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The biogeochemistry of nitrous oxide in permanently ice-covered lakes of the McMurdo Dry Valleys, Antarctica

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Abstract

This manuscript presents an overview of published work on nitrous oxide in the permanently ice-covered lakes of the McMurdo Dry Valleys, Antarctica. One of these lakes contains the highest concentration of nitrous oxide reported for natural aquatic systems (> 500 000% with respect to the global average mixing ratio in air). Recent data on nitrous oxide from the major lakes in this region of Antarctica are used to draw general conclusions regarding sources and sinks for this gas within the liquid water column, and to estimate exchanges with the atmosphere. Nitrous oxide maxima are usually found in regions where oxygen concentrations and redox potentials are decreasing (i.e. where high gradients exist); nitrous oxide is virtually absent in anoxic, and very low redox zones. These trends, together with positive relationships between apparent oxygen utilization (AOU) and apparent nitrous oxide production (ANP) indicate that nitrous oxide is primarily a product of nitrification; experiments showed that denitrification is a sink for this gas in anoxic water. ANP/AOU ratios are several orders of magnitude higher than that for the ocean. Yield ratios for nitrous oxide [ANP/(NO_2^- + NO_3^-)] averaged 4.2% (i.e. 1 atom of N appears in nitrous oxide for every 24 atoms appearing in oxidized N), greatly exceeding existing reports for pelagic systems, being similar to that from reduced sediments. Production and consumption rates, computed with a one-dimensional diffusion model, ranged from 0 to 5.3 nM-N d^{-1} and 0–2.7 nM-N d^{-1}, respectively. Rates were usually greatest in the region of largest oxygen and inorganic nitrogen gradients. Turnover times averaged 2917 and 1277 years for production and consumption which is in the range of the mixing times for the lakes. Areal flux from the lakes to the atmosphere (6.17 gN m^{-2} y^{-1}) is several hundred times greater than areal fluxes reported for oceanic systems. Owing to the relatively small combined surface area of these lakes, absolute atmospheric transfer (1.2×10^5 gN y^{-1}) is only a small fraction of annual global emission.

Keywords: Antarctic lakes, atmospheric flux, biogeochemistry, nitrous oxide

Introduction

Nitrous oxide (N_2O) is a long-lived (100–150 y; Cicerone 1989) atmospheric trace gas that contributes to the global radiation budget and stratospheric ozone depletion (Shine *et al.* 1990; Watson *et al.* 1990; Kroeze 1994). Data from Antarctic ice cores show that present day concentrations are higher than those over the past 45 000 y (Leuenberger & Siegenthaler 1992). Long-term data sets indicate that atmospheric nitrous oxide has been increasing between 0.2 and 0.3% y^{-1} for the past two decades (Rasmussen & Khalil 1986; Prinn *et al.* 1990). Despite the global importance of nitrous oxide, global budgets for this trace gas are still out of balance; between 30% and 50% of the known sinks are not balanced by sources (e.g. Cicerone 1989; Khalil & Rasmussen 1992; Robertson 1993).

Nitrous oxide has both biogenic and anthropogenic sources. Marine and natural soil systems are the major natural biogenic sources (Schlesinger 1991). Anthropogenic sources comprise land-use change, nylon production, fossil fuel burning and fertilizer usage (summarized by Kroeze 1994). In general, anthropogenically impacted sites have received more study than natural sites (Bouwman 1990) and terrestrial sites have been studied more intensively than aquatic sites.

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Nitrous oxide is produced microbially through nitrification, denitrification, and has been implied to be an intermediate in assimilatory nitrate reduction by certain algae; microbial consumption of nitrous oxide occurs only through denitrification (reviewed by Kaplan & Wofsy 1985). Research has shown that aquatic systems may be either sources or sinks for nitrous oxide (e.g. Oudot *et al.* 1990; Yoh 1990, 1992) depending upon dissolved oxygen concentration. Despite numerous studies on the influence of oxygen on nitrous oxide production and consumption, transformations in aquatic environments with low oxygen tensions remain equivocal (Downes 1988; von Schulthess *et al.* 1994; Priscu *et al.* 1996). Results from marine systems have generally shown that nitrous oxide is produced via nitrification in surface waters (e.g. Yoshinari 1976; Elkins *et al.* 1978; Nevison *et al.* 1995) whereas denitrification may be a source in oxygen depleted deep water (Yoshida *et al.* 1989). Overall, the ocean is thought to be a source of atmospheric nitrous oxide, most of which is produced by nitrification (Nevison *et al.* 1995). Owing to their individual nature and relatively wide range in trophic status, this scenario is not as obvious in lakes. Knowles *et al.* (1981) and Yoshinari & Wahlen (1985) have suggested that supersaturation of nitrous oxide in eutrophic systems results from denitrification whereas nitrous oxide in the water column of oligotrophic lakes is produced by nitrification (Lemon & Lemon 1981; Chan & Campbell 1980) or a combination of both (Yoh 1990, 1992).

Owing partially to the unresolved global nitrous oxide budget, and to the individual nature of freshwater systems, many studies have focused on sources and sinks of nitrous oxide and other greenhouse gases in regional systems such as groundwater (Ueda *et al.* 1993), estuaries (Middelburg *et al.* 1995), activated sludge (von Schulthess *et al.* 1994), artificially oxygenated lakes (Mengis *et al.* 1996), hydroelectric reservoirs (Rosa & Schaeffer 1994) and Antarctic lakes (Vincent *et al.* 1981; Priscu *et al.* 1996). Though these systems may each represent relatively small atmospheric sources, their collective input to the atmosphere deserves further attention. For example, nitrous oxide concentration in Lake Bonney, Antarctica exceeds 500 000% of air saturation producing locally elevated atmospheric levels (Priscu *et al.* 1996).

Antarctic lakes

Background

Antarctica is receiving increasing global attention, owing partially to its pristine nature and potential threats of pollution (Garrison & Siniff 1986; Savoie *et al.* 1993). Centred on the geographic south pole, Antarctica encompasses about 14×10^6 km^2, 95–98% of which is covered by ice and snow. The ice cover represents about 90% of the planet's ice volume and 70% of its fresh water. Numerous lakes exist on the Antarctic continent, all of which vary considerably in their physical and biogeochemical properties (Burton 1981; Heywood 1984; Green & Friedmann 1993). To my knowledge, the only published reports on nitrous oxide levels in Antarctic lakes have been for the permanently ice-covered lakes of the McMurdo Dry Valleys. The British Antarctic Survey (BAS), as part of a study on denitrification, found levels of nitrous oxide to be near detection limits in maritime Antarctic lakes (J.C. Ellis-Evans personal communication). Because of low concentrations, the BAS group did not focus their studies on nitrous oxide biogeochemistry. The remainder of this chapter will focus on the concentration and transformation of nitrous oxide in the permanently ice-covered Antarctic lakes adjacent to McMurdo Sound. The relatively few published manuscripts on nitrous oxide in these lakes is reviewed. This review is supplemented with new information collected over the past four years to assess general trends in nitrous oxide biogeochemistry. An attempt is made to define regulatory mechanisms, quantify rates and turnover times, and exchanges with the atmospheric nitrous oxide pool.

Fig. 1 Map showing location of the McMurdo Dry Valley region of Antarctica and lakes within these valleys.

Lakes of the McMurdo Dry Valleys

The dry valley region of southern Victoria Land (76° 30′ S to 78° 30′ S) is the largest ice-free expanse in Antarctica (~4500 km^2) (Fig. 1). Ice-free conditions result from a combination of low precipitation, blockage of ice flow from the polar plateau by the Transantarctic Mountains, solar heating caused by the low surface albedo of the valley floors, and warm dry catabatic winds descending from the polar plateau (Clow *et al.* 1988). A number of perennially ice-covered lakes, ranging in surface area from about 1 to 7 km^2, exist on the valley floors (Armitage & House 1962; Heywood 1972; Chinn 1993). These lakes contain liquid water columns up to about 80 m deep; other lakes in the region are frozen to the bottom (Chinn 1993). Variable amounts of glacial melt enter the lakes during the summer months and most lack outflows. Small moats often form in the summer occupying up to 3% of each lake's surface area. Water balance (ice + liquid water) is maintained by approximately 30 cm y^{-1} ablation from the ice surface (Clow *et al.* 1988). Owing to unique meteorological conditions, these lakes are the only ones on the planet that maintain a permanent ice cover (Wharton *et al.* 1993; McKay *et al.* 1985).

