

**Extreme Supersaturation of Nitrous Oxide in a Poorly Ventilated Antarctic Lake**



John C. Priscu; Malcolm T. Downes; Christopher P. McKay

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## Extreme supersaturation of nitrous oxide in a poorly ventilated Antarctic lake

**Abstract**—Lake Bonney, a permanently ice-covered Antarctic lake, has a middepth maximum  $N_2O$  concentration of  $41.6 \mu M N$  ( $>580,000\%$  saturation with respect to the global average mixing ratio of  $N_2O$ ) in its east lobe, representing the highest level yet reported for a natural aquatic system. Atmospheric  $N_2O$  over the lake was 45% above the global average, indicating that this lake is an atmospheric source of  $N_2O$ . Apparent  $N_2O$  production (ANP) was correlated with apparent oxygen utilization (AOU), and denitrification was not detectable, implying that nitrification is the primary source for this gas. The slope of a regression of ANP on AOU revealed that potential  $N_2O$  production per unit of potential  $O_2$  consumed in the east lobe of Lake Bonney is at least two orders of magnitude greater than reported for the ocean. The maximum yield ratio for  $N_2O$  [ $ANP/(NO_2^- + NO_3^-)$ ] in Lake Bonney is 26% (i.e. 1 atom of N appears in  $N_2O$  for every 3.9 atoms appearing in oxidized N), which exceeds previous reports for pelagic systems, being similar to values from reduced sediments. Areal  $N_2O$  flux from the lake to the atmosphere is  $>200$  times the areal flux reported for oceanic systems; most of this gas apparently enters the atmosphere through a small moat that occupies  $\sim 3\%$  of the surface of the lake and exists for  $\sim 10$  weeks in summer.

Nitrous oxide ( $N_2O$ ) contributes significantly to the global radiative budget and turnover of stratospheric ozone (Yung et al. 1976; Watson et al. 1990). Although atmospheric  $N_2O$  has been increasing  $0.2\text{--}0.3\%$   $yr^{-1}$  for the past two decades (Prinn et al. 1990), the magnitude of identified inputs remains ambiguous (e.g. Thiemens and Trogler 1991; Kim and Craig 1993). Research indicates that aquatic environments may be either sources or sinks for  $N_2O$ , depending largely upon dissolved  $O_2$  levels; mechanisms for  $N_2O$  transformations in low  $O_2$  aquatic

environments are highly equivocal (Downes 1988; Ward et al. 1989).

Most studies of marine systems have concluded that  $N_2O$  is produced via nitrification in surface waters (e.g. Yoshinari 1976; Nevison et al. 1995), whereas denitrification may be a source in oxygen-depleted deep water (Yoshida et al. 1989). On a global scale, the ocean is thought to be a source of atmospheric  $N_2O$ , most of which is produced by nitrification (Nevison et al. 1995). This paradigm is not as straightforward in lakes, presumably because of their relatively wide range of trophic states. For example, supersaturating levels of  $N_2O$  observed in several eutrophic lakes and sewage systems apparently arise from denitrification (Knowles et al. 1981; Yoshinari and Wahlen 1985), whereas  $N_2O$  in the water column of more oligotrophic lakes is thought to be produced by nitrification (Chan and Campbell 1980; Vincent et al. 1981) or a combination of both (Yoh 1990, 1992). Clearly, many questions remain regarding sources and sinks of  $N_2O$  in aquatic systems. During our studies of nitrogen transformations in permanently ice-covered antarctic lakes, we observed the highest concentration of  $N_2O$  yet reported for a natural aquatic system. We herein describe the vertical distribution of  $N_2O$  in the east lobe of Lake Bonney, Antarctica, discuss possible sources and sinks of this gas, and determine potential  $N_2O$  flux to the atmosphere.

Lake Bonney is in the Taylor Valley, an ablation area adjacent to McMurdo Sound and is one of several lakes in the region that contain liquid water. The lake has two lobes (east lobe,  $3.8 \text{ km}^2$ ; west lobe,  $2.1 \text{ km}^2$ ), each 40 m deep, and is permanently covered with  $\sim 4$  m of ice. The ice eliminates wind-induced turbulence, and together with low advective stream input, results in a liquid water col-

umn dominated by molecular diffusion (Spigel et al. 1990; Spigel and Priscu 1996). Lack of turbulence allows chemical gradients to exist over long periods and to develop at extremely low reaction rates, making Lake Bonney a unique system for the study of transformations of water column constituents.

All measurements were made in the east lobe of Lake Bonney between 1990 and 1993. Temperature and conductivity were obtained with a Martek 7 instrument;  $O_2$  was measured by Winkler titration (Parsons et al. 1984).  $NH_4^+$ ,  $NO_2^-$ , and  $NO_3^-$  were determined by wet chemistry on filtered (Whatman GF/F) samples (Parsons et al. 1984); the analyses were adjusted to accommodate a 10-ml sample size. Nutrient samples were diluted, when necessary, to seawater salinities or lower before analysis. Internal standards were recovered with virtually 100% efficiency.

$N_2O$  was measured with a Perkin-Elmer Sigma 4 gas chromatograph fitted with a 2-m stainless steel column of Chromosorb 102 (100–120 mesh) and operated at a column temperature of 55°C, with a carrier gas (95% Ar, 5%  $CH_4$ ) flow of 24 ml  $min^{-1}$ . Samples were injected into a sample loop (0.1, 0.5, or 1.0 ml, depending on concn) fitted to a 10-port, two-position valve. Plumbing was configured so that the sample passed through a 25-cm Poropak-T pre-column before entering the main column to retain acetylene (for denitrification experiments) and water vapor. After 1 min, the valve was switched to back-flush the precolumn while  $N_2O$  (and  $CO_2$ ) passed through the main column. Tests showed that elution times for  $N_2O$ ,  $CO_2$ ,  $C_2H_2$ , and  $H_2O$  were 0.5, 0.5, 1.3, and >6 min through the Poropak-T column and 2.5, 2.1, 3.4, and >12 min through both columns in series.  $N_2O$  and  $CO_2$  peaks showed no overlap using this arrangement.

