

SEDIMENT NITRIFICATION, DENITRIFICATION, AND
NITROUS OXIDE PRODUCTION IN AN ARCTIC LAKE

A
THESIS

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ABSTRACT

In order to examine the role of the sediment in the nitrogen budget of an arctic lake; nitrification, denitrification, and N_2O production were measured in Toolik Lake sediments using ^{15}N -labeling techniques and a C_2H_2 blockage technique. The sediment depth distribution of inorganic nitrogen concentrations, pH, and Eh were also determined. Inorganic nitrogen was found in low concentrations, NH_4^+ being the predominant nitrogen species. The sediments ranged from 435-2910% saturated with N_2O . Eh and pH measurements showed an oxidized surface sediment layer with deeper sediments becoming more reduced. The average estimated nitrification rate ($49 \text{ ng N}\cdot\text{cm}^{-3}\cdot\text{d}^{-1}$) was similar to the average denitrification rate ($44 \text{ ng N}\cdot\text{cm}^{-3}\cdot\text{d}^{-1}$). *In situ* N_2O production, from both denitrification and nitrification, ranged from 0-25 $\text{ng N}\cdot\text{cm}^{-3}\cdot\text{d}^{-1}$. Denitrification was stimulated with a large nitrate addition but not dramatically, suggesting other factors may be limiting.

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INTRODUCTION

The biological success of an organism depends, in part, on the supply of nutrients. Nitrogen, one of the principle constituents of cellular material, is necessary for protein synthesis. It is a major requirement of both autotrophic and heterotrophic organisms. Along with phosphorus, nitrogen is often reported as becoming limiting to primary production. The major pathways that regulate nitrogen cycling are organic matter mineralization, nitrification, denitrification, and nitrogen fixation. These microbial processes control nitrogen availability through chemical transformation of one form of nitrogen to another.

Arctic lakes are oligotrophic systems where primary production is low in response to the low nutrient supply (Hobbie, 1973). Lake productivity can be influenced by the sediment, which acts as a source or a sink for nutrients. Although it has been found that nitrogen is generally not limiting in arctic freshwater systems (Barsdate and Alexander, 1975), the supply of nitrogen in the sediment may contribute to nitrogen gain or loss in the water column. Studies on ponds near Barrow, Alaska (Tundra Biome, U.S. International Biological Program) indicate that the sediment plays a dominant role in supplying ammonium to the water column (Prentki *et al.*, 1980). After the conclusion of the Tundra Biome pond work, the scientists involved decided that the next step to understanding tundra freshwater ecosystems would be to study the processes regulating a deeper lake where the sediment processes would not be so completely dominant in controlling

the ecosystem. Toolik Lake, a deep arctic lake, was originally chosen as a study site for the aquatic portion of the NSF Division of Polar Programs Project RATE (Research on Arctic Tundra Environments) in 1975, which continued through 1977. The sequel to RATE was ALPS (Arctic Lake Process Studies), which began in 1978 and continued through 1980.

The general objective of ALPS was to determine the various factors that control the productivity and populations of an arctic lake. The Nitrogen Cycling component of Project ALPS, only one of seven components, was further broken down into water column and sediment studies. In general, the processes controlling whole lake ecosystems are poorly known, and an integrated project such as ALPS will provide a more complete picture of a whole lake system than single studies done on several different lakes.

The primary goal of this study, a part of the Nitrogen Cycling component of Project ALPS at Toolik Lake, was to attempt to measure rates of sediment nitrification, denitrification, and nitrous oxide production. The research was designed to determine the depth distribution of inorganic nitrogen concentrations, pH, and Eh; and to measure rates of nitrification, denitrification, and nitrous oxide production. A $^{15}\text{N-NO}_3^-$ dilution technique (Koike and Hattori, 1978) and a $^{15}\text{N-NH}_4^+$ tracer technique were used to measure rates of nitrification. Denitrification and nitrous oxide production were measured using the acetylene blockage technique (Yoshinari *et al.*, 1977).