The permanent ice cover is important to the biogeochemistry of the liquid water column in the lakes for many reasons. Wind-generated turbulence is non-existent resulting in (i) mixing at the molecular scale (Spigel *et al.* 1990, 1991; Spigel & Priscu, in press); (ii) highly restricted exchange of gases between the lakes and the atmosphere (Craig *et al.* 1992; Priscu *et al.* 1996); (iii) low light penetration (Priscu 1991; Fritsen *et al.* in press; Howard-Williams *et al.* in press); (iv) reduced rates of primary production (Lizotte & Priscu 1992a,b); and (v) diminished sediment deposition (Squyres *et al.* 1991; Adams *et al.* in press). The permanent ice-cover may also play a role for the paucity of higher trophic levels in the lakes; life is restricted to microorganisms. The lake ice also provides a growth habitat for microorganisms during periods of high ice porosity (Fritsen *et al.* in press).

The lakes in the McMurdo Dry Valleys have long and complex histories (Lyons *et al.* 1985; Chinn 1993; Lyons *et al.* submitted). They have been effaced several times by throughflow of ice from the polar plateau and invasion by Ross Sea ice (Denton *et al.* 1989; Hendy *et al.* 1979). Most of the present lake basins formed between 2000 and 15 000 y BP, reflecting climatic changes (Denton *et al.* 1989; Kellogg *et al.* 1979; Chinn 1993). Since delineation of the current basins, lake levels have risen and fallen considerably; the last major 'dry down' appears to have been between 1000 and 1200 y BP when some of the lakes appeared to have lost their ice covers and evaporated to complete dryness (Lyons *et al.* submitted). Concentration of salts during the dry periods followed by refilling has produced present day lakes with a range of salinities and salinity gradients (e.g. Spigel & Priscu 1996; Spigel & Priscu in press).

Published data on nitrous oxide in the dry valley lakes exist for Lake Vanda and the east lobe of Lake Bonney. This manuscript will present more recent results from these lakes as well as from Lakes Joyce, Bonney (west lobe), Joyce, Fryxell and Miers. Lakes Bonney, Hoare and Fryxell lie in the Taylor Valley and are the primary study lakes of a U.S. National Science Foundation Long Term Ecological Research (LTER) site (Fig. 1). Lake Joyce lies in the Pearse Valley against the Taylor Glacier whereas Lakes Vanda and Miers are located in the Wright and Miers Valley's, respectively. Location and general morphometric characteristics of the lakes are presented in Table 1; physical and chemical features are shown in Fig. 2 and will be discussed in more detail below. An excellent overview of the physical and hydrological characteristics of these lakes is presented by Chinn (1993). These sites are the major lakes containing liquid water in the McMurdo Dry Valleys and represent diverse physical, chemical and biological situations.

Overview of nitrous oxide studies in the dry valley lakes

The seminal work on nitrous oxide in Antarctic lakes was conducted in Lake Vanda (Vincent *et al.* 1981). Vincent and colleagues measured nitrous oxide levels ranging from 0.05 μM-N (48% above air saturation) immediately beneath the ice cover to a maximum of 4.29 μM-N (>20 000% above air saturation) in the saline bottom waters at 54 m. The nitrous oxide maximum coincided with the nitrate maximum and was several metres above the nitrite maximum. The highest levels of nitrous oxide corresponded to zones of high nitrification potential and a paucity of denitrification, leading these authors to conclude that nitrification was the source for this gas. Nitrous oxide levels decreased rapidly in the anoxic waters beneath the 54 m maximum coinciding with measurable rates of denitrification. Vincent *et al.* found the ratio of nitrous oxide to nitrate (an estimate of the amount of nitrous oxide produced per unit of ammonium oxidized) to be lowest in the upper water column and in the deep, anoxic layers beneath the nitrous oxide maximum. Such zonation led to the overall conclusion that the gas was lost in the near surface layer to the atmosphere through the ice cover or temporary moat, and that denitrification was a sink for the gas in the deep water. An abundance of ammonium (>100 μM), in concert with low dissolved reactive phosphorus levels (<0.01 μM) in the region of the nitrification maximum, led to the inference that nitrous oxide production via nitrification was limited by the supply of phosphorus. Phytoplankton photosynthesis in these lakes has also been shown to be limited by phosphorus (Priscu 1995).

Vincent *et al.* found that nitrite accumulated several metres beneath the nitrate maximum in a region where ammonium increased precipitously. This result was explained by possible differential inhibition of nitrite oxidation and ammonium oxidation (two primary steps in nitrification) by ammonium. Vincent *et al.* cite published

Table 1 Location and general characteristics for the study lakes. Z_{max} = maximum depth (m) from the hydrostatic water level (water level within the sampling hole); Ice_z = average ice thickness (m); A_o = estimated surface area (km^2); Volume = estimated liquid water volume ($\times$ 10^6 m^3). Data represent average conditions observed between 1989 and 1996.

Lake	Valley	Coordinates	Z_{max}	Ice_z	A_o	Volume
Joyce	Pearse	77°43′S, 161°33′E	35	4.8	0.8	4.9
WL Bonney	Taylor	77°43′S, 162°20′E	40	3.5–4.0	1.3	10.1
EL Bonney	Taylor	77°43′S, 162°20′E	40	3.5–4.0	3.5	54.7
Hoare	Taylor	77°38′S, 163°07′E	34	4.5	1.9	17.5
Fryxell	Taylor	77°37′S, 163°07′E	21	4.5	7.1	25.2
Vanda	Wright	77°32′S, 161°33′E	80	3.2	6.7	160.0
Miers	Miers	78°07′S, 163°54′E	20	4.3	1.1	2.9