The sample gas was detected with a  $^{63}Ni$  electron capture detector operated at 375°C according to the protocols outlined by Priscu and Downes (1985). Gas was collected directly from a 5-liter Niskin bottle connected to a 10-ml glass-barrel syringe with a short piece (~2 cm) of rubber tubing. Every precaution was taken to ensure that the samples did not come into contact with air or otherwise degas. Time-course experiments on highly supersaturated samples indicated that  $N_2O$  diffused through plastic-barrel syringes; hence, glass-barrel syringes were used. Water samples (5 ml) were analyzed following two or three equilibrations with high-purity He (McAulliffe 1971). All samples were analyzed within 2 h of collection at a lakeside laboratory. The instrument was calibrated with standards prepared daily by injecting known volumes of ultra-high-purity  $N_2O$  (Matheson) into gas calibration jars previously flushed with ultra-high-purity He (Matheson). Five standards with concentrations encompassing the range of sample  $N_2O$  were analyzed before and after each sample run. All standards were averaged to produce a curve used to compute sample concentration. Concentrations of all samples are presented as N in  $N_2O$ .

Denitrification potential was determined with the  $C_2H_2$  block assay (Yoshinari and Knowles 1976) on samples from 22, 25, and 30 m. Samples (100 ml) were slowly

pulled into 100-ml gas-tight syringes from the bottom of a Niskin bottle through a short piece of rubber tubing. Care was taken to avoid degassing of the sample during this procedure. High-purity acetylene (50 ml) was dissolved in each sample, and the samples were incubated in the dark near the temperature of collection. Five-milliliter samples were removed daily over a 5-d period for  $N_2O$  determination as described above. Ambient  $N_2O$  (no  $C_2H_2$  addition) concentration was also followed over time in a separate set of syringes containing water from 22, 25, and 30 m to detect possible net consumption by denitrification. Because ambient  $N_2O$  concentration in the 30-m sample was relatively low (<2  $\mu M$  N), 19  $\mu M$  N was added to the sample before incubation. Replicate 100-ml samples were included for all treatments.

$N_2O$  samples for the air above the lake were collected in replicate 30-ml glass serum vials that had been initially flushed with ultra-high-purity He. The flushed vials were filled with ambient air (600 ml), collected 30 cm above the lake ice at a centrally located station, using repeated injections from a 60-ml syringe (initially sparged with He). The vials were then allowed to stand open above the lake ice for an additional 24 h before they were capped with a serum stopper and aluminum seals. These air samples were run concomitantly with standardized air samples that had been collected in New Zealand to ensure that measurements made in Antarctica did not suffer from the point of calibration.

Percentage  $O_2$  and  $N_2O$  saturation represents the percentage of gas in the sample with respect to the amount that would be in the sample at air equilibrium. Sample equilibrium values for  $O_2$  and  $N_2O$  were obtained from Weiss (1970) and Weiss and Price (1980), respectively. The equilibrium equations presented by these authors for  $O_2$  and  $N_2O$  were derived for salinities ranging from freshwater to seawater (i.e. salinity of 0 to ~40‰). We verified the validity of extrapolating these equations to salinities in the deep-water samples of Lake Bonney (where salinity approaches 250‰) by direct  $N_2O$  measurement of selected high-salinity samples (20, 25, 30, 35 m) that had been sparged with air until equilibrium was reached. Equilibrated  $N_2O$  was measured with a gas chromatograph as described above;  $O_2$  was measured with a Coulximeter  $O_2$  sensor (Modern Controls) calibrated with air-equilibrated deionized water at known temperatures. Experimentally determined values were all within 10% of values obtained by extrapolation of the solubility equations presented by Weiss (1970) and Weiss and Price (1980).

Apparent  $N_2O$  production (ANP) and apparent oxygen utilization (AOU) were computed as  $[N_2O]_{\text{observed}} - [N_2O]_{\text{saturated}}$  and  $[O_2]_{\text{saturated}} - [O_2]_{\text{observed}}$  (Kaplan and Wofsy 1985; Butler et al. 1989). Although ANP and AOU imply activity, they are both state variables that are the net result of complex gain and loss processes.

$NH_4^+$  oxidation potential was measured as the difference between  $H^{14}CO_3^-$  uptake in control samples and samples amended with nitrapyrin (5 mg liter $^{-1}$ ), an inhibitor of  $NH_4^+$  oxidizer activity; carbon fixation was converted to  $NH_4^+$  oxidation assuming 0.1 mol of

