Biogeochemistry **38:** 281–301, 1997.

Sources and sinks of nitrous oxide (N_2O) in deep lakes

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Accepted 17 February 1997

Key words: aquatic nitrous oxide emissions, nitrous oxide consumption, nitrous oxide production

Abstract. As reported from marine systems, we found that also in 15 prealpine lakes N_2O concentrations were strongly correlated with O_2 concentrations. In oxic waters below the mixed surface layer, N_2O concentrations usually increased with decreasing O_2 concentrations. N_2O is produced in oxic epilimnia, in oxic hypolimnia and at oxic-anoxic boundaries, either in the water or at the sediment-water interface. It is consumed, however, in completely anoxic layers. Anoxic water layers were therefore N_2O undersaturated. All studied lakes were sources for atmospheric N_2O, including those with anoxic, N_2O undersaturated hypolimnia. However, compared to agriculture, lakes seem not to contribute significantly to atmospheric N_2O emissions.

Introduction

Nitrous oxide (N_2O) contributes to global warming and stratospheric ozone depletion (IPCC 1990). At present, the concentration of N_2O (310 ppb) in the atmosphere is increasing by 0.25% yr^{-1} (Machida et al. 1995). There are still significant uncertainties about the contribution of the individual sources to the atmospheric N_2O. It is mainly produced through microbial nitrogen transformations in soils and oceans. Aquatic systems are considered to be significant, but not the dominant sources of atmospheric N_2O (IPCC 1990). Mean marine surface water is near equilibrium (global mean saturation of about 103%) but in upwelling regions N_2O concentrations exceeded saturation up to about five-fold (Bange et al. 1996). The knowledge about the sources and sinks for marine N_2O is still rudimentary: Nitrification is considered to be an important source. In anoxic waters, denitrifiers reducing N_2O to N_2 act as a sink. However, also denitrification at oxic-anoxic boundaries could result in a net N_2O production (Codispoti et al. 1992), because O_2 inhibits the reduction of N_2O to N_2 more strongly than the reduction of NO_3^- to N_2O (Betlach & Tiedje 1981). Also other organisms such as methanotrophs (Yoshinari 1985)

or nitrate-ammonifiers (Smith 1982) have been shown to produce N_2O as by-product.

Because lakes cover a wide range of primary production and redox conditions and are much easier accessible than oceans, studies of the cycling of N_2O in lakes may contribute to a better understanding about production and consumption of N_2O in aquatic systems. Nevertheless, available information on production and consumption processes of N_2O in lakes is still limited (Knowles et al. 1981; Lemon & Lemon 1981; Vincent et al. 1981; Downes 1988; Yoh et al. 1988; Downes 1991; Mengis et al. 1996).

In this study we sampled 15 lakes at the end of summer stagnation to address the question how lake characteristics such as trophic state, morphometry and redox conditions influence N_2O production and consumption. Two of them were sampled several times throughout the year in order to study the seasonal N_2O cycling.

Study sites

Most of the 15 Swiss lakes, sampled in fall of 1995, were formed at the end of the last glacial period. They differ largely in size, trophic state and redox conditions in their hypolimnia (Table 1). Based on these characteristics, they were divided into four groups:

Group one: Deep ($>$100 m), oligo- to mesotrophic lakes that are oxic throughout the water column (if the layer close to the bottom is disregarded): Bodensee, Brienzersee, Lac Léman, Lac de Neuchâtel, Lago Maggiore, Vierwaldstättersee, Walensee, Zürichsee.

Group two: Deep ($>$100 m), eutrophic lakes with permanently anoxic water layers: Lago di Lugano (north basin), Zugersee.

Group three: Shallow ($<$40 m), meso- to eutrophic lakes with transiently and partially anoxic hypolimnia during summer stagnation: Alpnachersee, Greifensee, Rotsee.

Group four: Eutrophic lakes with permanently oxic hypolimnia due to artificial aeration: Baldeggersee, Sempachersee.

All lakes were sampled at the deepest station. These sampling sites are used in routine monitoring programs and are representative for the water column of these lakes. Effects of inflowing rivers and inlets from sewage treatment plants on the N_2O concentration within the lakes are likely to be neglectable at these sites.

Table 1. Lake characteristics.

Lake	ϕ N_2O [nM]	ϕ N_2O^{sat} [%]	N_2O^{sat} surface [%]	A [km^2]	V [km^3]	z_{max} [m]	tot-P [μg P/l]
Group 1							
Bodensee (Obersee)	22.0 (11.1–29.8)	147	108	475.5	47.7	254	30
Brienzersee	41.3 (12.1–47.9)	264	101	29.8	5.17	261	8
Lac Léman	25.7 (14.6–264.4)	167	117	582.4	89	310	50
Lac de Neuchâtel	14.4 (8.6–37.3)	103	102	217.9	14.17	153	20
Lago Maggiore	29.0 (10.4–43.3)	194	103	212.5	37.1	370	11
Vierwaldstättersee	22.2 (16.6–34.0)	153	168	113.6	11.8	214	6
Walensee	30.1 (15.7–39.2)	201	170	24.1	2.52	145	3
Zürichsee (Untersee)	23.7 (0.0–46.8)	156	112	68.2	3.30	136	40
Mean $\pm$ S.D.	**26.1 $\pm$ 7.8**	**173 $\pm$ 48**	**123 $\pm$ 29**				
Group 2							
Lago di Lugano (North basin)	14.5 (0.0–44.1)	99	144	27.5	4.69	288	169
Zugersee	27.8 (0.0–50.9)	175	125	38.3	3.18	198	157
mean $\pm$ S.D.	**21.2 $\pm$ 9.4**	**137 $\pm$ 54**	**135 $\pm$ 13**				
Group 3							
Alpnachersee	32.7 (18.9–72.3)	239	156	4.8	0.103	35	12
Greifensee	151.7 (7.6–1329.6)	798	265	6.2	0.148	32	90
Rotsee	87.5 (0.0–865.6)	744	144	0.48	0.004	16	60
mean $\pm$ S.D.	**90.6 $\pm$59.6**	**597 $\pm$ 308**	**188 $\pm$ 67**				
Group 4							
Baldeggersee	90.1 (16.3–144.6)	575	148	5.2	0.173	66	100
Sempachersee	44.6 (13.7–64.7)	293	145	14.1	0.693	87	90
mean $\pm$ S.D.	**67.4 $\pm$ 32.2**	**434 $\pm$ 199**	**147 $\pm$ 2**				

ϕ N_2O: volume weighted average [N_2O] in the water column, concentration range is shown in parentheses.
ϕ N_2O^{sat}: volume weighted average degree of N_2O saturation.
N_2O^{sat} surface: average degree of N_2O saturation in the mixed surface layer, calculated relative to an average atmospheric concentration of 310 ppb in dry air.
A, V, z_{max}, and tot-P are surface area, total lake volume, maximum depth, and volume weighted average total phosphorus concentration, respectively. Sampling dates are given in Figure 1.

Methods

Samples from different water depths were taken with 5-liter Niskin bottles. O_2 (Winkler titration), NH_4^+ (phenolhypochlorite method, VEB 1971) and NO_3^- (salicylic acid method, VEB 1971) were analyzed by standard methods. For N_2O analysis the water samples were transferred into glass serum bottles (125 ml) by plastic tubing. At least two bottle volumes were allowed to overflow.

The bottles were sealed with screw caps and butyl septa. Care was taken to exclude air bubbles during filling and sealing of the bottles. The samples received 200 μl NaOH (10 M) to increase the pH above 10 and were stored at 2 °C until analysis normally conducted within 7 hours after sampling. No change in dissolved N_2O was observed during storage of samples during three weeks.