Sediment N-Cycle

Lake sediments usually have a surface oxidized layer and become more reduced with sediment depth. This affects the microbial processes that can occur in a particular layer. The most abundant and stable form of nitrogen is N_2 , but its utilization is restricted to a relatively few organisms that can fix nitrogen. N-fixation is essential in balancing the nitrogen loss through denitrification and can occur in both oxic and anoxic zones. Ammonium is supplied to the sediments through organic matter mineralization that can occur in both oxic and anoxic zones. The ammonium diffuses up into the water column or farther down into the sediments depending upon the NH_4^+ gradients present. In the oxic layer, the ammonium can become nitrified to nitrite or nitrate. This nitrite and nitrate can diffuse upwards into the water column and serve as an additional nutrient source for autotrophs and can also diffuse down to a more reduced layer where it could provide the necessary substrate for denitrification.

The process of nitrification and denitrification also produces nitrous oxide (Yoshida and Alexander, 1970; Ritchie and Nicholas, 1972; CAST, 1976; Bremner and Blackmer, 1978; Walter *et al.*, 1979; and Blackmer *et al.*, 1980). Little is known about the environmental and physiological factors that regulate nitrous oxide production during denitrification and nitrification.

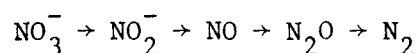
Only recently has N_2O production been studied quantitatively, and relatively few measurements of rates of its production and consumption

have been published. N_2O is a natural constituent of the atmosphere with a concentration ranging from 200-500 ppb. Because of nitrous oxide's destructive effects on the earth's ozone layer, more research on the factors regulating global N_2O cycling has been initiated. The earth's ozone layer protects the lower atmosphere from the harmful effects of ultraviolet light, preventing skin cancer and global warming. In the past decade there has been a substantial increase in the use of synthetically fixed nitrogen fertilizers which increase crop production but also affect other ecosystems. This increased use of fertilizers tends to increase the rates of nitrification and denitrification, thus affecting the rate of N_2O production. Wang *et al.* (1976) estimated that a doubling of the concentration of atmospheric nitrous oxide could raise the earth's surface temperature by $0.7^\circ C$.

Nitrification (ammonium oxidation) is the process by which chemototrophs generate energy. *Nitrosomonas* and *Nitrobacter* are the primary nitrifiers. *Nitrosomonas* oxidizes ammonium to nitrite, while *Nitrobacter* oxidizes nitrite to nitrate. Yoshida and Alexander (1970) observed N_2O evolution from autotrophic nitrifiers in conjunction with nitrification and found it to be enhanced by increasing nitrate concentrations, available phosphorus, and pH, or by lowering the temperature. Using ^{15}N -tracer studies, Ritchie and Nicholas (1972) found *Nitrosomonas europaea* could utilize nitrite as a terminal electron acceptor when the supply of oxygen was not adequate, thereby reducing nitrite to N_2O . *Nitrobacter* did not produce N_2O . With added

$(\text{NH}_4)_2\text{SO}_4$, N_2O production initially increased then decreased with pure cultures of *N. europaea*. This nitrite reductase system is thought to be a mechanism for removing nitrite accumulated intracellularly during ammonium oxidation. It could serve as an alternative to aerobic respiration under anaerobic conditions (Blackmer *et al.*, 1980). The latter may give the nitrifying bacteria an added survival benefit.

Denitrification (dissimilatory nitrate reduction) is a form of anaerobic respiration. Denitrification is not restricted to the deeper, more reduced zones of the sediment, but can also occur in the anoxic microzones within the oxic surface layer. Most denitrifiers are facultative anaerobes which prefer to use oxygen for respiration. During denitrification, nitrite, nitrate, or nitrous oxide are used as terminal electron acceptors and subsequently are reduced to nitrous oxide or dinitrogen. Dinitrogen is the major endproduct of denitrification, while nitrous oxide is usually a minor endproduct. The $\text{N}_2:\text{N}_2\text{O}$ endproduct ratio varies considerably, depending on the environmental conditions present. It is generally agreed that nitrate respiration follows the sequence:



Rolston *et al.* (1978) observed a small $\text{N}_2:\text{N}_2\text{O}$ ratio (5) early in denitrification and becoming much larger as denitrification proceeded. CAST (1976) reported a ratio of approximately 16 but concluded that N_2O production varied widely. Soil studies by Smith *et al.*

(1978), Blackmer *et al.* (1980), and Firestone *et al.* (1980) showed the $N_2:N_2O$ ratio to be strongly influenced by the physical environment and the physiological characteristics of the microbial community. Greater N_2O production was observed with increased concentrations of nitrate or nitrite, low pH, aerated soils, and low temperatures. A decrease and/or a reduction of N_2O was observed when levels of nitrate, nitrite, or oxygen were diminished.