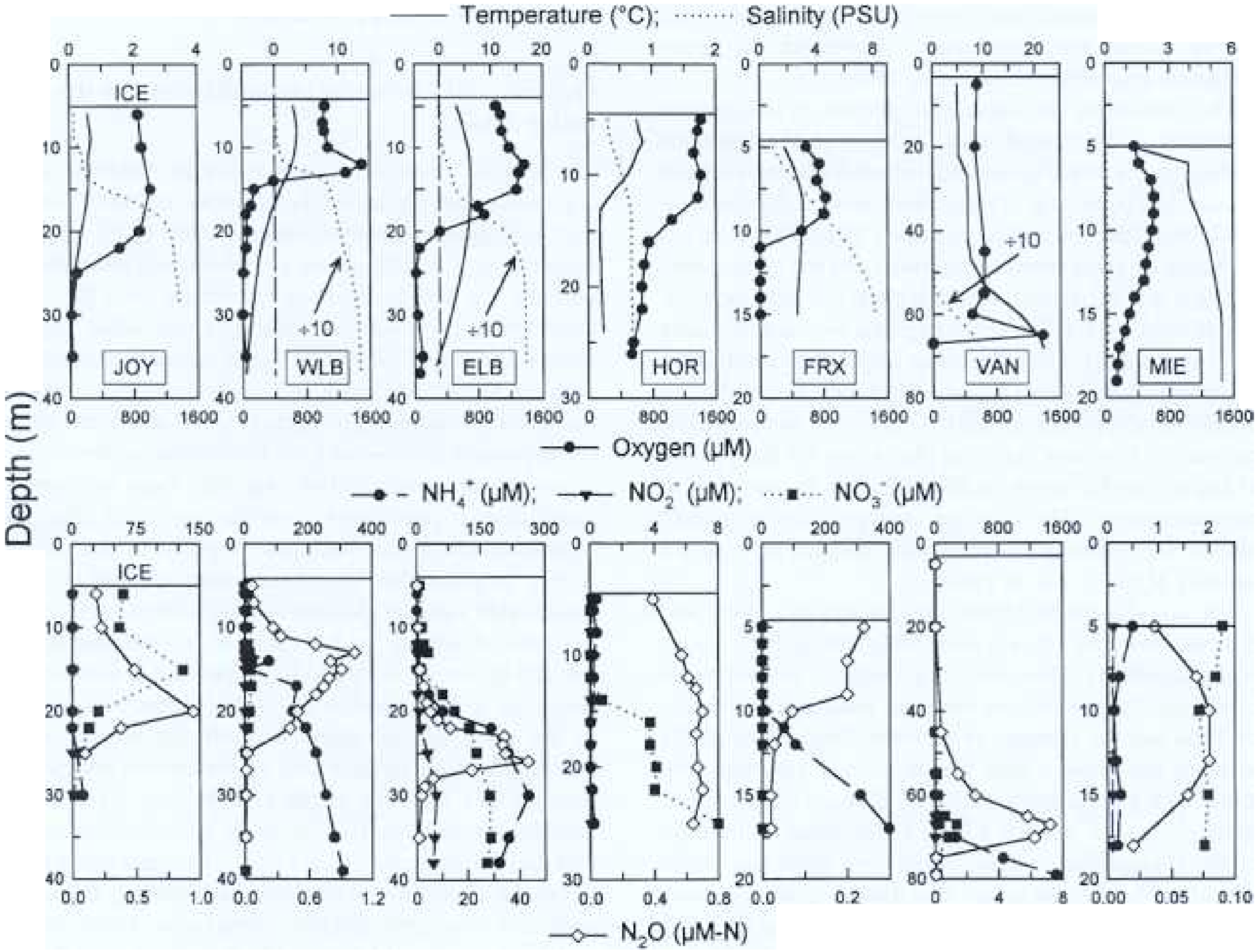

Fig. 2 Vertical profiles of physical and chemical parameters in seven lakes of the McMurdo Dry Valleys. JOY, Lake Joyce; WLB, west lobe of Lake Bonney; ELB, east lobe of Lake Bonney; HOR, Lake Hoare; FRX, Lake Fryxell; VAN, Lake Vanda; MIE, Lake Miers. Note that the salinity presented for Lakes Bonney and Vanda has been divided by 10; scale values should be multiplied by 10 to yield true values. PSU, practical salinity scale units. Also note that the temperatures in the deep waters of Lake Bonney are < 0 °C as indicated by the top x-axes offsets. Methods for collection and analysis of these parameters are presented in Priscu *et al.* (1996).

laboratory results showing that nitrite oxidizers are more sensitive to ammonium than ammonium oxidizers to explain the observed distributions of nitrate and nitrite in Lake Vanda. Differential inhibition of these processes by high pH is presumably negligible because pH rarely exceeds 8.0 in Lake Vanda and other dry valley lakes.

The seminal report of Vincent *et al.* on Lake Vanda led to a more intensive investigation of the sources and sinks of nitrous oxide by Priscu and co-workers. Though these later studies examined a number of lakes, the most intensive investigation was on Lake Bonney (Priscu *et al.* 1993; Ward *et al.* 1993; Priscu *et al.* 1996; Voytek 1996; Ward & Priscu in press). These studies showed that the east lobe of Lake Bonney had the highest level of nitrous oxide yet reported for a natural aquatic system. The highest nitrous oxide-N concentration measured between 1990 and 1993 was 41.6 μM, >580 000% above air saturation (assuming an atmospheric mixing ratio in air of 311 ppbv in 1992). The maximum occurred just beneath the chemocline and was associated with increasing ammonium and decreasing oxygen concentration (Priscu *et al.* 1996). Apparent nitrous oxide production (ANP = $[N_2O]_{observed}-[N_2O]_{saturated}$) was positively correlated with apparent oxygen utilization (AOU = $[O_2]_{saturated}-[O_2]_{observed}$). Denitrification (measured with the acetylene block assay; Yoshinari & Knowles 1976) was not detectable in the zone of maximum nitrous oxide concentration supporting the conclusion of Vincent *et al.* (1981) for Lake Vanda that nitrification was the sole source of the gas. Recent work using polyclonal antisera prepared against two denitrifying isolates from Lake Bonney further supports the paucity of denitrification in the deep water of east lobe of Lake Bonney (Ward & Priscu in press).

The slope of a linear regression of ANP on AOU revealed that potential nitrous oxide production per unit of potential oxygen consumed in the east lobe of Lake Bonney is at least two orders of magnitude greater than that reported for the ocean (Priscu *et al.* 1996). The maximum yield ratio for nitrous oxide [ANP/(NO_2^- + NO_3^-)] in this lake was 26% (i.e. 1 atom of N appears in nitrous oxide for every 3.9 atoms appearing in oxidized N). This ratio exceeds values for other pelagic systems, being similar to that in reduced sediments. Ammonium oxidizer activity, measured as the inhibition of $^{14}CO_2$ uptake by nitrapyrin, was detectable in the upper portion of the nitrous oxide peak but not in the lower region, implying that conventional nitrification ($NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$) is not responsible for the lower portion of the peak. Priscu *et al.* suggested that nitrifier denitrification, in which nitrite is reduced by autotrophic nitrifying bacteria to nitrous oxide under low dissolved oxygen (Downes 1988), is responsible for the lower portion of the peak. However, results from nitrapyrin amended CO_2 fixation experiments (nitrifier denitrification is thought to be coupled to CO_2 fixation; Poth & Focht 1985), together with high levels of nitrate and nitrite in the region of the deep portion of the peak, did not support the presence of such a pathway (Priscu *et al.* 1996).

Priscu (1995) and Priscu *et al.* (1996) suggested that nitrous oxide and other chemical gradients in the dry valley lakes may be remnants of microbial activity that existed during an earlier period of the lake's history. Considering a molecular diffusion coefficient of 10^{-9} m^2 s^{-1} and water column depths between 20 m and 80 m (Table 1), the mixing time for the dry valley lakes ranges from about 13 000 to 203 000 y. Because these lakes have apparently existed for >8000 y (Chinn 1993), it was concluded that certain chemical gradients could represent 'fossil' records of past metabolic activity.

Despite uncertainties regarding the biochemical pathways of nitrous oxide production in Lake Bonney, extreme supersaturation within the lake coupled with elevated atmospheric nitrous oxide levels in the air directly above the lake (45% above the global average), indicates that the east lobe of Lake Bonney is a source of atmospheric nitrous oxide. Priscu *et al.* (1996) modeled the transfer of nitrous oxide through the lake ice and the seasonal moat and estimated that 4.5 g N_2O-N m^{-2} y^{-1} (absolute flux = 1.04×10^5 g N_2O-N y^{-1}) is released to the atmosphere. Of this outward flux, only abut 0.03% (areal) and 5.4% (absolute) was through the permanent ice cover despite the area of the ice being about 97% larger than that of the moat. Based on the models employed, the ice is clearly an effective barrier to gas transport between the atmosphere and liquid lake water. The areal flux to the atmosphere (4.5 g N_2O-N m^{-2} y^{-1}) is more than 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). However, given the small surface area of Lake Bonney (Table 1), the absolute flux to the atmosphere was shown to be small on a global scale.

The role of nitrifying bacteria in dissolved inorganic nitrogen transformations in the dry valley lakes was further examined using a polymerase chain reaction (PCR) assay developed for the detection of ammonium oxidizing bacteria belonging to the beta and gamma-subclasses of the Proteobacteria (Voytek & Ward 1995; Voytek *et al.* in press; Voytek 1996). This procedure showed that ammonium oxidizing bacteria were present in all lakes with members of the gamma subclass present only in the saline lakes (Voytek 1996). The studies of Voytek showed that ammonium oxidizing bacteria were most abundant at depths above the pycnocline and were usually associated with lower concentrations of ammonium and elevated concentrations of nitrate and nitrite. The distribution of ammonium oxidizing bacteria corroborates other studies concluding that the primary nitrous oxide peak observed in the lakes is produced via nitrification.