To estimate N_2O concentration, an aliquot of 20 ml of water was displaced by Helium injection through the butyl septum. After equilibration at 30 °C by vigorously shaking for 20 min in a water bath, the N_2O concentrations in the Helium headspace was analyzed with a gas chromatograph (Dani 86.10) equipped with an electron capture detector and a packed column (Porapak Q). A mixture of Ar/CH_4 (95%/5%) was used as carrier gas. The column and the detector were held at 70 °C and 340 °C, respectively. Samples were injected with a 1 ml sample loop attached to a six-port gas-sampling valve. The time for an analysis was 11 min. Standards with known N_2O concentrations of 0.5 ppm (Scott Speciality Gases, New Jersey, USA) and 20 ppm (LINDE AG, Unterschleissheim, Germany) were used for calibration. Sample N_2O concentrations ($[N_2O]$) were calculated from the analyzed N_2O concentration in the headspace using the formula given by Butler & Elkins (1991). Replicate analysis (n = 12) of a sample with a $[N_2O]$ of 38 nM yielded a coefficient of variation of 3.8%. A non-linear response of the ECD-detector (Butler & Elkins 1991) had to be considered for samples with $[N_2O]$ exceeding 80 nM.

The degree of N_2O saturation was calculated as follows:

$$\text{degree of } N_2O \text{ saturation} = \{[N_2O]^{meas}/[N_2O]^{sat}\} \times 100 \quad [\%]$$

where $[N_2O]^{meas}$ stands for the measured concentration and $[N_2O]^{sat}$ for the saturation concentration of N_2O, taking into account the atmospheric concentration, the total pressure at the lake surface (corrected for the given altitude) and the solubility constant at the given water temperature (Weiss & Price 1980).

AOU ("apparent oxygen utilisation") and ΔN_2O were calculated as follows:

$$[AOU] = [O_2]^{sat} - [O_2]^{meas} \quad [\mu M]$$

$$\Delta[N_2O] = [N_2O]^{meas} - [N_2O]^{sat} \quad [nM]$$

$\Delta[N_2O]$ and [AOU] provide cumulative records of the net N_2O production and O_2 consumption, respectively, since the last contact of the investigated water-mass with the atmosphere (Elkins et al. 1978). All sampled lakes mixed when their surface temperature was about 4 °C. Thus, for the estimation of

hypolimnetic net N_2O production (ΔN_2O) and oxygen consumption (AOU), $[N_2O]^{sat}$ and $[O_2]^{sat}$ were defined as the saturation concentration at 4 °C.

Results

The results of the N_2O and O_2-analyses are presented in Figure 1. All surface waters were supersaturated with respect to the equilibrium with the atmospheric N_2O concentration ($[N_2O]$). In most lakes maximum $[N_2O]$ were observed either in the top 20 m or near the sediment surface. In lakes with anoxic hypolimnia, maximum $[N_2O]$ were found at the oxic-anoxic interface, whereas the anoxic water layers were undersaturated. Highest $[N_2O]$ were observed in lakes where redox conditions shifted from oxic to anoxic conditions in the hypolimnia during summer stagnation (lakes of group three). As indicated in Table 1, the average degree of N_2O saturation was lower in the surface waters of the oligo- and mesotrophic lakes (group 1, 123%) than in the eutrophic lakes of the other groups (135%, 188%, 147%).

Group 1: Deep, oligo- to mesotrophic lakes
In Lac Léman, Lac de Neuchâtel, Lago Maggiore, Zürichsee (if the sample close to the bottom was disregarded) and Vierwaldstättersee the hypolimnetic $[N_2O]$ increased with increasing depth whereas in Bodensee, Brienzersee and Walensee they were rather constant throughout their hypolimnia. The N_2O profile of Brienzersee and Vierwaldstättersee showed distinct peaks just below the thermocline (20 m). In all other lakes except Lac Léman at least one sample in the top 20 m of the water column exhibited elevated $[N_2O]$.

Group 2: Deep, eutrophic lakes with permanently anoxic hypolimnia
Although the surface waters of Lago di Lugano (north basin) and Zugersee were N_2O supersaturated, N_2O was undersaturated or even absent in the permanently anoxic part of the hypolimnia. In spring of 1994 we repeatedly observed very high $[N_2O]$ maxima ($>$200 nM) in the top 10 m of Zugersee (Figure 2). Close to the oxic-anoxic interface, the N_2O profiles exhibited small peaks in both Zugersee and Lago di Lugano (Figure 1).

Group 3: Shallow, eutrophic lakes with transiently and partially anoxic water layers
N_2O was present but undersaturated (ca. 60% saturation) in all samples of the anoxic part of the hypolimnion of Greifensee (15–30 m). In the anoxic layer of Rotsee $[N_2O]$ were also undersaturated. In both lakes the N_2O profiles exhibited distinct peaks at the lower end of the oxycline. In Rotsee a second peak was observed at the upper end of the oxycline. In Alpnachersee the

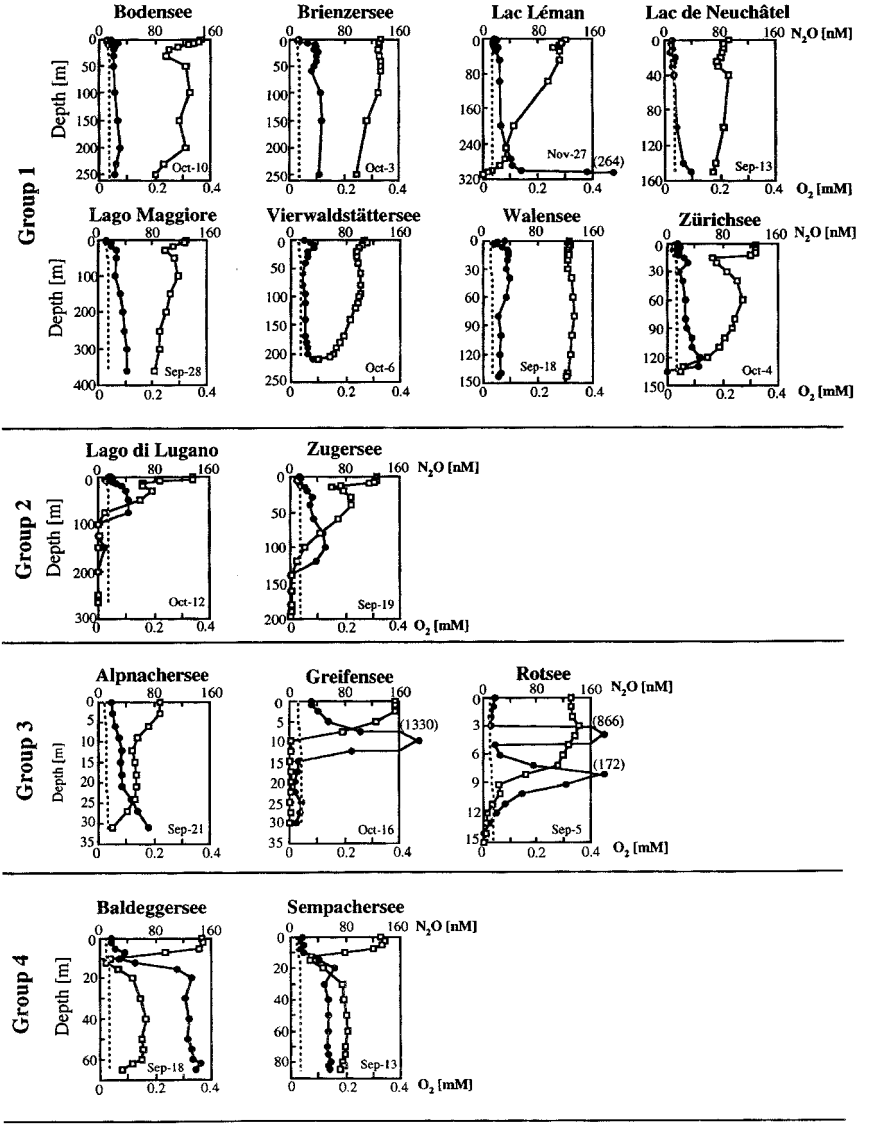


Figure 1. N_2O (—●—), N_2O^{sat} (- - - -) and O_2 (—□—) in all 15 sampled lakes (1995).

deepest water layer was still oxic at the time of sampling. N_2O was supersaturated throughout the water column and increased towards the sediment surface.