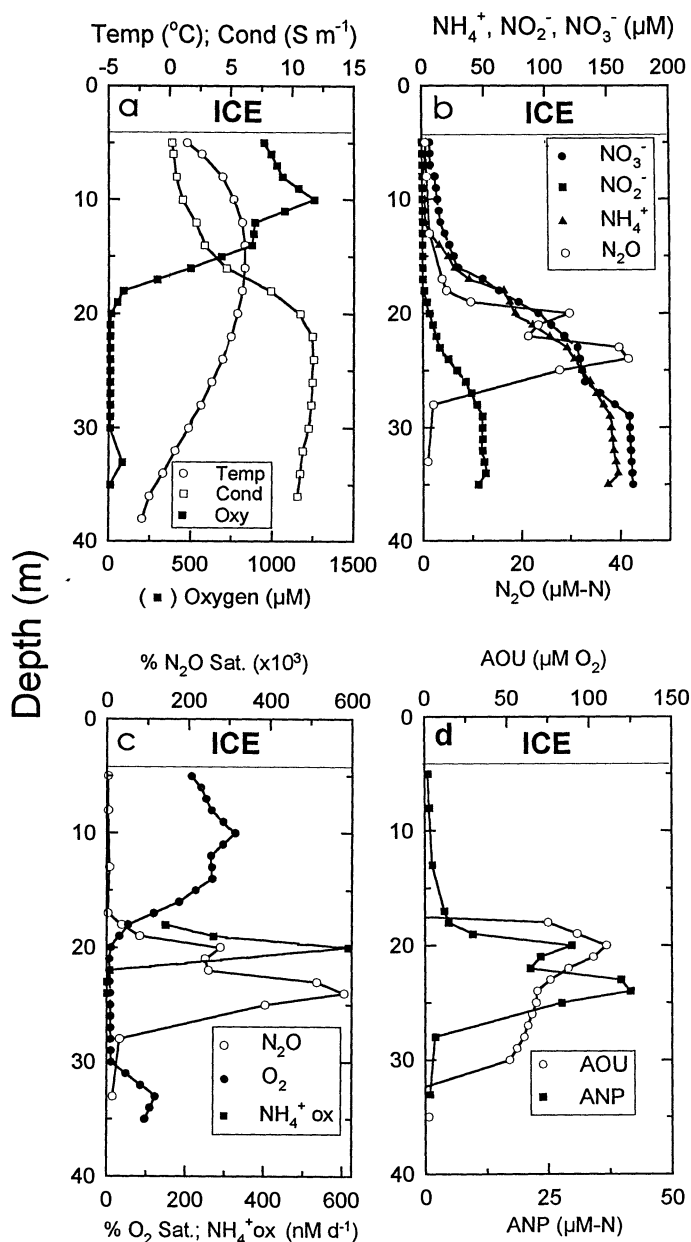


Fig. 1. Vertical profiles of various parameters at a central station in the east lobe of Lake Bonney made between October and December 1990–1992. All depths are relative to the piezometric liquid water level.  $\text{N}_2\text{O}$  saturation and ANP values are with respect to an air mixing ratio of 310.8 ppbv.  $\text{NH}_4^+_{\text{ox}}$  represents rates of potential  $\text{NH}_4^+$  oxidizer activity determined with the nitrapyrin assay. Details given in text.

$\text{HCO}_3^-$ -C fixed ( $\text{mol NH}_4^+$ -N oxidized) $^{-1}$  (Priscu and Downes 1985). Incubations were for 24 h in the dark at the temperature of collection; final  $^{14}\text{C}$  activity was between 37 and 74  $\text{kBq ml}^{-1}$ . The reaction was terminated by filtration of the sample through 0.22- $\mu\text{m}$  pore-size filters that were acidified and counted by standard liquid scintillation spectrometry. Phytoplankton photosynthesis (i.e.  $\text{CO}_2$  incorporation in the light over that in the dark) was extremely low or negligible at the depths where ni-

trapyrin experiments were conducted (Priscu 1995; Lizotte et al. 1996), minimizing any potential response of nitrapyrin on phytoplankton inorganic C metabolism (Dodds and Priscu 1991).

Temperature in the east lobe of Lake Bonney increased from  $\sim 0^\circ\text{C}$  just beneath the ice cover to a maximum of  $6.1^\circ\text{C}$  at 15 m and decreased to  $< -2^\circ\text{C}$  near the bottom (Fig. 1a). This unusual temperature profile results from solar heat accumulation in the high conductivity waters (primary chemocline, 17 m). The chemocline is a region where dissolved  $\text{O}_2$  levels drops from  $> 295\%$  saturation to  $< 7\%$  saturation (Fig. 1a,c) and where dissolved inorganic N increases rapidly (Fig. 1b). Distinct  $\text{N}_2\text{O}$  peaks occurred at 20 m and 24 m reaching 278,202% and 581,182%, respectively, relative to air saturation (Fig. 1b,c). These percentages are based on a global average mixing ratio for  $\text{N}_2\text{O}$  in air of 310.8 ppbv obtained by assuming a concentration of 310 ppbv in 1990 and an average atmospheric  $\text{N}_2\text{O}$  increase of  $0.25\% \text{ yr}^{-1}$  through 1991 (Watson et al. 1990; Prinn et al. 1990), the year that the vertical profile we present was measured. Numerous other profiles made during austral summer 1991 showed the same vertical bimodal distribution of  $\text{N}_2\text{O}$  and no obvious changes in concentration over time. The mixing ratio of  $\text{N}_2\text{O}$  in the air above the lake surface in October 1991 was  $451 \pm 25$  ppbv, 45% above the global average mixing ratio in 1991. On the basis of an air mixing ratio of 451 ppbv, the percent saturation of  $\text{N}_2\text{O}$  in lake water at 20 m would be 191,719% and at 24 m it would be 400,513%. Ammonium oxidizer activity, the presumed source of  $\text{N}_2\text{O}$  in another Antarctic lake (Vincent et al. 1981) and in the sea (Nevison et al. 1995), was detectable at the 20 m  $\text{N}_2\text{O}$  peak, but not in the region of the 24 m  $\text{N}_2\text{O}$  peak (Fig. 1c). ANP ranged from  $< 1 \mu\text{M N}$  in the near-surface and bottom waters to 30 and 42  $\mu\text{M N}$  at 20 and 24 m (Fig. 1d). Maximum ANP coincided with regions of high AOU.