The studies referenced above represent the extent of published research on nitrous oxide in lakes of the McMurdo Dry Valleys as of this writing. Most of this research focused on Lake Vanda and Lake Bonney. The remainder of this chapter will focus on nitrous oxide concentrations and biogeochemical relationships measured during the 1993–1994 and 1994–1995 austral winter, spring and summer (August–December) in seven major lakes in the McMurdo Dry Valley ecosystem.

Recent data from the dry valley lakes

The lakes of the McMurdo Dry Valleys encompass a wide range of physical and chemical conditions (Fig. 2). Temperatures range from –4.6 °C near the bottom of the west lobe of Lake Bonney to >20 °C in the deep water of Lake Vanda. Mid- to deep-water temperature maxima are associated with regions of high salinity. Salinities range from freshwater just beneath the ice covers to brine (>150 PSU) in the deep waters of Lakes Bonney and Vanda. Lakes Hoare and Miers have relatively freshwater throughout the water column (salinities < 1 PSU). Dissolved oxygen concentration decreases with depth in all lakes. Oxygen levels in the near-surface waters range from 400 to 1500 μM and reach 300% of air saturation in certain lakes (Fig. 3). A study of oxygen dynamics in Lake Hoare concluded that supersaturation results primarily from gas transferred to the lakewater in glacial melt followed by gas occlusion during the formation of new ice; a small fraction (~11%) comes from biological production in excess of consumption (Craig *et al.* 1992). The bottom waters of Lakes Joyce, Fryxell and Vanda are highly anoxic and contain noticeable levels of hydrogen sulfide. Negative redox potentials occur in these anoxic waters reaching a minimum of –46 mV in Lake Fryxell (Fig. 3; Downes & Priscu in press). Oxygen is also depleted below the chemocline in both lobes of Lake Bonney, though the redox remains poised near 200 mV in the west lobe and 500 mV in the east lobe.

Dissolved inorganic nitrogen (ammonium + nitrite + nitrate) is usually < 7 μM in the surface water of all lakes except Joyce where surface levels exceed 50 μM (Fig. 2). Ammonium concentration increases with depth in all lakes with strong chemoclines reaching almost 2 000 μM in Lake Vanda. Nitrite is low (<1 μM) in most lakes but shows peaks at 17 m and 70 m in the west lobe of Lake Bonney and at 70 m in Lake Vanda. These nitrite peaks are located several meters beneath peaks in nitrate and nitrous oxide, a trend similar to that observed by Vincent *et al.* (1981). Nitrite increases beneath the chemocline in the east lobe of Lake Bonney reaching 45 μM at 30 m, just below the nitrous oxide maximum.

Nitrate levels beneath the chemocline show evidence of denitrification in lakes with highly reduced (low oxygen and redox) bottom waters (i.e. Lakes Joyce, Fryxell and Vanda). Moderately reducing oxygen and redox conditions also support denitrification below the chemocline in the west lobe of Lake Bonney (discussed in detail later). No bulk denitrification occurs below the chemocline in the east lobe of Lake Bonney, where low oxygen concentration and high redox potential exists (Fig. 2, Priscu *et al.* 1996), resulting in large pools of nitrate and nitrite.

Nitrous oxide is present as mid-water maxima in all lakes except Fryxell (Fig. 2). Peak concentrations exceed (>500%) air saturation in all lakes. The highest values were 703 000% and 148 000% above air saturation for the maxima in Lakes Bonney and Vanda, respectively. These saturation values are higher than those previously reported for the nitrous oxide maxima in these lakes (Priscu *et al.* 1996; Vincent *et al.* 1981). Differences from previous reports may have resulted from variation in sample storage, calibration methods, errors involved with collecting samples in regions of large gradients, or from biological production. Experiments on water from the deep maximum in the east lobe of Lake Bonney showed that nitrous oxide levels remained constant over 10 days in sealed vials (Priscu *et al.* 1996; Priscu unpublished) implying extremely low net production rates. I believe that the differences result from one or more of the variables discussed above rather than biological activity.

Nitrous oxide maxima were often associated with regions of decreasing dissolved oxygen (Fig. 3). This relationship is shown most clearly in profiles of apparent oxygen utilization (AOU) and apparent nitrous oxide production (ANP) (Fig. 3). Note that only positive AOU and ANP values are semantically meaningful terms to define 'utilization' of oxygen and 'production' of nitrous oxide (i.e., AOU = $[O_2]_{saturated}-[O_2]_{observed}$; ANP = $[N_2O]_{observed}-[N_2O]_{saturated}$). For example, Lake Hoare never shows net consumption of oxygen (AOU is negative throughout the water column). Likewise, the negative ANP value at the deepest point in Lake Fryxell does not represent nitrous oxide production. Negative values of AOU and ANP are presented along with positive values in Fig. 3 to show general tendencies through the water column. It should also be noted that although ANP and AOU imply activity, they are both state variables that are the net result of complex gain and loss processes.

It is possible that profiles of certain gases may have arisen by abiotic processes during historical dry down cycles (Lyons *et al.* submitted) or gas introduction via glacial melt (Craig *et al.* 1992). Concentration of gases via physical means should have the same effect on all gases, hence the ratio of a biological conservative gas (such as argon) with nitrous oxide will depict zones of sources and sinks of nitrous oxide. Profiles of nitrous oxide to argon ratios (Fig. 4) are similar to profiles of nitrous oxide concentration, percent air saturation, and ANP, supporting a biological origin for this gas.

Nitrous oxide relationships among lakes

General features about nitrous oxide dynamics in the McMurdo dry valley lakes were determined by examining