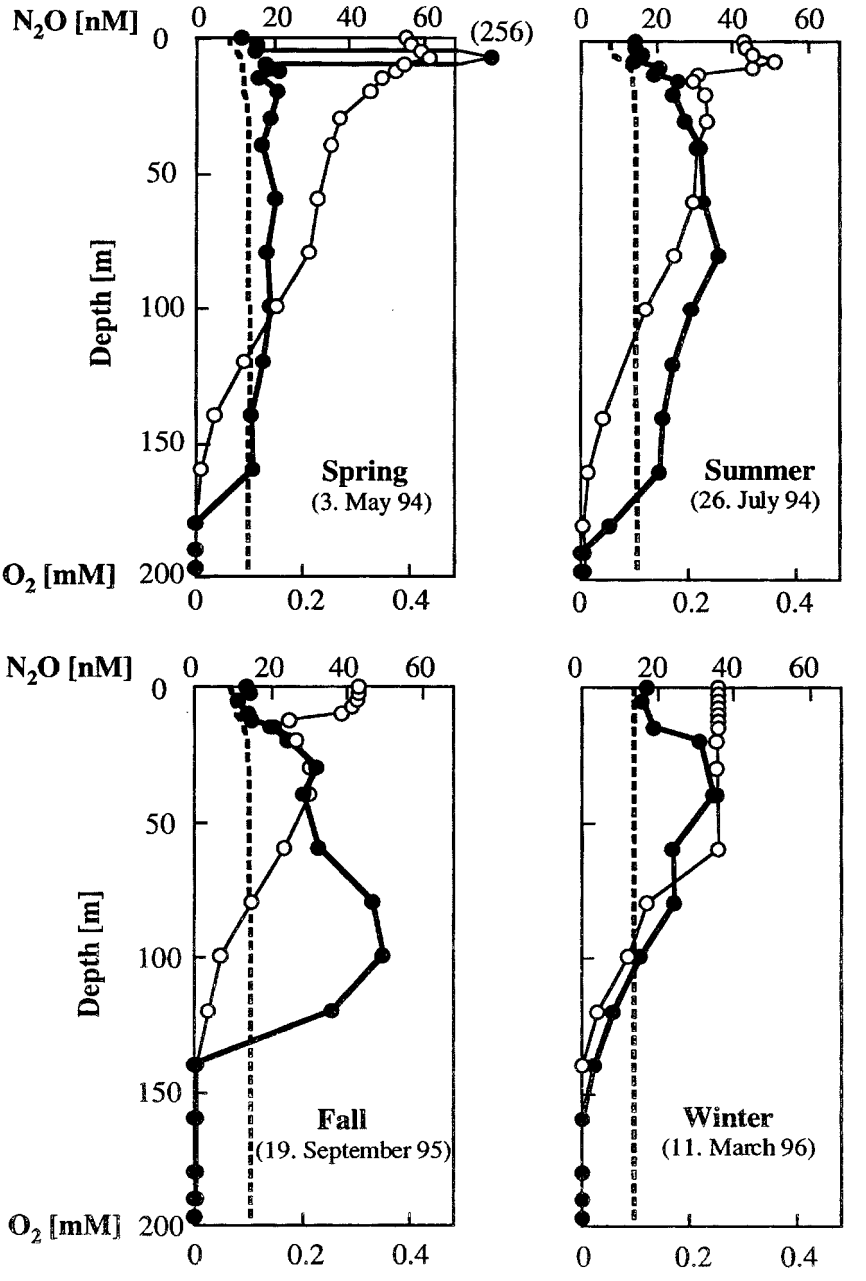


Figure 2. Seasonal variation of N_2O in Zugersee: N_2O(—●—), N_2O^{sat} (– –) and O_2 (—○—).

Group 4: Eutrophic, aerated lakes.
Surface water [N_2O] were lower than hypolimnic [N_2O], but nevertheless exceeded saturation. In both lakes, the hypolimnetic [N_2O] were rather constant with values of about 130 nM and 55 nM in Baldeggersee and Sempachersee, respectively. Hypolimnetic [N_2O] in Baldeggersee exceeded all values observed in the other lakes if extreme peak values observed in Lac Léman, Greifensee, Rotsee and Zugersee are disregarded.

Case study in Alpnachersee and Zugersee
Alpnachersee and Zugersee were sampled on several occasions during 1994 and 1995. Zugersee is a 200 m deep, meromictic eutrophic lake. At depths exceeding 160 m, the water is permanently anoxic. Representative depth profiles of N_2O and O_2 are shown in Figure 2. N_2O was always absent at depths exceeding 180 m and supersaturated at the lake surface. In spring of 1994 a distinct N_2O peak was observed in the epilimnion (Figure 2). In fall of 1995 the profile exhibited a weak peak at the lower end of the oxycline.

Alpnachersee is 35 m deep and mesotrophic. At the end of November 1994 its deepest water layers became anoxic one month before overturn reached the lake bottom. In spring and summer of 1994 (Figure 3) the [N_2O] in the oxic hypolimnion were generally supersaturated with values up to 80 nM. After O_2 was depleted at depths exceeding 27 m, [N_2O] increased in the deepest water layers from 60 nM (November 29, 1994) to 1200 nM (December 22, 1994) and 3000 nM (December 23, 1994). One week later (January 3, 1995), [N_2O] decreased to only 45 nM in the homogeneously mixed water column.

Discussion

N_2O production in oxic epilimnia
In many lakes [N_2O] maxima were observed in their epilimnion. Under oxic conditions denitrification or NO_3^--ammonification are unlikely as possible N_2O sources. Different explanations about the source of N_2O in oxic surface waters of lakes or oceans have been suggested: Weathers (1984) showed that N_2O can be produced by green algae. Based on incubation experiments, Law et al. (1993) demonstrated that denitrifying bacteria living on the surface of macroalgae can produce N_2O in oxic waters.