Description of Study Area

Toolik is a large, deep, oligotrophic lake located on Alaska's North Slope at $68^{\circ} 38'N$ and $149^{\circ} 36'W$. It lies in the foothills north of the Brooks Range within the Trans-Alaskan Pipeline corridor. Toolik is a kettle lake with five basins separated by rocky shoals. It has an area of 3.06 km^2 and is located at an elevation of 720 m. The average depth is 7.45 m, and the maximum depth is 25.3 m. There is one inlet and one outlet, but during spring runoff as many as five inlets were observed. Unlike typical arctic lakes, Toolik Lake stratifies during most summer seasons. Ice covers the lake from October to June.

Nitella, a macroalga (phylum Chlorophyta), forms meadows on the sediment between 2-7 m depth. The surface sediments, 0-12 cm, are quite flocculent, being an average of 90% water. Most cores that were taken had a red iron oxide layer and a crusty black manganese oxide layer. During the summer, sediment temperature ranged from a low of $4^{\circ}C$ in May to a high of $7^{\circ}C$ in August at 2 to 10 m in the study area.

Most sediment cores were taken in the mouth of Camp Bay (Figure 1) in 10 m of water. In August 1980, a sediment transect of 2 m, 5 m, and 10 m was taken in the bay. Permanent buoys were used to mark sampling locations during the ice-free period.

Smith Lake, a small, shallow, subarctic lake, was also sampled. It is located within the University of Alaska's arboretum near Fairbanks. Nitrogen cycling within the Smith Lake water column has been well described by several studies (Dugdale, 1965; Goering and Dugdale, 1966; and Alexander and Barsdate, 1971). Once freeze-up occurs in October, ammonium concentrations increase through organic matter mineralization with a subsequent increase in nitrate concentrations due to nitrification. From mid-February to mid-April, anoxic conditions prevail, and a rapid decline in nitrate concentrations occur. Goering and Dugdale (1966) explain this rapid disappearance of nitrate as denitrification.

After the initial observations of Toolik Lake sediment N_2O data, some doubts occurred as to whether the acetylene blockage technique had in fact measured N_2O production. The acetylene blockage technique was then checked at Smith Lake where the nitrogen cycle is well understood. The Smith Lake water column was sampled on two dates during February 1981, and the samples were treated with and without nitrate and ammonium to determine if the acetylene blockage technique was actually measuring N_2O production.

