r = 0.43, p = 0.05) in September (Table 1).

### Table 1. Comparisons of correlations (r) of N₂O saturation to other variables and their significances (p).

<table>
<thead>
<tr>
<th></th>
<th>CH₄</th>
<th>DO⁺</th>
<th>CO₂⁺</th>
<th>NO₃⁻</th>
<th>N₂O⁺</th>
<th>NH₄⁺</th>
<th>TₓP⁺</th>
<th>SO₂⁺</th>
<th>HCO₃⁻</th>
<th>Temp</th>
<th>pH</th>
<th>TDS⁺</th>
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<tbody>
<tr>
<td>19–20 July</td>
<td>r</td>
<td>0.85</td>
<td>-0.19</td>
<td>0.54</td>
<td>0.25</td>
<td>-0.29</td>
<td>-0.09</td>
<td>0.08</td>
<td>-0.18</td>
<td>-0.23</td>
<td>-0.22</td>
<td></td>
</tr>
<tr>
<td></td>
<td>p</td>
<td>&lt;0.01</td>
<td>0.36</td>
<td>0.11</td>
<td>0.60</td>
<td>&lt;0.01</td>
<td>0.22</td>
<td>0.16</td>
<td>0.67</td>
<td>0.37</td>
<td>0.26</td>
<td>0.28</td>
</tr>
<tr>
<td>22–23 Sept.</td>
<td>r</td>
<td>0.29</td>
<td>0.37</td>
<td>-0.21</td>
<td>0.59</td>
<td>0.21</td>
<td>0.05</td>
<td>0.11</td>
<td>-0.38</td>
<td>0.43</td>
<td>0.38</td>
<td>0.52</td>
</tr>
<tr>
<td></td>
<td>p</td>
<td>0.19</td>
<td>0.10</td>
<td>0.01</td>
<td>0.36</td>
<td>0.83</td>
<td>0.65</td>
<td>0.08</td>
<td>0.05</td>
<td>0.08</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>19 July</td>
<td>r</td>
<td>0.85</td>
<td>-0.46</td>
<td>0.59</td>
<td>0.86</td>
<td>-0.12</td>
<td>0.58</td>
<td>-0.22</td>
<td>-0.10</td>
<td>0.74</td>
<td>0.03</td>
<td>-0.52</td>
</tr>
<tr>
<td></td>
<td>p</td>
<td>&lt;0.01</td>
<td>0.10</td>
<td>0.03</td>
<td>&lt;0.01</td>
<td>0.69</td>
<td>0.03</td>
<td>0.44</td>
<td>0.74</td>
<td>&lt;0.01</td>
<td>0.92</td>
<td>0.06</td>
</tr>
<tr>
<td>20 July</td>
<td>r</td>
<td>0.91</td>
<td>-0.75</td>
<td>0.69</td>
<td>-0.27</td>
<td>0.76</td>
<td>0.48</td>
<td>-0.23</td>
<td>-0.33</td>
<td>-0.19</td>
<td>-0.79</td>
<td>-0.68</td>
</tr>
<tr>
<td></td>
<td>p</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>0.01</td>
<td>0.40</td>
<td>&lt;0.01</td>
<td>0.12</td>
<td>0.47</td>
<td>0.30</td>
<td>0.55</td>
<td>&lt;0.01</td>
<td>0.02</td>
</tr>
</tbody>
</table>

† DO, dissolved oxygen; Tₚ, total phosphorus; TDS, total dissolved solids.

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Wang et al.: Field Observations of N₂O Saturations in Lake Taihu, China 1861
Differences in denitrification and N₂O production are significant not only between day and night (Laursen and Seitzinger, 2004), but also on the scale of a few hours, as measured here. Sampling protocol (time and frequency) may result in significant biases for N₂O concentrations determined in lakes during N₂O diel variations. Here, maximum values of N₂O saturations were approximately a factor of 2 greater than minimum values within a day (Fig. 2), suggesting that sampling time may cause an error of up to 50% if the result of one-time sampling was taken to represent daily mean values.

The correlative analyses (Table 1) indicate that the anthropogenic N load is not the primary factor regulating N₂O production in the lake over very short time scales. As Lake Taihu is a eutrophic water body, generally N₂O production is related to anthropogenic N inputs (Wang et al., 2009). This is in agreement with the widely accepted notion that N₂O emitted from eutrophied aquatic systems is generally anthropogenically derived (Seitzinger et al., 2000; Garnier et al., 2006). However, temporally, N₂O saturations correlated with NO₃⁻, but not with NH₄⁺ in September, and with neither NO₃⁻ or NH₄⁺ in July (Table 1). Additionally, the correlations showed significant variability from 19 to 20 July (Table 1). These observations are not in accord with the generally accepted mechanism of enhancement of DIN to N₂O, which regards increases in N₂O (as a product of nitrification and denitrification) as a consequence of increases in reagent (DIN) concentrations. The conclusion drawn here is in congruence with the observations of Cole and Caraco (2001) in the Hudson River—some factors other than riverine DIN concentrations regulate N₂O flux. It is also in agreement with Beaulieu et al. (2009)’s finding that only 29% of the variation in N₂O production rates can be explained by the NO₃⁻ concentration in freshwater streams.

Diurnal variations of N₂O saturation and seasonal effects show that N₂O production is sensitive to biogeochemical processes in water and sediments. Generally, denitrification and N₂O production are thought to be primarily regulated by O₂ dynamics related to microalgal photosynthesis (Christensen et al., 1990; Risgaard-Petersen et al., 1994; Laursen and Seitzinger, 2004). Here, benthic microalgal photosynthesis is inhibited by wind-driven sediment resuspension (McCarthy et al., 2007), and would not be expected to drive diurnal fluctuations of denitrification and N₂O production. However, N₂O saturations show a distinct diel pattern on 19 to 20 July. The positive significant correlations with CH₄, NO₃⁻, NH₄⁺, HCO₃⁻, and TDS on 19 July (Table 1) imply that N₂O production was likely related to organic matter decomposition at the sediment–water interface. Gardner et al. (1987) emphasized that recycled N from organic matter decomposition is important in controlling nitrification and denitrification. Both Kemp et al. (1990) and Rysgaard et al. (1994) contend that denitrification in sediments is mainly controlled by nitrification of regenerated NH₄⁺ at O₂ concentrations above 100% of atmospheric saturations, which could be maintained by intense photosynthesis (though this process would still be influenced by water phase NO₃⁻ concentrations).

In summary, while it is clear that large-scale changes (~25-fold) in N₂O fluxes in Lake Taihu are a function of variable N loading (Wang et al., 2009), biogeochemical processes concerning O₂ and N transformation at the sediment–water interface have significant (~twofold) impacts on the regulation of N₂O production over very short time scales. Production of N₂O is complex and cannot be defined using only these data. Further, high temporal resolution research focused on developing a comprehensive understanding of N₂O production, including natural and anthropogenic loading and biogeochemical transformation processes, is needed.

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**Fig. 3.** Diurnal variations of geochemical parameters for 22 to 23 Sept. 2003. DO, dissolved oxygen; EC, electrical conductivity; TDS, total dissolved solids; TP, total phosphorus.
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