The extremely high [N_2O] of 866 nM observed in Rotsee at a depth of 4 m (Figure 1) and repeatedly observed high [N_2O] in the top 10 m of Zugersee (Figure 2) in spring were closely related to O_2 maxima. This seems to support suggestions of Weathers (1984) and Law et al. (1993), indicating that N_2O may have been produced either directly by algae or by denitrifying bacteria living on them. This might also explain the smaller peaks observed in the less

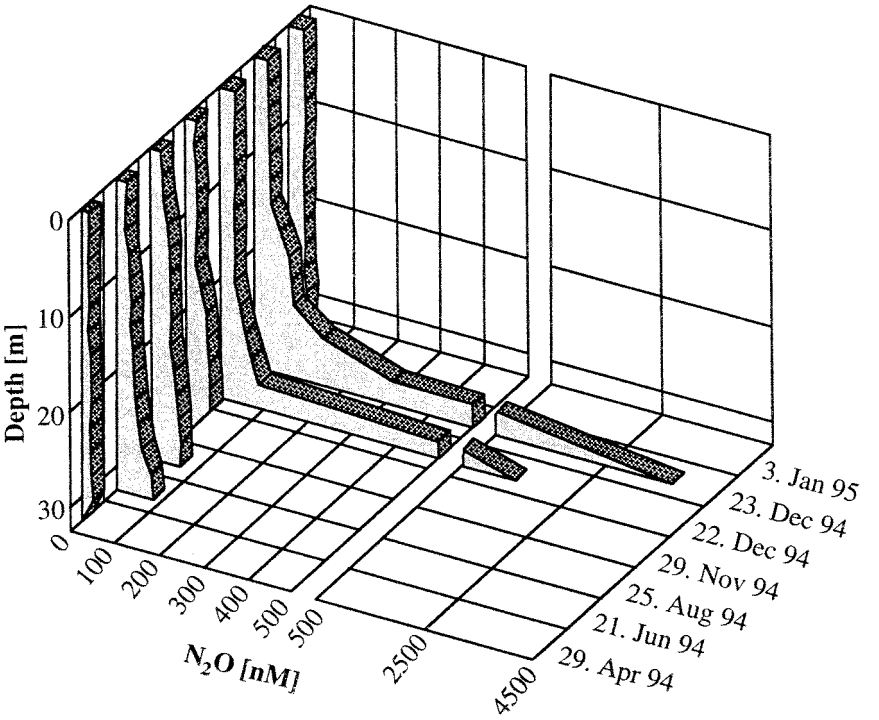


Figure 3. Seasonal variation of [N_2O] in Alpnachersee.

productive Bodensee (8 m) and Vierwaldstättersee (10 m), although in these lakes the observed N_2O maxima were not accompanied by an O_2 maximum. N_2O maxima at the same level as O_2 maxima in surface waters were also found in the Tropical Atlantic Ocean and were attributed to N_2O production by assimilative NO_3^- reduction (Outdot et al. 1990). In Rotsee, a shallow lake with a large littoral zone (≈40% of total lake surface), the very high epilimnetic [N_2O] may be partially attributed to release of N_2O from littoral sediments and subsequent horizontal transport into the water column. N_2O production in epilimnetic sediments was also suggested by Butler et al. (1988) to explain observed N_2O supersaturation in surface waters of a coastal lagoon.

N_2O production in oxic hypolimnia

The small N_2O peaks observed in Lac de Neuchâtel and Zürichsee occurred at too large depths (18–25 m) to be produced by or on actively growing algae. In fact, these N_2O peaks occurred where O_2 concentrations ([O_2]) were minimal. In oceans N_2O peaks close to O_2 minima were often observed and were related to high nitrification rates (Butler et al. 1989).

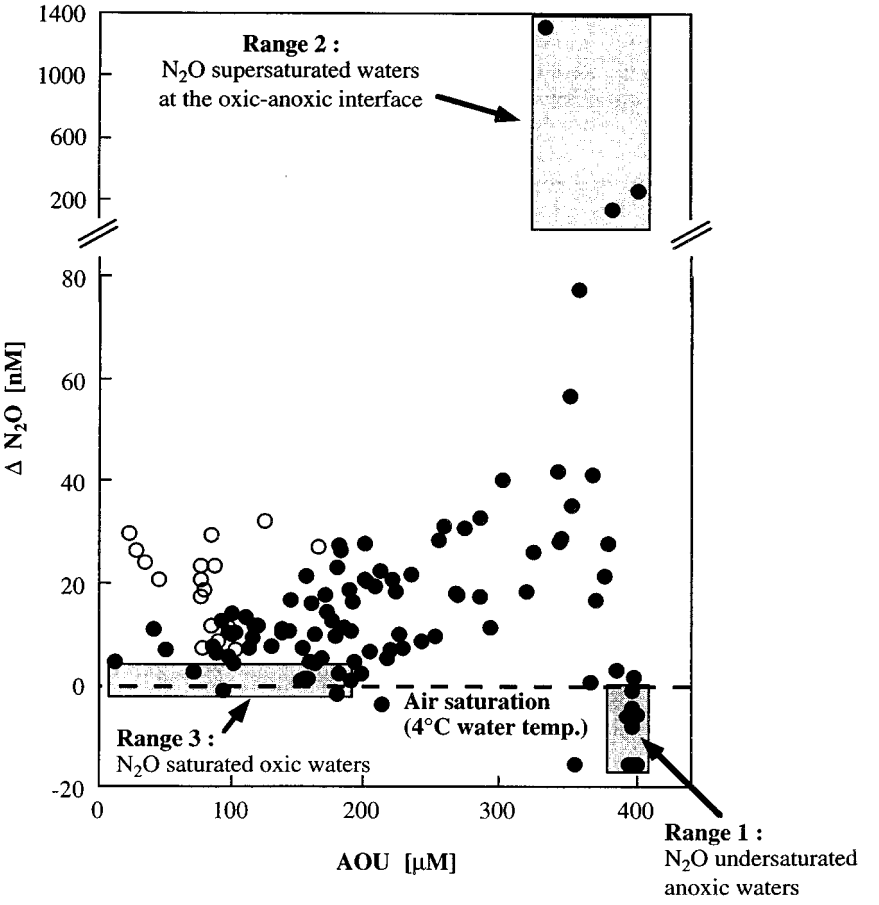


Figure 4. ΔN_2O versus AOU. Results from the mixed surface layer (<10 m) and the two aerated lakes Baldeggersee and Sempachersee were not included. The open circles show the results from oligotrophic Brienzersee and Walensee.

In Figure 4 [ΔN_2O] were plotted versus [AOU] from all lakes except the oxygenated Baldeggersee and Sempachersee. Results obtained from the mixed surface layer (depth <10 m) are not included in this figure. This figure shows a considerable amount of scatter, although in some lakes good linear correlation between ΔN_2O and AOU were found (Table 2). The scatter is partly due to the different [ΔN_2O]/[AOU] ratios determined for the different lakes. In the oligotrophic Brienzersee and Walensee no correlation between ΔN_2O and AOU was observed. In these oligotrophic lakes, [N_2O] clearly exceeded those observed in meso- and eutrophic lakes at low [AOU] (<100 μM). At present, we have no explanation for this phenomenon.

Table 2. Regression equations of ΔN_2O [nM] vs AOU [μM] for marine systems (modified from Nevison et al. 1995) and for five lakes (this study, samples from the mixed surface layer and with low O_2 concentrations (<50 μM) were not included).