A linear regression of ANP on AOU for points within the zone of  $\text{O}_2$  utilization (positive AOU), although positive, is not significantly different from zero if all data points are included (slope =  $0.093 \mu\text{M N} (\mu\text{M O}_2)^{-1}$ ;  $r^2 = 0.012$ ,  $P = 0.78$ ) (Fig. 2). However, if the samples forming the deeper  $\text{N}_2\text{O}$  maximum (23, 24, 25 m) are omitted, the slope of a linear regression becomes significantly different from zero (slope,  $0.547 \mu\text{M N} (\mu\text{M O}_2)^{-1}$ ;  $r^2 = 0.796$ ,  $P = 0.016$ ). Note that data from 23, 24, and 25 m group together and fall outside the 99% confidence belt for the latter regression.

Linear relationships between ANP and AOU were first observed in the subsurface waters of the Atlantic Ocean (Yoshinari 1976), leading to the suggestion that  $\text{N}_2\text{O}$  is produced in association with  $\text{NH}_4^+$  oxidation by nitrifying bacteria (an  $\text{O}_2$ -consuming process); this contention was corroborated by others with data from other regions of the sea (e.g. Butler et al. 1989; Law and Owens 1990), global oceanic estimates (Nevison et al. 1995), cultures of nitrifying bacteria (Goreau et al. 1980), and isotopic  $\text{N}_2\text{O}$  ratios (Yoshida 1988). Interestingly, the slopes of the regression between ANP and AOU for Lake Bonney exceed the oceanic average ( $\sim 2.51 \times 10^{-4} \mu\text{M N} (\mu\text{M O}_2)^{-1}$

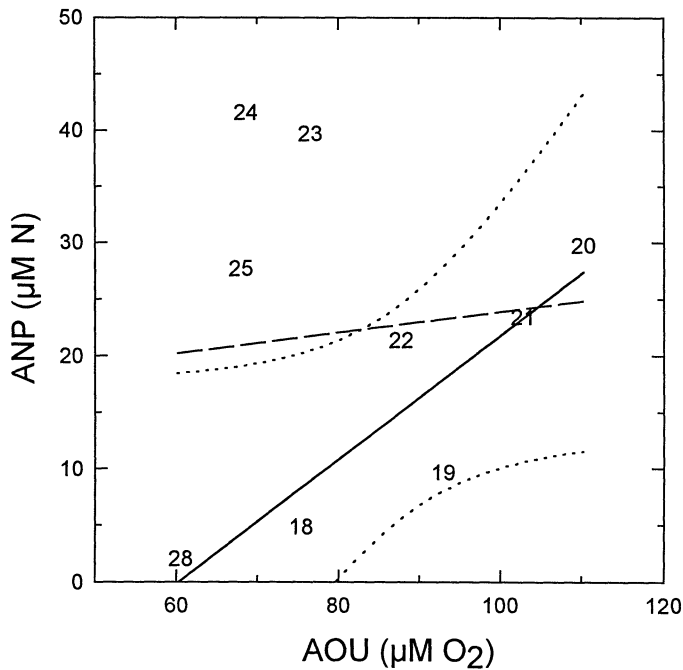


Fig. 2. Relationship between apparent  $\text{N}_2\text{O}$  yield (ANP) and apparent oxygen utilization (AOU). Numbers designate the depth of sample collection. Dashed line is the least-squares linear fit through all data; solid line is the linear least-squares fit when the 23, 24, and 25 m samples are omitted. Dotted lines represent the 99% confidence belt for the latter regression.

(Nevison et al. 1995) by two to three orders of magnitude, depending on whether the deep points are omitted. Lake Bonney thus has a considerably higher potential for  $\text{N}_2\text{O}$  production per unit  $\text{O}_2$  consumed than does the ocean.

Variation in the slopes of regressions between ANP and AOUs may relate to differences in the composition of organic matter being oxidized, differences in the yield for production of  $\text{N}_2\text{O}$ , mixing of different fluid layers, and additional sources of  $\text{N}_2\text{O}$  in regions of active assimilatory nitrate reduction (Elkins et al. 1978). Mixing and additional sources do not apply to Lake Bonney because fluid mixing is near the molecular level (Spigel et al. 1990; Spigel and Priscu 1996) and the zone of measurable phytoplankton primary production, presumably the primary pathway for assimilatory  $\text{NO}_3^-$  reduction, extends only to a depth of  $\sim 18$  m (Priscu et al. 1990; Lizotte et al. 1996; Priscu 1995).

Acetylene block experiments designed to measure denitrification potential on samples from 22, 25, and 30 m revealed no  $\text{N}_2\text{O}$  production in the presence of acetylene (slopes not significantly different from zero;  $P \geq 0.05$ ) (Fig. 3a). Samples from these depths also showed no significant (slopes not significantly different from zero;  $P \geq 0.05$ ) production or consumption of  $\text{N}_2\text{O}$  without acetylene addition (Fig. 3b). These results indicate that bulk denitrification does not occur in the low- $\text{O}_2$  water in the east lobe of Lake Bonney. The efficacy of our assay was proven on samples from below the chemocline in the west lobe of Lake Bonney, which showed significant produc-