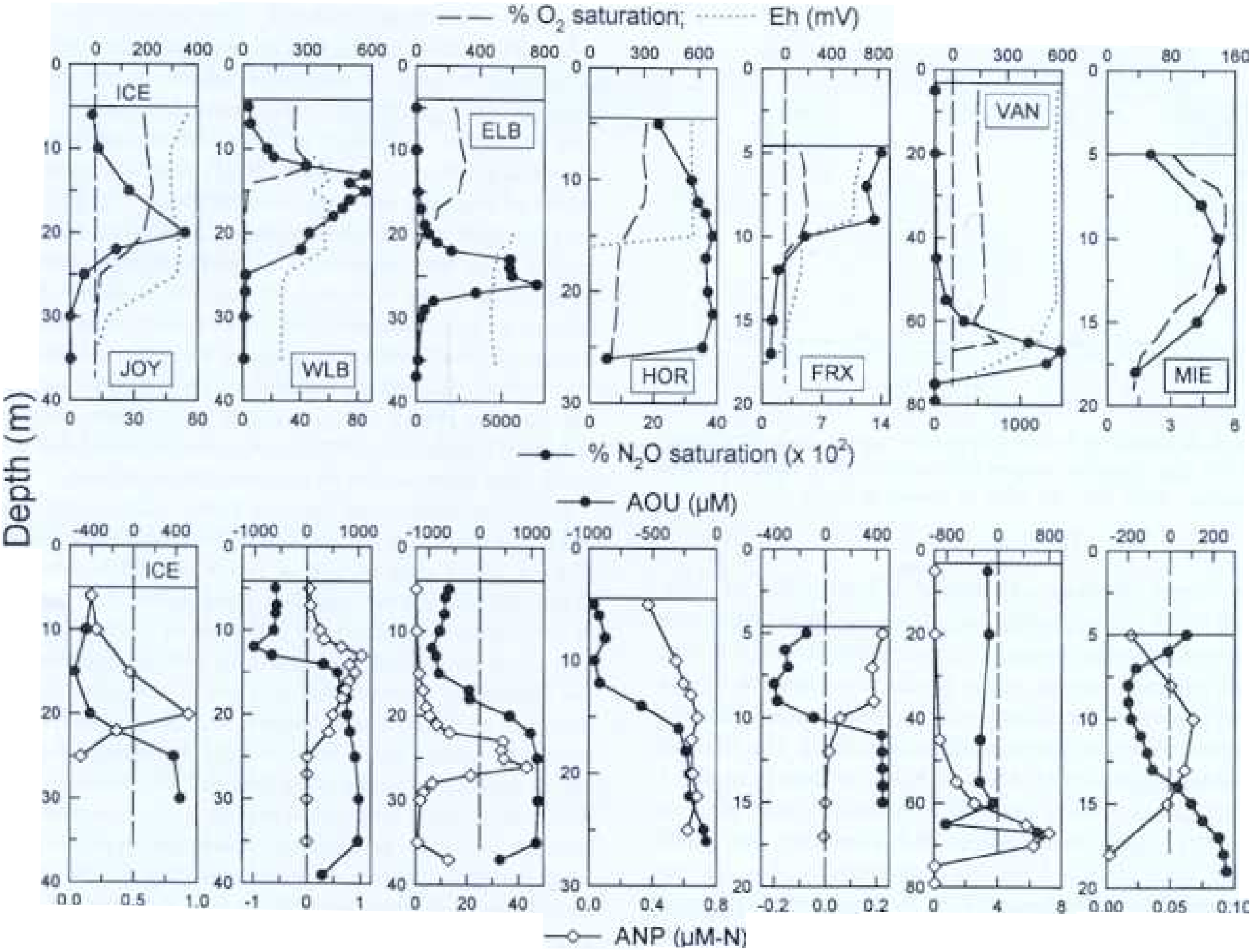

Fig. 3 Vertical profiles of oxygen and nitrous oxide saturation, redox potential (Eh), apparent oxygen utilization (AOU) and apparent nitrous oxide production (ANP). AOU = $[O_2]_{saturated}-[O_2]_{observed}$; ANP = $[N_2O]_{observed}-[N_2O]_{saturated}$. Details for calculation of oxygen and nitrous oxide saturation are given by Priscu *et al.* (1996); redox methods are presented in Downes & Priscu in press). Vertical dashed lines represent zero on the x-axes. Lake identification as in Fig. 2 Eh was not measured in Lake Miers. Note that the axis values for percent nitrous oxide saturation must be multiplied by 100.

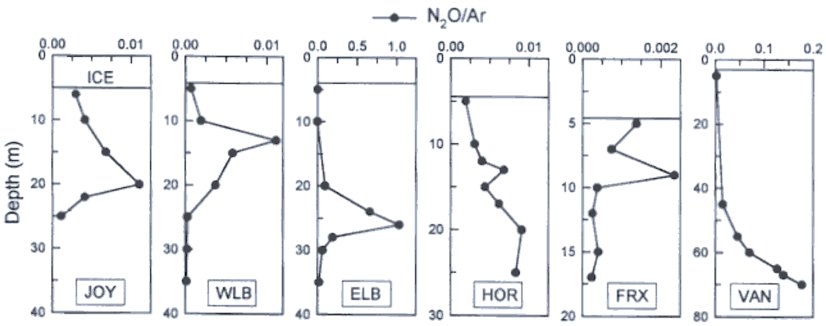

Fig. 4 Profiles of nitrous oxide/argon ratios. Argon was measured with a Hewlett-Packard 5890-II gas chromatograph fitted thermal conductivity detector and a 30 m (I.D. = 0.55 mm) DB-Mol column; Helium was the carrier gas (5 ml min^{-1}). The oven was held at −50 °C for 1 min then ramped (20 °C min^{-1}) to 220 °C for 1 min. Injector and detector temperatures were 250 °C and 300 °C, respectively. The instrument was calibrated using injections of laboratory air and noble gas standard. Collection of argon samples followed the same protocol as for nitrous oxide; 20 ml sample in a 40 ml Helium purged serum vial (see Priscu *et al.* 1996). Calculations of argon concentration were based on the solubility data of Weiss (1970). Nitrous oxide methodology is presented elsewhere (Priscu & Downes 1985; Priscu *et al.* 1996). Lake identification as in Fig. 2 Argon was not measured in Lake Miers.

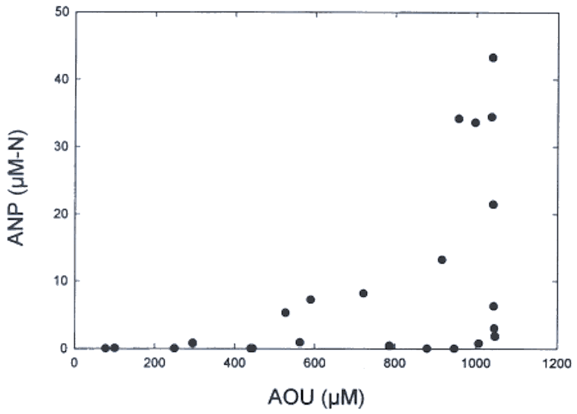

Fig. 5 Relationship between apparent nitrous oxide production (ANP) and apparent oxygen utilization (AOU). Data represent positive values from all lakes as shown in Fig. 3

data from all lakes collectively. A scatter plot of ANP and AOU, incorporating data from all lakes within the zone of apparent oxygen utilization (positive AOU only) and apparent nitrous oxide production (positive values only), reveals increasing nitrous oxide production in regions of net oxygen consumption (Fig. 5). The slope of a linear regression of ANP on AOU for data from Fig. 5 is 0.022 µM N_2O-N (µM O_2)$^{-1}$ (different from zero at $p<0.01$). Linear relationships between ANP and AOU were first observed in the subsurface waters of the Atlantic Ocean (Yoshinari 1976), leading to the suggestion that nitrous oxide is produced in association with ammonium oxidation by nitrifying bacteria (an oxygen consuming process). Subsequent studies verified this contention using data from other regions of the sea (e.g. Elkins *et al.* 1978; Butler *et al.* 1989; Law & Owens 1990), estimates of global oceanic production (Nevison *et al.* 1995), cultures of nitrifying bacteria (Goreau *et al.* 1980) and isotopic ratios (Yoshida *et al.* 1984; Yoshida 1988). The slope of ANP on AOU for the dry valley lakes is almost two orders of magnitude greater than the oceanic average (~2.5×10^{-4} µM N_2O-N (µM O_2)$^{-1}$; Nevison *et al.* 1995) indicating that the Antarctic lakes have a considerably higher potential for nitrous oxide production per unit oxygen consumed than the ocean.

The positive relationship shown in Fig. 5 indicates that nitrification is the primary source of nitrous oxide in the dry valley lakes. Given this inference, yield ratios for nitrous oxide can be estimated from the relationship between ANP and oxidized nitrogen concentration (e.g. Kaplan & Wofsy 1985). This relationship provides an estimate of the proportion of nitrous oxide produced by ammonium oxidizing bacteria per unit of ammonium oxidized. The yield ratio for the dry valley lakes estimated from a regression of ANP on ambient nitrate + nitrite is 4.2% (slope = 0.042; $p<0.01$) (Fig. 6). A majority of the data pairs occur at oxidized nitrogen concentrations below 50 µM (inset in Fig. 6). The yield ratio for the lower oxidized nitrogen concentrations shown in the inset is 2.9% (slope = 0.029; $p<0.01$). These percentages infer that 1 atom of N appears in nitrous oxide for every 24 atoms appearing in oxidized N (1 atom for every 35 atoms at oxidized nitrogen concentrations <50 µM). The average yield ratio for the dry valley lakes is considerably higher than that reported for pelagic marine systems (range 0.05–0.9%; reviewed by Kaplan & Wofsy 1985) being similar to more reduced systems such as sediments (Jørgenson *et al.* 1984). The average yield for the lakes is within that reported for liquid cultures of marine nitrifying bacteria which reaches about 10% at low oxygen tension (Goreau *et al.* 1980). Goreau *et al.* showed that the yield ratio increased as oxygen tension decreased.