Region	Regression equation	$r^{\dagger}$	n‡	Reference
Oceans				
NW Atlantic	$\Delta N_2O = 0.099 \times AOU - 2.04$			Yoshinari (1976)
Tropical central Pacific	$\Delta N_2O = (0.092 + 0.014 \times T^*) \times AOU - 10.5$			Elkins et al. (1978)
NW Atlantic	$\Delta N_2O = 0.089 \times AOU - 0.437$			Cohen & Gordon (1979)
NE Pacific, 0–800 m	$\Delta N_2O = 0.076 \times AOU - 0.928$			Cohen & Gordon (1979)
NE Pacific, 100–2500 m	$\Delta N_2O = 0.218 \times AOU - 46.25$			Cohen & Gordon (1979)
E tropical north Pacific, 0–125 m	$\Delta N_2O = 0.140 \times AOU + 0.909$			Cohen & Gordon (1979)
E tropical north Pacific, 700–3000 m	$\Delta N_2O = = 0.152 \times AOU - 31.33$			Cohen & Gordon (1979)
East Indian and west Pacific	$\Delta N_2O = (0.125 + 0.0099 \times T^*) \times AOU - 13.5$			Butler et al. (1989)
Upwelling, NW Indian Ocean, AOU $<$ 197 μM	$\Delta N_2O = 0.033 \times AOU + 5.5$			Law & Owens (1990)
Upwelling, NW Indian Ocean, AOU $>$ 197 μM	$\Delta N_2O = 0.31 \times AOU - 49.4$			Law & Owens (1990)
Lakes				
Alpachersee	$\Delta N_2O = 0.269 \times AOU - 33.57$	0.96	9	This study
Lac Léman	$\Delta N_2O = 0.075 \times AOU - 0.65$	0.92	11	This study
Lago di Lugano	$\Delta N_2O = 0.093 \times AOU + 3.46$	0.88	9	This study
Lago Maggiore	$\Delta N_2O = 0.123 \times AOU + 4.33$	0.91	11	This study
Zürichsee	$\Delta N_2O = 0.082 \times AOU + 0.83$	0.84	14	This study

†: correlation coefficient ‡: number of samples *: temperature [°C]

Table 2 summarizes all lakes, where a good linear correlation (correlation coefficeint > 0.8) between ΔN_2O and AOU was found. The calculated regression coefficients varied between 0.075 and 0.269 nM $\Delta N_2O/\mu$M AOU. Hahn (1974) and Yoshinari (1976) were the first who reported similar striking linear correlations between $[N_2O]$ and $[O_2]$ in samples obtained from different depths in the North Atlantic Ocean. Numerous studies from other marine systems confirmed these observations (Cohen & Gordon 1979; Law & Owens 1990; Outdot et al. 1990). The relation is usually given as:

$$\Delta[N_2O] = a + b \times [AOU] \quad (1)$$

In some studies (Naqvi & Noronha 1991; Elkins et al. 1978; Butler et al. 1989) consideration of temperature (T) as a variable ($\Delta[N_2O] = a + \{b + c \times T\} \times [AOU]$) improved the correlation, whereas in other studies it did not (Law & Owens 1990). Apart from $[N_2O]$ also $[NO_3^-]$ was linearly correlated with AOU. Thus, it was postulated that N_2O production was highly correlated with NO_3^- regeneration and that nitrification was the main source for N_2O in marine systems (Cohen & Gordon 1979; Broecker & Peng 1982).

Although a linear correlation between $[\Delta N_2O]$ and [AOU] in oxic deep waters has now been established for almost all marine environments, the reported regression coefficients (b in equation 1) varied between 0.033–0.31 nM $\Delta[N_2O]/\mu$M [AOU], and hence differed tenfold (Nevison et al. 1995). The regression coefficients determined for lakes in this study agree nicely with published regression coefficients for marine systems (Table 2). The observed differences in the regression coefficients from different aquatic systems are not yet fully understood. Various factors were suggested to contribute to the variability (Outdot et al. 1990): Differences in the composition of organic material that is oxidized in deep waters or differences in the yield for production by nitrifiers could contribute to varying $\Delta[N_2O]$/[AOU] ratios. In addition, mixing of different water masses or additional N_2O sources as denitrification or assimilative NO_3^- reduction may also affect the $\Delta[N_2O]$/[AOU] ratios. The similarity between $[\Delta N_2O]$/[AOU] ratios determined for some lakes in this study and those reported for oceans may indicate that N_2O in lakes is produced by similar mechanisms as in marine systems. No significant correlation between the $[\Delta N_2O]$/[AOU] ratios and the trophic state of the lakes was found.

N_2O production at oxic-anoxic interfaces

It was shown by Rönner (1983), Naqvi & Noronha (1991) and Codispoti et al. (1992) that the linear correlation between N_2O and O_2 breaks down at the oxic-anoxic boundary where usually the highest $[N_2O]$ are found. Also in this study we found the highest $[N_2O]$ at the oxic-anoxic interface

except for the mentioned peak values in surface waters. Figure 4 shows that at the oxic-anoxic interface ([AOU] = 350–400 μM) very high [N_2O] were observed (range 2 in Figure 4). These high [N_2O] suggest enhanced net N_2O production at the oxic-anoxic interface. Various processes may contribute to this enhanced production. It was shown by Goreau et al. (1980) that N_2O production by nitrifiers is maximal at low [O_2]. On the other hand, at low [O_2], N_2O can also accumulate due to denitrification because O_2 inhibits the N_2O reduction to N_2 more strongly than the NO_3^- reduction to N_2O (Betlach & Tiedje 1981). Based on observed enrichment of ^{15}N in N_2O Naqvi & Noronha (1991) proposed that the coupling of both nitrification and denitrification trough NO (NH_4^+ oxidation to NO by nitrifiers and subsequent NO reduction to N_2O by denitrifiers) may be the dominant mechanism for N_2O production at oxic-anoxic boundaries in the ocean. N_2O production by a similar nitrification-denitrification couple was previously also suggested by Codispoti & Christensen (1985).

In addition, other microorganisms adapted to low [O_2] or anoxic conditions, e.g. methanotrophs (by oxidizing NH_4^+, Yoshinari 1985) or nitrate-ammonifiers (Smith 1982), have been shown to produce N_2O as by-products. In fact, the profiles of [NH_4^+], [NO_3^-] and [CH_4] obtained from Greifensee and the north basin of Lago di Lugano (Figure 5) show steep gradients near the oxycline where the N_2O peaks were observed. Thus, it is likely that in these water layers nitrification, denitrification, nitrate-ammonification and methane-oxidation may have simultaneously contributed to the observed N_2O net production.

The seasonal cycling of N_2O in Alpnachersee supported the hypothesis that N_2O is produced at oxic-anoxic interfaces. The deepest water layer of Alpnachersee turned anoxic at the end of November 1994. Shortly after O_2 was completely depleted, the [N_2O] increased dramatically between November 29 and December 23 (Figure 3). Similarly dramatic increases in [N_2O] were observed in other lakes (Knowles et al. 1981; Yoh et al. 1988) and in the Baltic Sea (Rönner 1983). In all these studies such extremely high [N_2O] (up to 20000% saturation) were temporal phenomena and occurred shortly before or after O_2 was completely depleted.

Such phenomena may be explained by the onset of denitrification in water layers containing still trace [O_2]. Because O_2 inhibits the reduction of N_2O to N_2 more strongly than the reduction of NO_3^- to N_2O (Betlach & Tiedje 1981), this could explain N_2O accumulation during the early stage of denitrification. One week after the observed [N_2O] maximum, the water column was homogeneously mixed due to the onset of winter turnover, resulting in a [N_2O] of about 45 nM throughout the water column. This is equal to a decrease in the total dissolved N_2O in the water column of about 3700 mol.