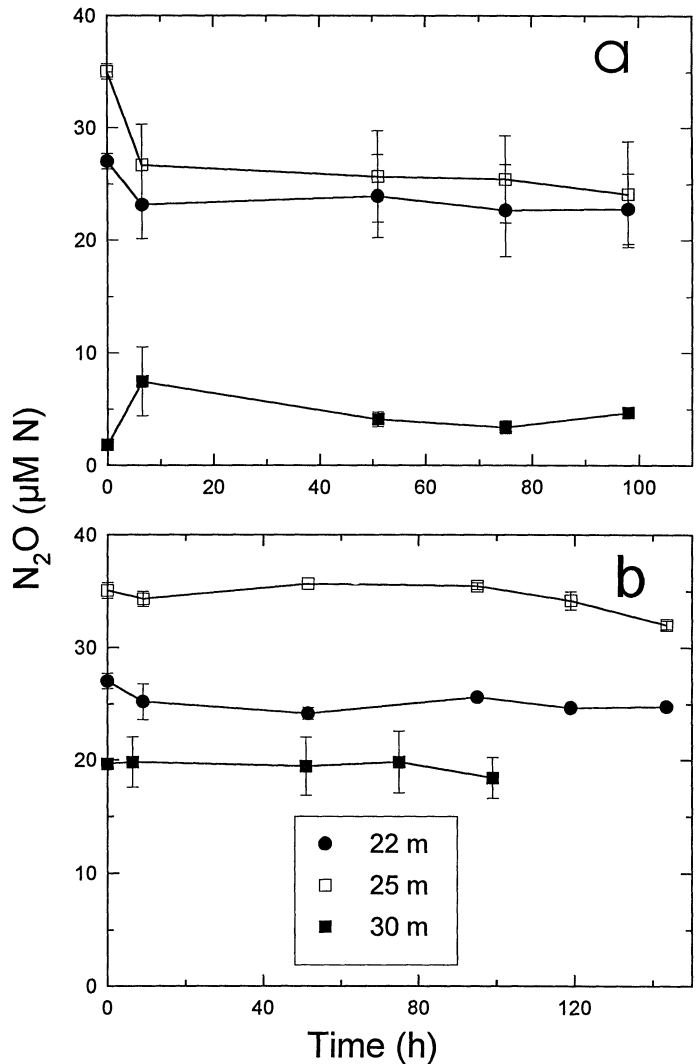


Fig. 3. Time-course changes in  $\text{N}_2\text{O}$  concentration in the presence (a) and absence (b) of 50% acetylene for samples from 22, 25, and 30 m.  $\text{N}_2\text{O}$  ( $19 \mu\text{M N}$ ) was added to the 30-m sample shown in panel b at time zero to ensure against potential depletion by denitrification during the experiment. Error bars denote the range of two replicate samples; when bars are not shown, they are smaller than the symbol.

tion of  $\text{N}_2\text{O}$  in the presence of acetylene and significant consumption of  $\text{N}_2\text{O}$  in samples amended with this gas (data not shown). The presence of high levels of oxidized nitrogen and no measurable denitrification in the east lobe indicates that nitrification is the source of  $\text{N}_2\text{O}$  and that no biochemical sink exists.

Assuming that nitrification is the sole source of  $\text{N}_2\text{O}$  in the east lobe of Lake Bonney, yield ratios for  $\text{N}_2\text{O}$  can be estimated from the relationship between ANP and oxidized nitrogen concentration (e.g. Kaplan and Wofsy 1985). This relationship represents the proportion of  $\text{N}_2\text{O}$  produced per unit  $\text{NH}_4^+$  oxidized. The yield ratio in the east lobe of Lake Bonney, estimated from the slope of a regression of ANP on ambient  $\text{NO}_2^- + \text{NO}_3^-$ , is 8.5% (slope = 0.0853,  $r^2 = 0.14$ ,  $P = 0.18$ ) (Fig. 4). The yield

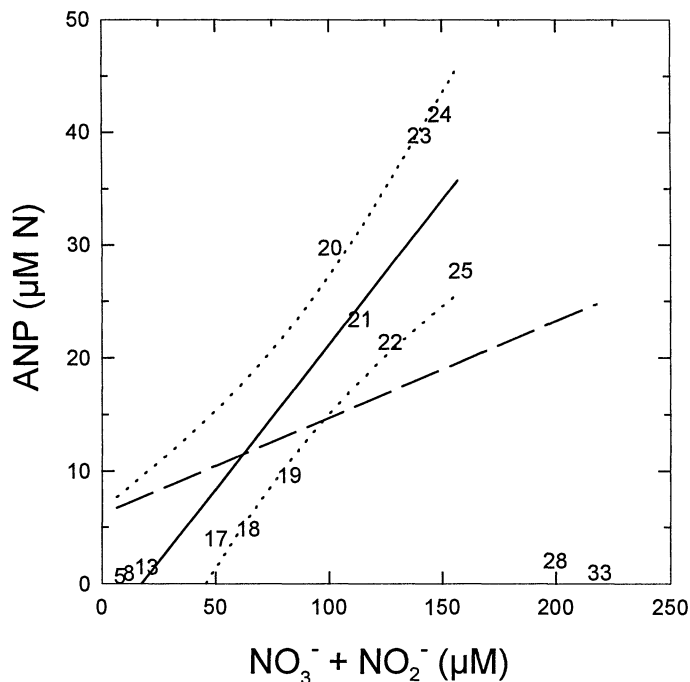


Fig. 4. Relationship between apparent  $\text{N}_2\text{O}$  yield (ANP) and oxidized inorganic nitrogen concentration ( $\text{NO}_3^- + \text{NO}_2^-$ ). Numbers designate the depth of sample collection. Dashed line is the linear least-squares fit through all data points; solid line is the linear least-squares fit when the 28-m and 33-m samples are omitted. Dotted lines represent the 99% confidence belt for the latter regression.