Collective data from the dry valley lakes show that ANP was highest at oxygen levels between 25 and 250 µM (Fig. 7a). ANP also peaked at redox potentials between about 350 and 550 mV (Fig. 7b). Presumably, the majority of ammonium oxidized by nitrifiers at higher oxygen and Eh is converted completely to nitrate as shown in the laboratory experiments of Goreau *et al.* (1980). The decrease in ANP at low oxygen and Eh is presumably caused by nitrous oxide utilization by denitrifiers. Experiments conducted in the west lobe of Lake Bonney show that experimental addition of nitrous oxide to water from beneath the water column maximum was depleted over time, presumably from denitrification (Fig. 8). The slopes for nitrous oxide decrease at 25 m and 30 m were –0.0086 and –0.0094 µM-N h^{-1}, respectively; both significantly different from zero ($p<0.05$). The addition of 10 µM acetate did not alter significantly the depletion rate at 25 m. Acetylene block experiments corroborate the presence of denitrification below the chemocline in the west lobe of Lake Bonney (Fig. 9 a,b). Rates of nitrous oxide accumulation in the presence of ~20% acetylene, an inhibitor of nitrous oxide reductase (Yoshinari & Knowles 1976), were –0.002, 0.007, 0.007 and 0.001 µM-N h^{-1} at 13, 15, 20 and 25 m, respectively. All of these rates are positive and significantly different from zero ($p<0.001$) except that at 13 m ($p=0.21$), indicating that denitrification occurs only below 13 m. The rate of denitrification at 25 m was stimulated significantly by the addition of 25 µM nitrate. Stimulation of denitrification, in concert with the paucity of nitrate at 25 m in the lake (Fig. 2), indicates that denitrification is limited by available nitrate in the bottom water of the west lobe of Lake Bonney. Interestingly, the acetylene block experiment shows potential denitrification at 15 m, coincident with the lower zone of the nitrous oxide maxima.

Numerical analysis of nitrous oxide dynamics

Most of the nitrous oxide relationships presented thus far in this section are based upon static variables (e.g.

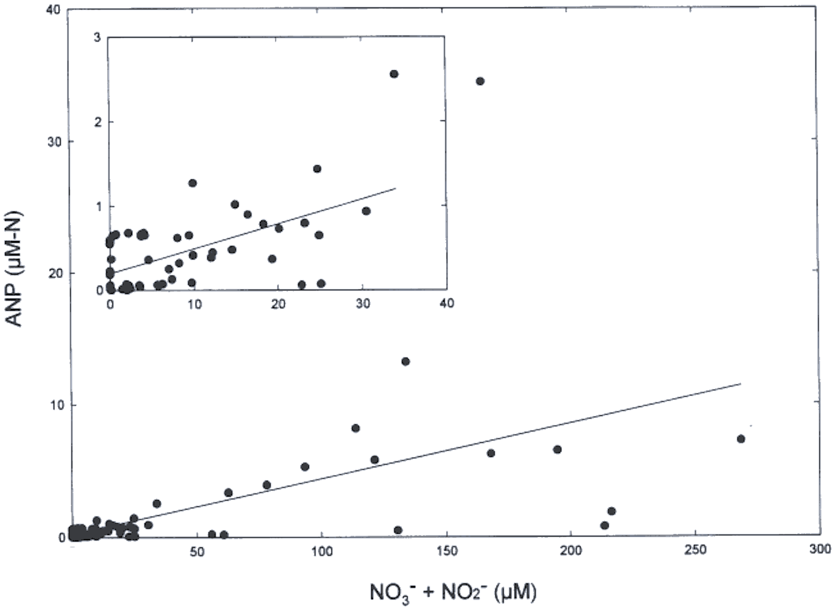

Fig. 6 Relationship between apparent nitrous oxide production (ANP) and oxidized inorganic nitrogen (NO_2^- + NO_3^-). Lines represent linear least-squares fits through the data. Data represent positive values from all lakes. The inset shows the relationship at a smaller scale.

bulk concentrations, ANP, AOU). To better understand nitrous oxide dynamics in the dry valley lakes, a 1-D diffusion model was used to estimate rates of generation and loss in the liquid water column. The model assumes that the nitrous oxide concentration is in a steady state. Maximum nitrous oxide concentration in the east lobe of Lake Bonney between 1991 and 1995 varied by ~ 5% and showed no clear temporal trend (Priscu, unpubl. data) supporting the assumption of steady-state, at least over this period. The model is of the form

$$\frac{\partial C}{\partial t} = \frac{1}{A}\frac{\partial}{\partial z}\left(DA\frac{\partial C}{\partial z}\right) + R \,. \tag{1}$$

Assuming steady-state and simplifying the model can be rewritten as

$$R = -\frac{1}{A}\frac{\mathrm{d}}{\mathrm{d}z}\left(DA\frac{\mathrm{d}C}{\mathrm{d}z}\right) \tag{2}$$

where C = nitrous oxide concentration, t = time, z = depth (measured positive downward from the lake surface), A = lake area enclosed within a specified z-depth contour (1 m), D is the molecular diffusion coefficient for nitrous oxide (2.1×10^{-9} m^2 s^{-1}), and R is a residual term representing changes in concentration owing to reactions other than diffusion within the water column. For the purpose of this analysis, a negative R-value represents consumption of nitrous oxide by denitrification whereas a positive R-value represents production of nitrous oxide primarily by nitrification. Advective inputs are low in these lakes and should not influence the R-term. The choice of molecular diffusion is based on numerous CTD casts in these lakes (particularly the east lobe of Lake Bonney) which revealed no turbulence at cm scales (Spigel *et al.* 1990, 1991; Spigel & Priscu in press), the small fraction of the lake surface exposed to the energy of the wind, and the relatively low and seasonal advective stream input. Details of this model are presented elsewhere (Priscu *et al.* 1986).

Turnover rates were obtained by dividing the R-values by the corresponding concentration of nitrous oxide for each layer; turnover times represent the inverse of turnover rates. Positive turnover times indicate that nitrous oxide is being generated, negative values represent losses. It should be noted that some R-values are based on small differences between large values. Hence, large errors may be associated with certain peaks.

Vertical profiles of R-values are presented in Fig. 10. Major sources of nitrous oxide correlate with peak concentrations, as would be expected from the mechanics and assumptions of the model. The utility of this model is that it provides estimates of the rate of nitrous oxide production and consumption. Nitrous oxide is most dynamic in lakes with strong oxygen, redox and dissolved inorganic nitrogen gradients; the highest rates occur in the zones where these gradients are steepest. The seven study lakes can be divided into three groups based on their maximum rates of nitrous oxide production. Production rates are in the range 0.002–0.006 nM-N d^{-1} in Lakes Hoare and Miers; 0.02–0.1 nM-N d^{-1} in Lakes Joyce, Bonney (west lobe), Fryxell and Vanda; and >4 nM-N d^{-1} for the east lobe of Lake Bonney.