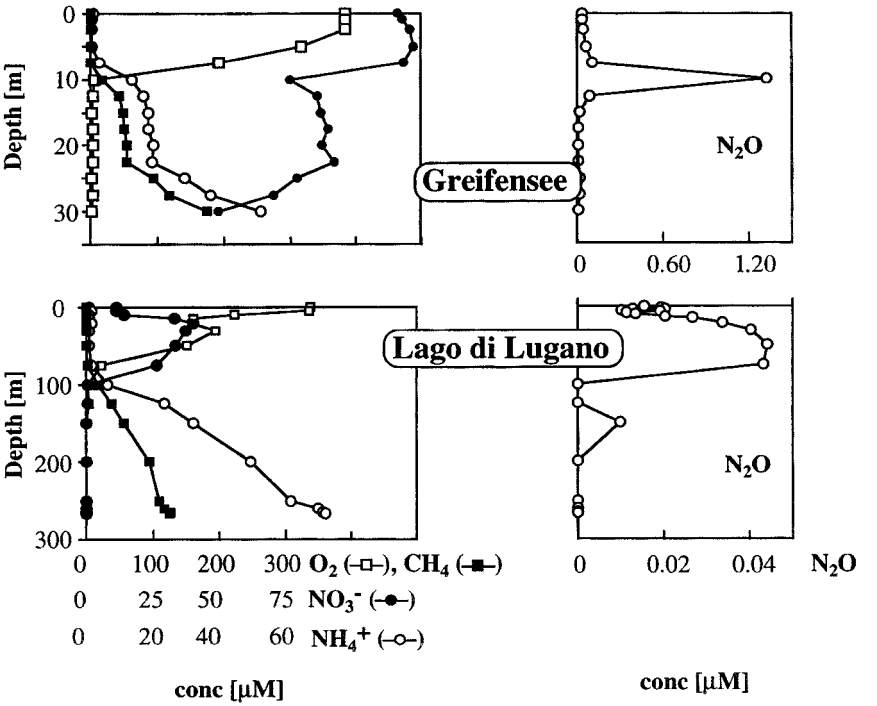


Figure 5. O_2, CH_4, NH_4^+, NO_3^- and N_2O characteristics in Greifensee (16 Oct 1995) and Lago di Lugano (12 Oct 1996).

In the following, the question is discussed, whether this decrease in the N_2O content can be explained by N_2O evasion into the atmosphere. Based on wind measurements from a nearby weather station (average wind speed 10 m above ground = u_{10} = 1.7 m s^{-1}) the transfer velocity of N_2O ($v_{tot}^{N_2O}$) during this period was estimated. Based on the formula proposed by Schwarzenbach et al. (1993) the water side mass transfer coefficient of O_2 ($v_w^{O_2}$) was calculated as:

$$v_w^{O_2}[\text{cm s}^{-1}] = 4 \times 10^{-4} + 4 \times 10^{-5} \times u_{10}^2 \quad (2)$$

where u_{10} is in [m s^{-1}]. This formula is based on numerous laboratory and field studies and gives an empirical relationship between u_{10} and $v_w^{O_2}$. For u_{10} = 1.7 m s^{-1} it yields $v_w^{O_2}$ = 0.45 m d^{-1}. Since the gas exchange of both N_2O and O_2 is dominated by transfer through the water boundary layer and because the molecular diffusion coefficient in water (D_w) of N_2O and O_2 (1.08×10^{-5} cm^2 s^{-1} for N_2O and 1.26×10^{-5} cm^2 s^{-1} for O_2 at 5 °C, Lerman 1979) are similar, $v_w^{O_2}$ equals roughly $v_{tot}^{N_2O}$:

$$v_{tot}^{N_2O} \approx v_w^{O_2} \times \{D_w^{N_2O}/D_w^{O_2}\}^{0.5} \approx 0.45\text{m d}^{-1} \quad (3)$$

Because existing approaches to estimate transfer velocity based on wind measurements differ by a factor of 2, we doubled the calculated $v_{tot}^{N_2O}$ in order to get a rough estimate of the upper boundary of the average transfer velocity of N_2O (v_{tot}^{max,N_2O} = 0.9 m d^{-1}) during this period. Based on this estimate of v_{tot}^{max,N_2O}, at maximum 60% of the lost N_2O could have been exported to the atmosphere. Thus, a significant fraction of N_2O must have been reduced to N_2 within the lake during this period (23 December 1994–3 January 1995).

In conclusion, results obtained from Alpnachersee confirmed, that N_2O is produced at oxic-anoxic interfaces. They also revealed, that in lakes with a shift from oxic to anoxic conditions, this N_2O net production can temporally be very high. This might also explain why the highest [N_2O] in the 15 lakes were found in Greifensee and Rotsee. Both lakes mix completely in winter but get anoxic in the hypolimnia during summer stagnation.

N_2O consumption in anoxic water layers

Figure 4 shows that under completely anoxic conditions, N_2O is depleted (range 1 in Figure 4), probably due to consumption by denitrification. In Zugersee for example, the anoxic water layers at depths exceeding 180 m acted as a N_2O sink throughout the year, since N_2O was always absent (Figure 2). The average N_2O supply from water layers above 180 m to the anoxic zone estimated by Fick's first law and measured eddy diffusion coefficients (Wüest & Gloor 1995) yielded a flux of 0.24 μmol m^{-2} d^{-1}. The presence of a N_2O sink in anoxic waters led to the hypothesis that eutrophic lakes may act as sinks for atmospheric N_2O (Lemon & Lemon 1981). Knowles et al. (1981) based this argument on N_2O depth profiles observed in Canadian lakes. These profiles showed N_2O undersaturation in the anoxic water layers and decreasing [N_2O] with increasing depth. Based on these gradients they concluded that N_2O was diffusing from the epilimnion into the anoxic hypolimnion where it was reduced to N_2 by denitrifiers. The surface waters were slightly undersaturated with N_2O. Similarly slightly undersaturated surface waters were also found in marine systems as in areas of the subtropical gyres and the North Atlantic (Butler et al. 1989; Nevison et al. 1995). However, in these studies N_2O undersaturation was mainly explained by seasonal cooling of the surface waters during winter and not by N_2O consumption.

Contrary to the studies of Lemon & Lemon (1981) and Knowles et al. (1981), our results indicate, that the surface layers of all sampled lakes were supersaturated with N_2O (Table 1). Hence, at the time of sampling these lakes acted as sources for atmospheric N_2O, although in four lakes (Greifensee, north basin of Lago di Lugano, Rotsee, Zugersee) the anoxic parts of the

hypolimnia and in the other lakes the anoxic sediments acted as sinks for N_2O. More N_2O was therefore produced during summer stagnation in the oxic part of the water column than was transported to the anoxic water layers and subsequently reduced to N_2. This argument is confirmed by Figure 4. It shows that N_2O undersaturated, anoxic water layers in the hypolimnia (range 1 in Figure 4) were always separated from waters saturated with O_2 and N_2O (range 3) by N_2O supersaturated water layers.

This separation is eliminated during winter overturn. As a consequence of mixing, the [N_2O] may become undersaturated at the lake surface and therefore the lake may act as a sink for atmospheric N_2O during winter. However, with the exception of Lago di Lugano (north basin), in the lakes with anoxic hypolimnia the volume weighted average degree of N_2O saturation exceeded 100% at the end of summer stagnation (Table 1). Therefore, physical mixing during winter overturn will not result in undersaturated surface waters, even if the increase in saturation with decreasing water temperature is taken into account. Meromictic lakes do not mix completely during winter. Thus, in Lago di Lugano (north basin) and Zugersee, the N_2O depleted water layers are not mixed into the whole water column and therefore do not contribute to a decrease of surface [N_2O]. In conclusion, our results do not support the hypothesis that lakes with anoxic deep waters would act as sinks for atmospheric N_2O.

It is interesting to note that highest average hypolimnetic [N_2O] (if the results from the two shallow eutrophic Greifensee and Rotsee are disregarded) were observed in the artificially aerated Baldeggersee and Sempachersee. Their hypolimnia became regularly anoxic during summer stagnation before artificial aeration during winter and oxygenation during summer was started (Gächter & Meyer 1990). Since then, the hypolimnetic [O_2] always exceed 60 μmol liter^{-1}. Two factors may have contributed to the high hypolimnetic [N_2O]. First, oxygenation eliminated anoxic conditions in the hypolimnia that formerly favoured N_2O reduction to N_2 by denitrifiers. Secondly, oxic conditions likely stimulate nitrification and hence N_2O production in the hypolimnetic water.