increases to 25.6% if data from below the ANP maximum (28 and 33 m) are excluded from the regression (slope = 0.256,  $r^2 = 0.83$ ,  $P < 0.001$ ). The yield ratios at 28 and 33 m, which are clearly outliers with respect to other depths (they fall well outside the 99% C.L. of the latter regression), may be affected by potentially toxic levels of metals that have accumulated in the deep water of the east lobe (Spigel and Priscu 1996). These yield ratios are higher than any reported in the literature for pelagic marine systems (range, 0.05–0.9%; reviewed by Kaplan and Wofsy 1985), being similar to that observed in highly reduced sediments (Jørgenson et al. 1984). Work on liquid cultures of marine nitrifying bacteria (Goreau et al. 1980) has shown that the  $\text{N}_2\text{O}$  yield ratio increased inversely with  $\text{O}_2$  tension but that the yield reached only ~10%, even at  $\text{O}_2$  tensions <1%. The high yield shown by the regression of ANP to oxidized N and its dependence on  $\text{O}_2$  in Lake Bonney is confirmed by the relationship between ANP/oxidized N and ambient  $\text{O}_2$  (Fig. 5). These data show that the  $\text{N}_2\text{O}$  yield ratio increased with decreasing  $\text{O}_2$ , reaching ~30% at  $\text{O}_2$  levels <10  $\mu\text{M}$ ; there was no dependence of the  $\text{N}_2\text{O}$  yield ratio with  $\text{O}_2$  above ~50  $\mu\text{M}$   $\text{O}_2$ . Although the transition at 50  $\mu\text{M}$   $\text{O}_2$  is similar to that found in pelagic marine systems (Kaplan and Wofsy 1985), the yield ratios for Lake Bonney exceed those in pelagic marine systems by 25-fold above 50  $\mu\text{M}$   $\text{O}_2$  and 3-fold below 50  $\mu\text{M}$   $\text{O}_2$ .

The absence of nitrapyrin-sensitive  $\text{NH}_4^+$  oxidizer ac-

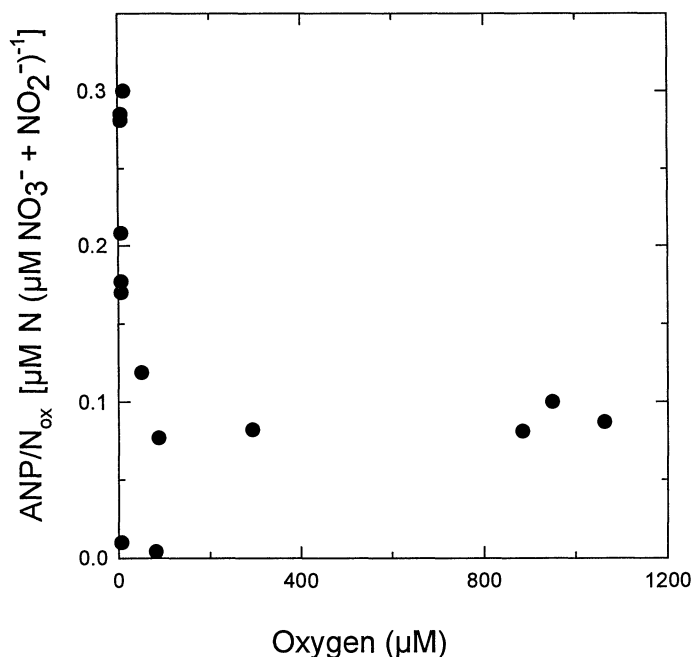


Fig. 5. Relationship between apparent  $\text{N}_2\text{O}$  yield normalized to the concentration of oxidized inorganic nitrogen ( $\text{ANP}/\text{N}_{\text{ox}}$ ) and dissolved oxygen.

tivity at 24 m, together with the outlying ANP-AOU relationship for the  $\text{N}_2\text{O}$  maximum at 24 m (Fig. 2), implies that conventional nitrification ( $\text{NH}_4^+ \rightarrow \text{NO}_2^- \rightarrow \text{NO}_3^-$ ) is not responsible for the  $\text{N}_2\text{O}$  peak at 24 m. Downes (1988) discussed the potential importance of nitrifier denitrification in which  $\text{NO}_2^-$  is reduced by autotrophic nitrifying bacteria to  $\text{N}_2\text{O}$  under low  $\text{O}_2$  (<31  $\mu\text{M}$   $\text{O}_2$ ). This process is thought to be coupled to  $\text{CO}_2$  fixation (Poth and Focht 1985) and should have been detected as nitrapyrin inhibition. Despite the potential for nitrifier denitrification, lack of nitrapyrin sensitivity together with high levels of  $\text{NO}_3^-$  and  $\text{NO}_2^-$  in this region do not support the presence of such a pathway. Owing to low eddy diffusion rates, some of the gradients we observed in Lake Bonney may represent biological activity that existed during an earlier period of the lake's history (Priscu 1995). On the basis of a molecular diffusion coefficient of  $10^{-9}$   $\text{m}^2 \text{s}^{-1}$  and a water column depth of 40 m, the diffusion time for Lake Bonney is >50,000 yr. Our use of molecular diffusion is based on numerous CTD casts in the east lobe of Lake Bonney, which revealed no turbulence at centimeter scales (Spigel and Priscu unpubl. data); on the small fraction of the lake surface exposed to the energy of the wind; on the relatively low and seasonal advective stream input; and on published data that show that in most stratified hypolimnia, mixing is molecular almost everywhere except in isolated patches and along boundaries where wind-, river-, and convective-driven motions obtain enough energy for isolated overturning events or instabilities (Spigel and Imberger 1987; Imberger and Ivey 1991). Because the lake has apparently existed for >10,000 yr (Chinn 1993), we conclude that certain chemical gra-

dients could represent “fossil” records of past metabolic activity.