Estimated turnover time of nitrous oxide varies down the water column and shows no clear correlation with R-values (Fig. 10). Average water column turnover time for production (positive values) ranges from 592 y in the west lobe of Lake Bonney to 5901 y in Lake Vanda. Values

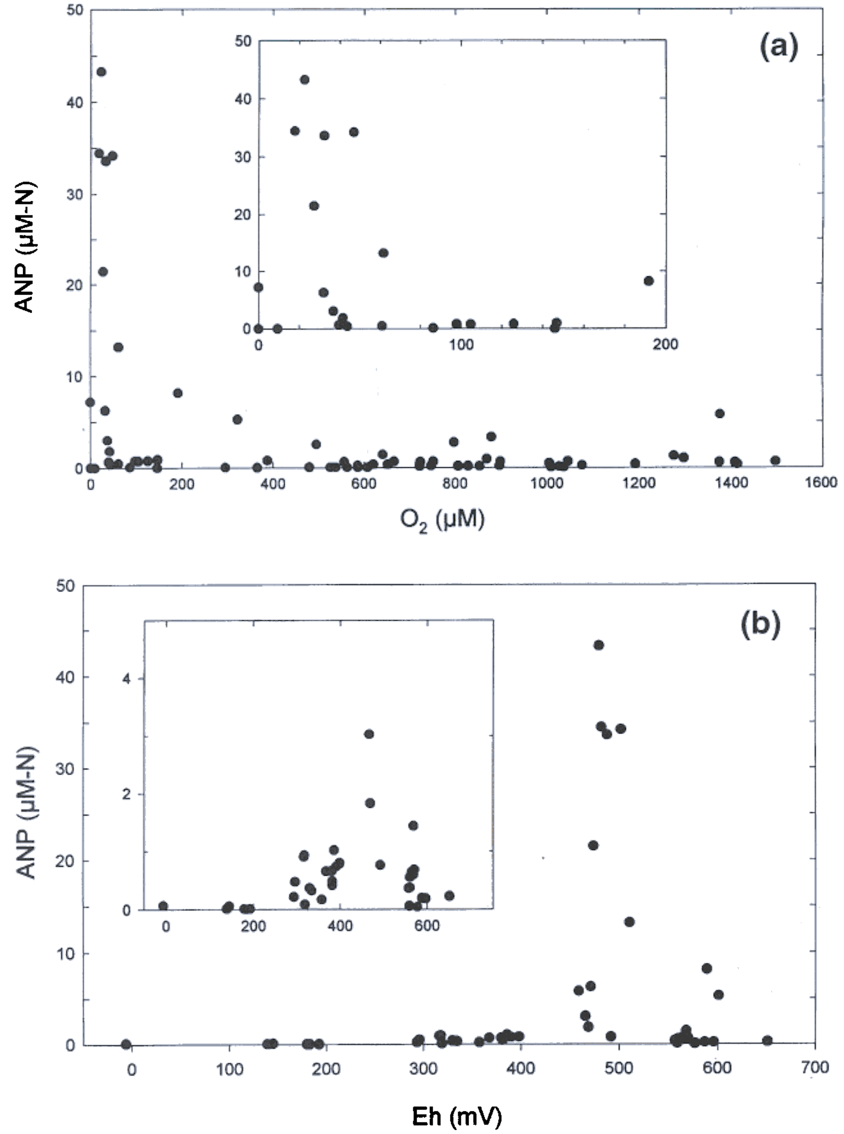

Fig. 7 Relationship between dissolved oxygen concentration and apparent nitrous oxide production (ANP, positive values only) (a), and between ANP and redox potential (b). The data represent all lakes. The insets show the relationships on a smaller scale.

> 35 000 y were computed at certain depths in Lakes Vanda and Miers. Long turnover times, which reflect low production and consumption rates relative to concentration, are within the range for the mixing time of the lakes. Owing to diffusion at the molecular level, and consequent mixing times on the order of tens of thousands of years, any nitrous oxide produced has the potential to accumulate and form distinct gradients. Hence, these poorly-ventilated, low-dispersive systems can display large concentration gradients despite low production and consumption rates.

Atmospheric sources and sinks

Concentration of nitrous oxide in the water just beneath the ice covers of all lakes is always supersaturated with respect to the mixing ratio in air (Fig. 2) making the lakes potential sources of atmospheric nitrous oxide. A previous study on gas diffusion in Lake Bonney showed that the permanent ice cover represents a highly effective barrier to atmospheric ventilation of nitrous oxide (Priscu *et al.* 1996). Specifically, the study concluded that only about 0.03% of the areally based transport was through the ice cover, albeit the ice represents more than 97% of the lake's surfaces. Considering the low permeability of the ice, fluxes through the seasonal moat alone can be used to estimate of atmospheric input.

Numerous models exist to compute air-water transfer of gases (e.g. Broeker & Peng 1974; Liss & Merlivat 1986; Erickson 1993; Wanninkhof *et al.* 1996). 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 1988). Nevison *et al.* (1995) computed global oceanic nitrous oxide fluxes

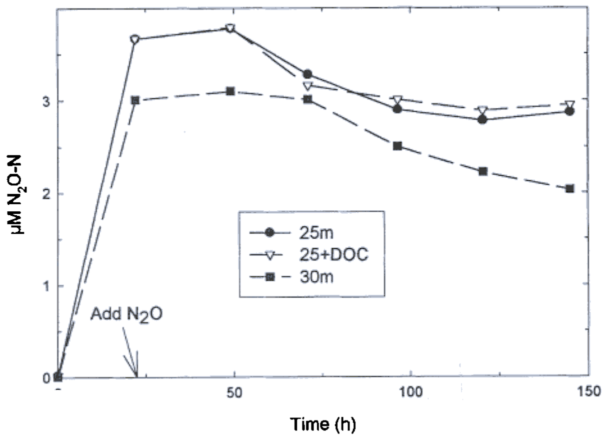

Fig. 8 Time-course changes in nitrous oxide concentration for 25 m and 30 m samples from the west lobe of Lake Bonney. Samples were incubated under *in situ* light and temperature in duplicate 100 ml air-tight syringes. Nitrous oxide-N (~ 3 μM) was added to each syringe 24 h into the incubation (denoted by arrow). One of the 25 m samples was amended with 10 μM acetate (+DOC). Each point represents the mean from replicate syringes. Ambient (time zero) nitrous oxide nitrogen concentration at 25 m and 30 m was 0.021 and 0.009 μM, respectively.

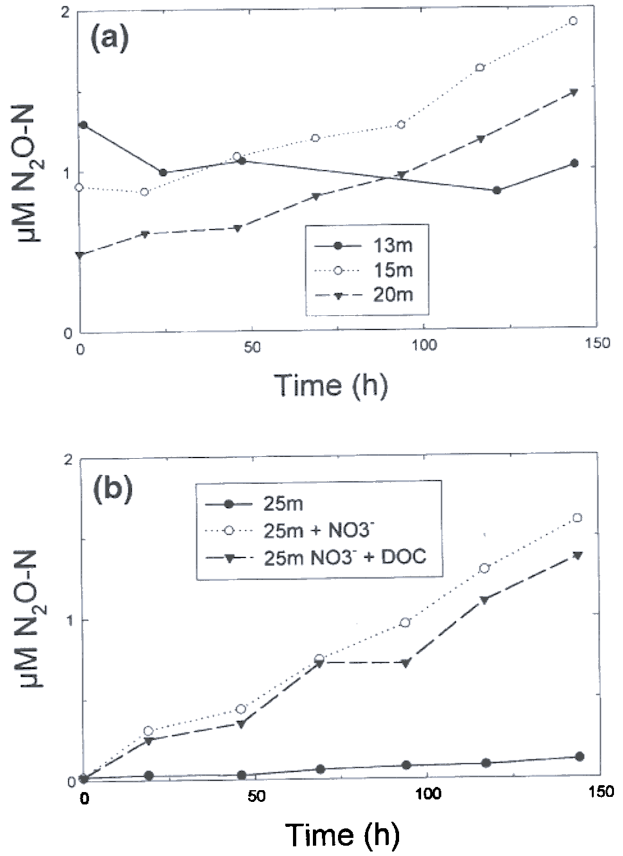

Fig. 9 Nitrous oxide production during acetylene block experiments for 13, 15, 20, and 25 m samples from the west lobe of Lake Bonney. The 25 m sample was amended with 25 μM NO_3^- (+NO_3^-) and 25 μM NO_3^- + 10 μM acetate (NO_3^- +DOC) at time zero. Each point represents the mean from replicate samples. Experimental details are presented in Priscu *et al.* (1996).

using several of these models and reported a propagated uncertainty of about 70%. An estimate of the outward flux of nitrous oxide across the air–water interface for the moats of the dry valley lakes was made using transfer velocity relationships and Schmidt number scaling (Liss & Merlivat 1986; Erickson 1993; Nevison *et al.* 1995) as outlined by Priscu *et al.* (1996). Assumptions include that (i) the peripheral summer moat occupies 3% of each of the lakes surface area for 10 weeks per year (Wharton *et al.* 1986; J.C. Priscu, personal observation), (ii) the average wind speed in the dry valleys during the moat period is 7 m s^{-1} (Clow *et al.* 1988), (iii) the moat water maintains a temperature of 1 °C, and (iv) the atmospheric mixing ratio in 1993 was 313 ppbv (Prinn *et al.* 1990; Watson *et al.* 1990). These calculations further assume that the nitrous oxide concentration measured just beneath the ice is in equilibrium with the moat water, and the nitrous oxide gradient between moat water and the atmosphere is maintained throughout the moat period.