Quantification of hypolimnetic N_2O production

N_2O is nearly inert in the presence of oxygen, because reduction of N_2O to N_2 is unlikely to occur. This missing N_2O sink in oxic hypolimnia is probably responsible for the observed increase in deep-water [N_2O] during summer stagnation (Downes 1991; Mengis et al. 1996). This finding leads to two conclusions: First, the hypolimnetic [N_2O] in lakes with a permanently oxic water column should be maximal at the end of summer stagnation. Second, the N_2O accumulation in the hypolimnia during summer permits an estimate

of the net N_2O production in the hypolimnion or at the sediment surface during the stagnation period:

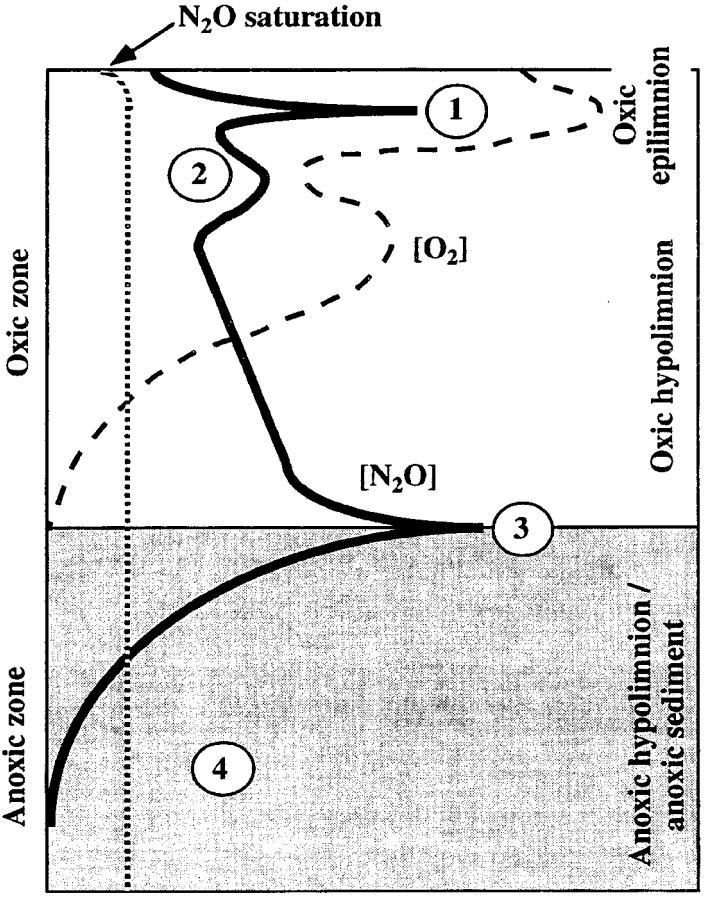
$$N_2O^{\text{production}}_{\text{hypolimnion}} = \frac{([N_2O]^{\text{meas}} - [N_2O]^{\text{sat}}) \times V}{T \times A} \quad (4)$$

V, A and T stand for the hypolimnetic volume and sediment area and the duration of the stagnation period, respectively. Butler et al. (1988) used a similar mass-balance model to quantify N_2O production in a meromictic coastal lagoon. The calculated production is related to the hypolimnetic sediment surface, because it was shown that the sediment-water interface is often an important N_2O source (Law et al. 1992; Koike & Terauchi 1996; Mengis et al. 1996).

This value underestimates the true gross production because it does not take into account losses due to diffusion of N_2O across the thermocline and consumption by anoxic sediments. On the other hand, it may overestimate gross production by assuming that the hypolimnetic [N_2O] was in equilibrium with the atmosphere at the beginning of the summer stagnation. To minimize this error we applied the above formula only to those six lakes that mixed completely during winter overturn. In fact, [N_2O] were within 100–125% saturation at all depths in Alpnachersee, Baldeggersee and Sempachersee at the end of winter overturn. Thus, in these lakes most of the N_2O accumulated in the water column during summer stagnation must have been consumed or exported to the atmosphere during winter overturn. Table 3 summarizes the estimated N_2O production rates. They lie well within published benthic N_2O production rates observed by others in rivers, lakes and coastal marine waters.

Conclusion

Net N_2O production was observed at three different sites in the water column (Figure 6): Epilimnion, oxic hypolimnion and at oxic-anoxic interfaces. Production in the epilimnion (process 1 in Figure 6) was occasionally observed in eutrophic lakes and seems to be attributed to the presence of actively growing algae. Net N_2O production in the oxic hypolimnion (process 2 in Figure 6) may be due to nitrification and inhibition of N_2O reduction in the presence of O_2. Net N_2O production at the oxic-anoxic interface (process 3 in Figure 6) was observed in all lakes with anoxic hypolimnia. Various bacteria, e. g. nitrifiers, denitrifiers, methanotrophs and nitrate-ammonifiers may contribute to the N_2O production at the oxic-anoxic interface. Net N_2O consumption (process 4 in Figure 6) was only observed in anoxic layers and was attributed to reduction of N_2O to N_2.



Process 1 : N_2O production in the oxic epilimnion, attributed to actively growing algae

Process 2 : N_2O production in the oxic hypolimnion, attributed to nitrification

Process 3 : N_2O production at oxic-anoxic interfaces, attributed to nitrifiers, denitrifiers, (methanotrophs, nitrate-ammonifiers)

Process 4 : N_2O consumption in anoxic hypolimnia/sediment, attributed to denitrifiers (reduction of N_2O to N_2)

Figure 6. Scheme of N_2O (and O_2) profiles in lakes.

Table 3. Estimated benthic N_2O fluxes.

Location	Benthic N_2O Flux [μmol m^{-2} h^{-1}]	
Coastal marine		
Narragansett Bay	0.02–0.92	Seitzinger 1988
Tama Bay	0.95	Nishio et al. 1983
Tamar estuary	0.31–1.1	Law et al. 1992
Tokyo Bay	0.06–0.07	Koike & Terauchi 1996
Oligo-/mesotrophic lakes		
Lake Ernest	0.35	Seitzinger 1988
Lake Lacawac	0.04	Seitzinger 1988
Alpnachersee	0.09	This study
Brienzersee	0.84	This study
Lac de Neuchâtel	0.01	This study
Walensee	0.31	This study
Eutrophic, aerated lakes		
Baldeggersee	0.3–0.7	Mengis et al. 1996
Baldeggersee	0.69	This study
Sempachersee	0.34	This study
Rivers		
Potomac	0.6–5.0	Seitzinger 1988
Willamette	0.03–0.70	Wissmar et al. 1987

All sampled lakes were sources for atmospheric N_2O throughout the year. Based on a mass balance calculation, we estimated net N_2O production rates in six lakes. If these rates are extrapolated to the total surface area of all Swiss lakes, about 3.5×10^6 mol N_2O would be produced annually. Estimated N_2O emissions by agriculture are about 4.8×10^8 mol N_2O yr^{-1} (Grud & Fuhrer 1995). Thus, although lakes were identified as N_2O sources, limnetic N_2O emissions seem not to contribute significantly to the local N_2O load of the atmosphere.