Despite uncertainties regarding the biochemical pathways of  $N_2O$  production in Lake Bonney, extreme supersaturation within the lake, coupled with the elevated atmospheric  $N_2O$  levels that occurred in the air above the lake, indicates that the lake is a source of atmospheric  $N_2O$ . Numerous models exist to compute air–water transfer of gases (e.g. Liss and Merlivat 1986; Erickson 1993), each based on different premises. The gas transfer coefficients used in these models are modeled primarily as a function of surface wind speed, with an estimated error of at least 50% (Erickson 1993). Nevison et al. (1995) computed global oceanic  $N_2O$  fluxes using several of these models and reported a propagated uncertainty of ~70%. An estimate of the outward flux of  $N_2O$  across the air–water interface for the moat of Lake Bonney was made using the transfer velocity relationship of Liss and Merlivat (1986). We assumed that the peripheral summer moat occupies ~3% of the lake surface area for about 10 weeks per year (Wharton et al. 1986). Flux from the summer moat was combined with an estimate of  $N_2O$  flux through the permanent ice cover of the lake. The latter considers information from an  $O_2$  ice-flux model developed for Lake Hoare (Craig et al. 1992), a permanently ice-covered lake located ~10 km east of Lake Bonney.

The flux of  $N_2O$  across the air–water interface of the moat can be expressed as

$$F = K(pN_2O_w - pN_2O_a) = K\Delta pN_2O. \quad (1)$$

$F$  ( $\text{mol cm}^{-2} \text{h}^{-1}$ ) is flux from water to atmosphere,  $K$  ( $\text{mol natm}^{-1} \text{cm}^{-2} \text{h}^{-1}$ ) is the gas transfer coefficient,  $pN_2O_w$  ( $\text{natm}$ ) is  $N_2O$  partial pressure in surface water, and  $pN_2O_a$  ( $\text{natm}$ ) is  $N_2O$  partial pressure in the water-saturated atmospheric boundary layer.  $K$  is the product of the solubility of the gas ( $\text{mol cm}^{-3} \text{natm}^{-1}$ ) and the gas transfer velocity ( $\text{cm h}^{-1}$ ). Solubility is a function of salinity and temperature; gas transfer velocity can be thought of as the rate of molecular and turbulent diffusion through the air–water interface (Liss and Merlivat 1986; Erickson 1993).

$pN_2O_w$  (5,948  $\text{natm}$ ) was computed by dividing the  $N_2O$  concentration measured immediately beneath the ice cover, which was assumed to be in equilibrium with the moat water (0.677  $\mu\text{M N}$ ), by the solubility of  $N_2O$  in freshwater at 1°C and 1 atm ( $5.691 \times 10^{-14} \text{mol cm}^{-3} \text{natm}^{-1}$ ; Weiss and Price 1980). The global average mixing ratio in air of 310.8 ppbv was used for  $pN_2O_a$ . The dry-gas mole fraction (ppbv) was converted to partial pressure using the vapor pressure of freshwater at 1°C (4.58 mm Hg); hence,  $\Delta pN_2O = 5,601 \text{natm}$ .

If we assume an average wind speed at Lake Bonney of 7  $\text{m s}^{-1}$  (Clow et al. 1988), the relationship of Liss and Merlivat (1986), together with the scaling factor presented by Nevison et al. (1995), yields a transfer velocity of 5.754  $\text{cm h}^{-1}$ . This transfer velocity times the solubility of  $N_2O$  at 1°C in freshwater yields a value for  $K$  of  $3.274 \times 10^{-13} \text{mol cm}^{-2} \text{h}^{-1} \text{natm}^{-1}$ ; hence,  $F = 1.83 \times 10^{-9} \text{mol N}_2\text{O cm}^{-2} \text{h}^{-1}$ , which converts to 4.50  $\text{g N}_2\text{O-N m}^{-2} \text{yr}^{-1}$ . When corrected for east lobe moat size and period, the

outward flux from the moat was  $9.86 \times 10^4 \text{g N}_2\text{O-N yr}^{-1}$ . This value decreases by 2.5% if the elevated atmospheric  $N_2O$  level (451 ppbv) measured over the lake surface is used in the calculation instead of the global average. We stress that this flux calculation assumes that  $N_2O$  concentration in the 5-m water (that just beneath the ice) and moat water was in equilibrium and that the  $N_2O$  concentration gradient between moat water and the atmosphere was maintained throughout the moat period. These assumptions have not been tested.

Outward gas flux through the permanent ice cover is difficult to measure directly owing to complex dynamics of gas exsolution upon freezing and unknown absolute gas concentration within the ice cover. However, given the approximate annual steady-state dynamics of the ice cover (the same thickness of new ice formed at the lake water–ice interface is lost from the ice–air interface via ablation each year), loss of  $N_2O$  to the atmosphere through the ice cover should be proportional to the concentration of  $N_2O$  in the water immediately below the ice cover. We estimated outward  $N_2O$  flux with results from a model of  $O_2$  flux through the permanent ice cover of Lake Hoare (Craig et al. 1992), ~10 km from Lake Bonney, by scaling it to  $N_2O$  according to the following general relationship:

$$\text{FLUX\_OUT\_N}_2\text{O} = \text{FLUX\_OUT\_O}_2 \times ([N_2O]/[O_2]). \quad (2)$$

$\text{FLUX\_OUT\_O}_2 = [(\text{biological production of } O_2 \text{ within the lake}) + (\text{meltwater FLUX\_IN\_O}_2)]$ , and  $[N_2O]$  and  $[O_2]$  are ambient levels of these gases measured just beneath the ice, which is a function of equilibrium solubility and saturation level.