The annual estimated areal (m^{-2}) flux of nitrous oxide from the moats to the atmosphere ranges from 0.01 gN m^{-2} y^{-1} in Lake Miers to 2.48 gN m^{-2} y^{-1} in Lake Hoare; average for all lakes = 0.88 gN m^{-2} y^{-1} (Table 2). Areal flux from Lakes Hoare, Fryxell and Bonney (east lobe) accounts for more than 80% of the combined areal flux. Fluxes, corrected for moat area and duration, ranged from 57 gN y^{-1} for Lake Miers to 58 496 gN y^{-1} for Lake Fryxell (average for all lakes = 16 420 gN y^{-1}). Again Lakes Hoare, Fryxell and Bonney account for a majority (89%) of the total absolute flux to the atmosphere. The combined flux to the atmosphere for all lakes is 6.17 gN m^{-2} y^{-1} (absolute flux = 114 937 gN y^{-1}).

The areal flux from the dry valley lakes is several hundred times greater than that reported for the ocean (0.01–0.03 gN m^{-2} y^{-1}; Cohen & Gordon 1979; Nevison *et al.* 1995) and almost 100 times greater than estuarine sediments (0.01–0.14 gN m^{-2} y^{-1}; Middelburg *et al.* 1995). Despite the high nitrous oxide flux per unit area, the relatively small combined surface area of the moats (~0.7 km^2) and their short duration yields an absolute flux of only about 1×10^5 gN y^{-1}. This absolute flux is well below that for other global sources such as nylon production (2×10^9 gN y^{-1}; Thiemens & Trogler 1991), global biomass burning ($0.1–0.3 \times 10^{12}$ gN y^{-1}; Crutzen & Andreae 1990), human waste ($0.2–1.6 \times 10^{12}$ gN y^{-1}; Prinn *et al.* 1990) and global oceanic production ($4–11 \times 10^{12}$ gN y^{-1}; Elkins *et al.* 1978; Nevison *et al.* 1995) making fluxes from these lakes only a minute fraction of total atmospheric sources

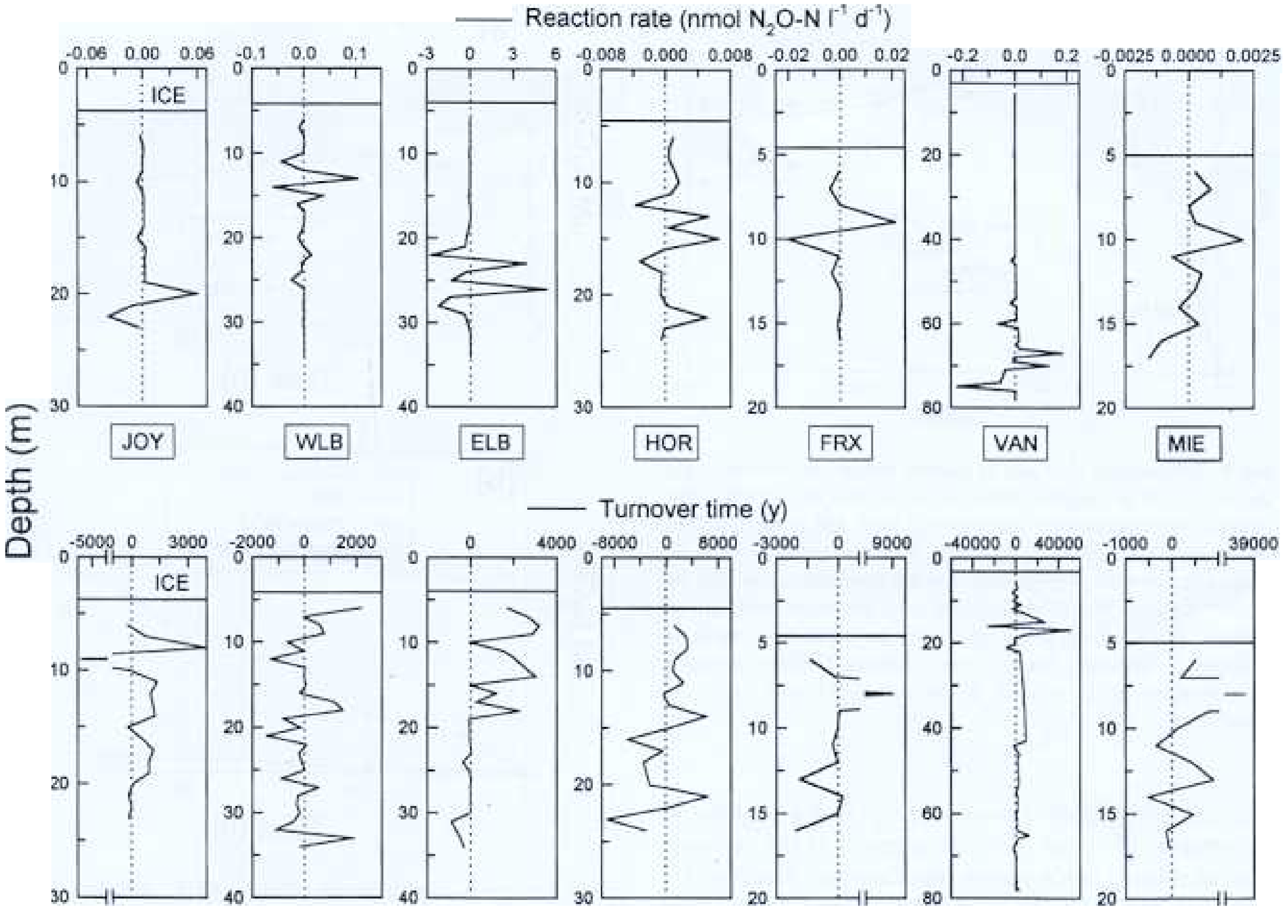

Fig. 10 Vertical profiles of reaction rates (R-values) and turnover times for nitrous oxide computed from a 1-D diffusion model. Positive and negative values represent gains and losses for 1 m thick layers of water. Vertical dashed lines represent zero on the *x*-axes. Lake identification is as in Fig. 2

Table 2 Estimates of atmospheric nitrous oxide flux from moat water of seven Antarctic lakes.

	Flux	
Lake	gN m^{-2} y^{-1}	gN y^{-1}
Joyce	1.08	4902
WL Bonney	0.22	1611
EL Bonney	0.77	15476
Hoare	2.48	27793
Fryxell	1.43	58496
Vanda	0.17	6602
Miers	0.01	57
Total	6.17	114937

of nitrous oxide (0.01–2.2 × 10^{12} gN y^{-1}; Watson *et al.* 1990).

Conclusions

The lakes of the McMurdo Dry Valleys represent small, intense sources of nitrous oxide. However, owing to their small combined surface area, they supply only a very small fraction of the global input. The unique habitat caused by permanent ice cover provides systems ideally suited to study environmental factors influencing biogeochemical transformations of nitrous oxide in aquatic systems. The low mixing rates and large gradients found in many of the Antarctic lakes makes them conceptually similar to many soil systems (e.g. Grant *et al.* 1993). Results from these pristine lakes could help resolve some of the uncertainty that exists regarding microbial production and consumption of nitrous oxide and overall global balance of this gas. Given the global concern for Antarctic conservation, these systems can be expected to remain unimpacted by human exploitation. Hence, Antarctic systems serve as globally unique sites for long-term studies of biogeochemical transformations of nitrous oxide and other globally important compounds.

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