Acknowledgements

We thank the following institutes for their generous help in the field and for providing data: Laboratorio di studi ambientali Ticino, Lugano; Kant. Laboratorium Zug, Steinhausen; Service de la protection de l'environment

de Neuchâtel, Peseux; Wasserversorgung Zürich, Zürich; Institut für Seenforschung, Langenargen (Germany); Station hydrobiologie lacustre, INRA, Thonon (France); Instituto Italiano di Idrobiologia, Pallanza (Italy); Kant. Umweltschutzamt Luzern, Luzern; Kant. Gewässer- und Bodenschutzlabor Bern, Bern; Limnology department of EAWAG, Dübendorf; Swiss meteorological institute (SMA). E. Grieder, R. Illi, A. Mares, B. Ribi, T. Schaller and F. Vazquez helped during the field campaign. We aknowledge the helpful suggestions of M. Downes, S. Rysgaard, A. Wüest, and two anonymus reviewers to the manuscript.

References

Bange HW, Rapsomanikis S & Andreae MO (1996) Nitrous oxide in coastal waters. Global Biogeochem. Cycles 10: 197–207

Betlach MR & Tiedje JM (1981) Kinetic explanation for accumulation of nitrite, nitric oxide and nitrous oxide during bacterial denitrification. Appl. Environ. Microbiol. 42: 1074–1084

Broecker WS & Peng TH (1982) Tracers in the Sea. Eldigio

Butler JH, Pequegnat JE, Gordon LI & Jones RD (1988) Cycling of methane, carbon monoxide, nitrous oxide, and hydroxylamine in a meromictic, coastal lagoon. Estuarine Coastal Shelf Sci. 27: 181–203

Butler JH, Elkins JW, Thompson TM & Egan KB (1989) Tropospheric and dissolved N_2O of the West Pacific and East Indian Oceans during the El Nino Southern Oscillation event of 1987. J. Geophys. Res. 94: 14865–14877

Butler JH & Elkins JW (1991) An automated technique for the measurement of dissolved N_2O in natural waters. Mar. Chem. 34: 47–61

Codispoti LA & Christensen JP (1985) Nitrification, denitrification and nitrous oxide cycling in the eastern tropical south pacific ocean. Mar. Chem. 16: 277–300

Codispoti LA, Elkins JW, Yoshinari T, Friederich GE, Sakamoto CM & Packard TT (1992) On the nitrous oxide flux from productive regions that contain low oxygen waters. In: Desai BN (Ed) Oceanography of the Indian Ocean (pp 271–284). Balkema

Cohen Y & Gordon LI (1979) Nitrous oxide production in the ocean. J. Geophys. Res. 84: 347–353

Downes MT (1988) Aquatic nitrogen transformations at low oxygen concentrations. Appl. Environ. Microbiol. 54: 172–175

Downes MT (1991) The production and consumption of nitrate in an eutrophic lake during early stratification. Arch. Hydrobiol. 122: 257–274

Elkins JW, Wofsy SC, McElroy MB, Kolb CE & Kaplan WA (1978) Aquatic sources and sinks for nitrous oxide. Nature 275: 602–606

Gächter R & Meyer JS (1990) Mechanisms controlling fluxes of nutrients across the sediment/water interface in a eutrophic lake. In: Baudo R. et al. (Eds) Sediments: Chemistry and Toxicity of In-Place Pollutants (pp 131–162). Lewis

Goreau TJ, Kaplan WA, Wofsy SC, McElroy MB, Valois FW & Watson SW (1980) Production of NO_2^- and N_2O by nitrifying bacteria at reduced concentrations of oxygen. Appl. Environ. Microbiol. 40: 526–532

Grud A & Fuhrer J (1995) Treibhausgasemissionen der schweizerischen Landwirtschaft. Agrarforschung 2: 217–220

Hahn J (1974) The north atlantic as a source of atmospheric N_2O. Tellus 26: 160–168

IPCC (Intergovernmental Panel on Climate Change) (1990) Climate Change. Cambridge, pp. XXI and 25–26

Knowles R, Lean DRS & Chan YK (1981) Nitrous oxide concentrations in lakes: Variations with depth and time. Limnol. Oceanogr. 26: 855–866
Koike I & Terauchi K (1996) Fine scale distribution of nitrous oxide in marine sediments. Mar. Chem. 52: 185–193
Law CS & Owens NJP (1990) Significant flux of atmospheric nitrous oxide from the northwest Indian Ocean. Nature 346: 826–929
Law CS, Rees AP & Owens NJP (1992) Nitrous oxide: Estuarine sources and atmospheric flux. Estuarine Coastal Shelf Sci. 35: 301–314
Law CS, Rees AP & Owens NJP (1993) Nitrous oxide production by estuarine epiphyton. Limnol. Oceanogr. 38: 435–441
Lemon E & Lemon D (1981) Nitrous oxide in freshwaters of the Great Lakes Basin. Limnol. Oceanogr. 26: 867–879
Lerman A (1979) Geochemical Processes: Water and Sediment Environments. Wiley
Machida T, Nakazawa T, Fujii Y, Aoki S & Watanabe O (1995) Increase in the atmospheric nitrous oxide concentration during the last 250 years. Geophys. Res. Lett. 22: 2921–2924
Mengis M, Gächter R & Wehrli B (1996) Nitrous oxide emissions to the atmosphere from an artificially oxygenated lake. Limnol. Oceanogr. 41: 548–553
Naqvi SWA & Noronha RJ (1991) Nitrous oxide in the arabian sea. Deep-Sea Res. 38: 871–890
Nevison CD, Weiss RF & Erickson III DJ (1995) Global oceanic emissions of nitrous oxide. J. Geophys. Res. 100: 15809–15820
Nishio T, Koike I & Hattori A (1983) Estimates of denitrification and nitrification in coastal and estuarine sediments. Appl. Environ. Microbiol. 45: 444–450
Outdot C, Andrie C & Montel Y (1990) Nitrous oxide production in the tropical Atlantic Ocean. Deep-Sea Res. 37: 183–202
Rönner U (1983) Distribution, production and consumption of nitrous oxide in the Baltic Sea. Geochim. Cosmochim. Acta 47: 2179–2188
Schwarzenbach RP, Gschwend PM & Imboden DM (1993) Environmental Organic Chemistry. 1st edn. Wiley
Seitzinger SP (1988) Denitrification in freshwater and coastal marine ecosystems: Ecological and geochemical significance. Limnol. Oceanogr. 33: 702–724
Smith MS (1982) Dissimilatory reduction of NO_2^- to NH_4^+ and N_2O by a soil *Citrobacter sp*. Appl. Environ. Microbiol. 43: 854–860
VEB (1971) Ausgewählte Methoden der Wasseruntersuchung. Bd. 1, VEB Gustav Fischer Verlag, Jena (Germany)
Vincent WF, Downes MT & Vincent CL (1981) Nitrous oxide cycling in Lake Vanda, Antartica. Nature 292: 618–620
Weathers PJ (1984) N_2O evolution by green algae. Appl. Env. Microbiol. 48: 1251–1253
Weiss RF & Price BA (1980) Nitrous oxide solubility in water and seawater. Mar. Chem. 8: 347–359
Wüest A & Gloor M (1995) Bottom boundary mixing in lakes: The role of the near-sediment density stratification. Proceedings of IUTAM-Symposium, Broome (Australia)
Wissmar RC, Lilley MD & deAngelis M (1987) Nitrous oxide release from aerobic riverine deposits. J. Freshwat. Ecol. 4: 209–218
Yoh M, Terai H & Saijo Y (1988) Nitrous oxide in freshwater lakes. Arch. Hydrobiol. 113: 273–294
Yoshinari T (1976) Nitrous oxide in the sea. Mar. Chem. 4: 189–202
Yoshinari T (1985) Nitrite and nitrous oxide production by *Methylosinus trichosporium*. Can. J. Microbiol. 31: 139–144