Meltwater input was estimated from the lake ice ablation rate (30  $\text{cm yr}^{-1}$ ; Clow et al. 1988) and an ice density of 0.917  $\text{g cm}^{-3}$ ; the relationship assumes annual steady-state ice thickness and water level, which were approximated during the study period. When considering these values and assumptions, we found the average annual meltwater input into Lake Bonney to be 0.03  $\text{kg cm}^{-2} \text{yr}^{-1}$ .  $\text{FLUX\_IN\_O}_2$  was then determined assuming that the incoming meltwater was in equilibrium with the atmosphere.

The biological contribution of  $O_2$  in Lake Hoare through photosynthesis was estimated to be ~11% of  $\text{FLUX\_IN\_O}_2$  (Craig et al. 1992). Because phytoplankton production and meltwater input in Lake Hoare are close to those in the east lobe of Lake Bonney (Priscu 1995; Priscu unpubl. data), we used this value as an estimate of biological  $O_2$  production in Lake Bonney. Hence, the  $\text{FLUX\_OUT\_O}_2$  through the ice cover of Lake Bonney can be computed as

$$\text{FLUX\_OUT\_O}_2 = 1.11 \times 0.03 \text{kg cm}^{-2} \text{yr}^{-1} \times 10.22 \text{cm}^3 (\text{STP}) \text{kg}^{-1}, \quad (3)$$

where 1.11 represents photosynthetic  $O_2$  production in the lake (11%), 0.03  $\text{kg cm}^{-2} \text{yr}^{-1}$  is meltwater  $O_2$  flux into the lake, and 10.22  $\text{cm}^3 (\text{STP}) \text{kg}^{-1}$  is the atmospheric equilibrium solubility of  $O_2$  at 0°C and 760 mm Hg, which applies to meltwater entering the lake. The  $\text{FLUX\_OUT\_O}_2$  through the ice cover, based on the above relationships, is 0.34  $\text{cm}^3 (\text{STP}) \text{cm}^{-2} \text{yr}^{-1}$ .

The FLUX\_OUT\_N<sub>2</sub>O was then estimated as:

$$\begin{aligned} \text{FLUX\_OUT\_N}_2\text{O} &= [1.11 \times 0.03 \text{ kg cm}^{-2} \text{ yr}^{-1} \times 10.22 \text{ cm}^3 \text{ O}_2 \text{ (STP) kg}^{-1}] \\ &\quad \times [(19.19 \times 0.41 \times 10^{-3} \text{ cm}^3 \text{ N}_2\text{O (STP) kg}^{-1}) \\ &\quad \div (2.21 \times 10.22 \text{ cm}^3 \text{ O}_2 \text{ (STP) kg}^{-1})] \\ &= 1.19 \times 10^{-4} \text{ cm}^3 \text{ N}_2\text{O (STP) cm}^{-2} \text{ yr}^{-1} \end{aligned} \quad (4)$$

where 19.19 represents the level of N<sub>2</sub>O supersaturation (1,919%) just beneath the ice cover in Lake Bonney (Fig. 1c),  $0.41 \times 10^{-3} \text{ cm}^3 \text{ N}_2\text{O (STP) kg}^{-1}$  is the atmospheric equilibrium solubility of N<sub>2</sub>O at 0°C and 760 mm Hg (Weiss and Price 1980), 2.21 represents the level of O<sub>2</sub> supersaturation (221%) just beneath the ice cover in Lake Bonney (Fig. 1c), and the other factors are as presented in Eq. 3. The outward flux of N<sub>2</sub>O converted to units of mass is  $1.49 \times 10^{-3} \text{ g N m}^{-2} \text{ yr}^{-1}$ , which, considering an east lobe lake-ice area of  $3.8 \times 10^{-6} \text{ m}^2$  during the moat-free period and  $3.7 \times 10^6 \text{ m}^2$  during the 10-week moat period, yields an absolute outward flux of  $5.63 \times 10^3 \text{ g N yr}^{-1}$ .

The annual areal (m<sup>-2</sup>) flux of N<sub>2</sub>O from the east lobe of Lake Bonney (moat at an atmospheric mixing ratio of 310.8 ppbv, plus ice transfer;  $4.50 \text{ g N m}^{-2} \text{ yr}^{-1} + 1.49 \times 10^3 \text{ g N m}^{-2} \text{ yr}^{-1}$ ) is >200 times greater than the annual areal flux computed for various regions of the ocean (e.g. Prinn et al. 1990; Nevison et al. 1995). Our calculations show that most of the atmospheric N<sub>2</sub>O flux comes from the summer moat despite its relatively small surface area and duration, indicating the importance of ice cover as a barrier to gas transport from the liquid water of the lake to the air (areal fluxes from the lake ice were ~0.03% of that from the moat). However, numerous temporal cracks may develop in the lake ice (Wharton et al. 1993; Priscu 1991) that can act as direct conduits of gases between the atmosphere and water column. Because gas flux through these cracks may be considerable and is virtually impossible to quantify, our estimates of gas flux through the ice (and consequently the total flux) should be considered conservative.

John C. Priscu

Department of Biology  
Montana State University  
Bozeman 59717

Malcolm T. Downes

National Institute for Water and Atmospheric Research  
Riccarton, P.O. Box 8602  
Christchurch, New Zealand

Christopher P. McKay

Space Science Division  
NASA Ames Research Center  
Moffett Field, California 94035

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