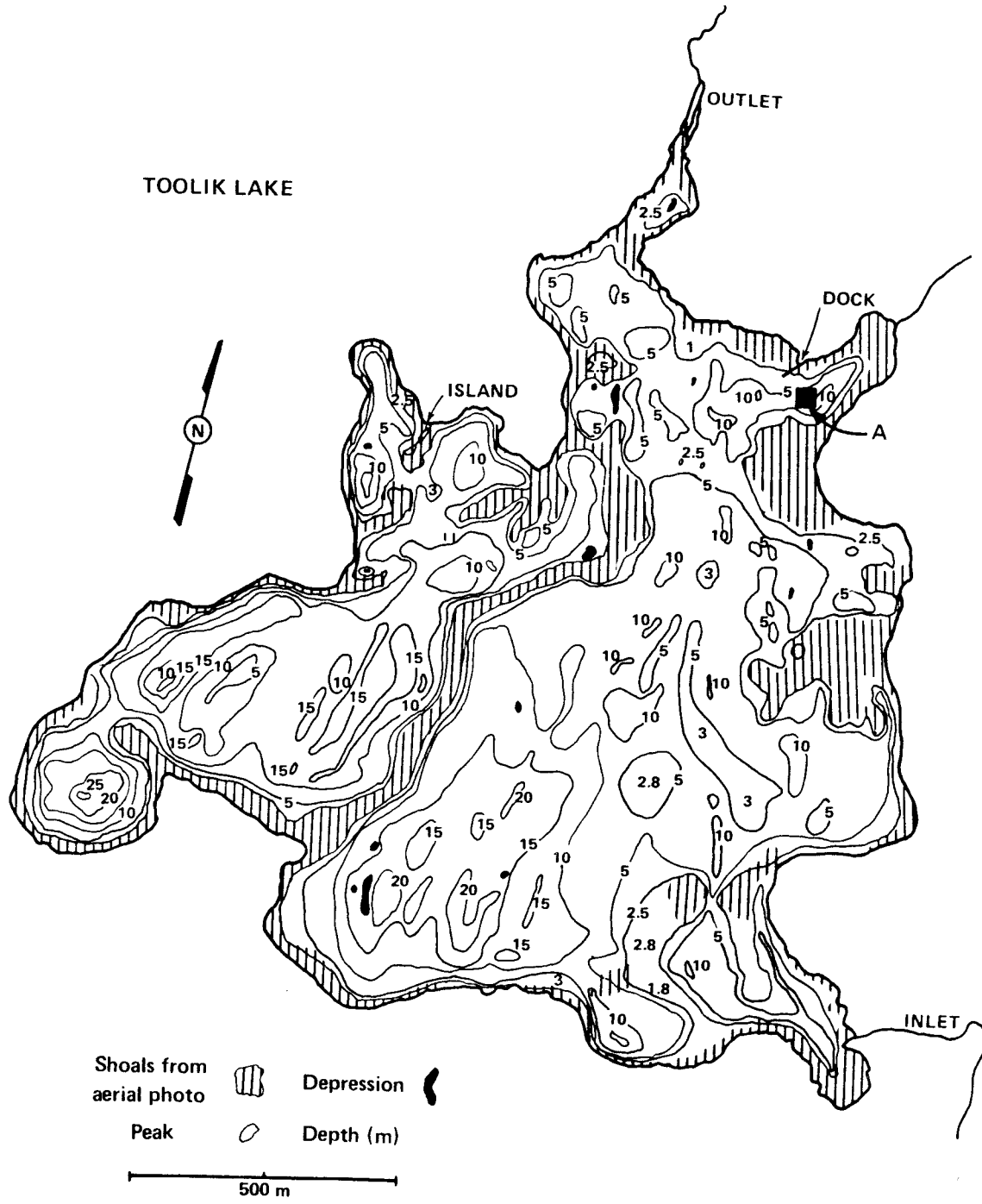


Figure 1. Toolik Lake map showing depth contours and sampling site (A).

METHODS

Sediment cores were obtained with a KB gravity corer modified to fit a three-inch core tube. The cores were immediately brought back to the field laboratory to be sectioned for experiments, nutrient analysis, pH, and Eh. Sediment cores were kept for experiments and for analysis only if they were apparently undisturbed in the core tube.

Interstitial water was collected *in situ* from equilibrators (Hesslein, 1976) and from cores with Reeburgh (1967) core squeezers. Nitrate, nitrite, ammonium, and exchangeable ammonium determinations were made according to Strickland and Parsons (1969) in the field laboratory. Exchangeable ammonium was extracted with 2 M KCl for 24 h (Blackburn, 1979). Organic nitrogen was determined after ignition at 750°C. A Coleman nitrogen analyzer, which is an automated Dumas combustion, was used for total nitrogen determinations on dried sediment.

Simultaneous Eh and pH measurements were made with an Orion combination pH electrode and an Orion Eh electrode. The electrodes were inserted at least 2 cm beneath the surface of the core to the depth of interest, in an effort to eliminate atmospheric contamination.

The relationship between Eh (pE) and pH can be shown graphically in a pE-pH diagram. These diagrams show the regions of stability and boundary lines for the various chemical species in water and indicate which species will predominate under a given condition of pE and pH. The Nernst equation, which expresses the relationship between the standard redox potential of a given redox couple, its observed potential

and the concentration ratio of its electron donor and acceptor, was used to calculate the line boundaries of a pE-pH diagram. The equation is:

$$E_H = E_o + \frac{RT}{nF} \ln \frac{[\text{electron acceptor}]}{[\text{electron donor}]}$$

where R = the gas constant, T = °K, n = the number of electrons, F = the Faraday constant, and can be simplified to:

$$E_H = E_o + \frac{RT}{nF} \text{pH}$$

where $E_o = \frac{\Delta F^\circ}{nF}$, and ΔF° = the change in free energy. In converting Eh to pE, the following equation was used:

$$\text{pE} = \frac{F}{\ln 10 RT} E_h \quad \text{or} \quad \text{pE} = -\text{pH} + \log K$$

where $\log K = \log ([\text{electron acceptor}]/[\text{electron donor}])$ (Stumm and Morgan, 1970). Reactions used to define the stability diagram are as follows:

1. $\text{NO}_3^- + 6\text{H}^+(\text{W}) + 5\text{e}^- = 1/2 \text{N}_2(\text{g}) + 3(\text{H}_2\text{O}) \quad \Delta F^\circ = 143.64$
2. $\text{NO}_3^- + 10\text{H}^+(\text{W}) + 8\text{e}^- = \text{NH}_4^+ + 3\text{H}_2\text{O} \quad \Delta F^\circ = 162.64$
3. $\text{N}_2 + 8\text{H}^+(\text{W}) + 6\text{e}^- = 2\text{NH}_4^+ \quad \Delta F^\circ = 38.00$
4. $\text{NO}_2^- + 8\text{H}^+(\text{W}) + 6\text{e}^- = \text{NH}_4^+ + 2\text{H}_2\text{O} \quad \Delta F^\circ = 124.13$
5. $\text{NO}_3^- + 2\text{H}^+(\text{W}) + 2\text{e}^- = \text{NO}_2^- + \text{H}_2\text{O} \quad \Delta F^\circ = 38.51$

Values of Eh and pH were then plotted on the pE-pH diagram.

Nitrification was measured with a $^{15}\text{N-NO}_3$ dilution technique (Koike and Hattori, 1978) and with a $^{15}\text{N-NH}_4^+$ tracer method. Sediment core samples were sectioned into 3 cm increments and placed in test tubes with 10 ml of enriched labeled lake water containing $30 \mu\text{g}$ at $\text{N-NH}_4^+ \cdot \text{liter}^{-1}$ and $10 \mu\text{g}$ at $\text{N-NO}_3^- \cdot \text{liter}^{-1}$. Labeled nitrogen as NH_4^+ or NO_3^- was added as a 30% enrichment of ^{15}N . Samples were incubated for 0, 24, and 48 h on the sediment surface and at the designated times were filtered. The filtrate was frozen until further analysis. Both the dilution and tracer samples were analyzed for $^{15}\text{N-NO}_3^-$ on a modified Bendix Time of Flight, model 17-210 mass spectrometer. A 1 ml carrier, $5 \mu\text{mol N-NO}_3^- \cdot \text{cm}^{-3}$ was added to the filtrates, and the nitrate was then reduced to nitrite by a Cu-Cd column (Strickland and Parsons, 1969). The Cu-Cd column was approximately 95% efficient in nitrate reduction.

Two different chemical methods were used for the reduction of nitrite to dinitrogen, one following Koike and Hattori's (1978) method and one following Schell's (1978) method. In using Koike and Hattori's (1978) technique, the sample pH was adjusted to 10 by the addition of 4 M KOH and was then reduced to a 1 ml volume with low heat. Nitrite was then reduced to dinitrogen in a vacuum with the addition of 2 ml sulfamic acid. Schell's (1978) method involved converting nitrite to a diazonium salt with the addition of aniline and then coupling it with B-naphthol to form 1-benzenazo-B-naphthol, a bright orange dye. The dye was extracted with CCl_4 and absorbed onto a filter and subsequently

was then reduced to dinitrogen by a modified Dumas combustion (Barsdate and Dugdale, 1965). Once nitrite was reduced to dinitrogen, the ^{15}N : ^{14}N ratio was analyzed on the Bendix mass spectrometer that had a precision of 0.01% (T. Chapman, personal communication). The ^{15}N : ^{14}N ratio was calculated using the following equation (Hauck *et al.*, 1958):

$$\text{atom \% } ^{15}\text{N} = \frac{100R - \frac{^{15}\text{N (carrier)}}{^{14}\text{N (carrier)}}}{1 + (R - \frac{^{15}\text{N (carrier)}}{^{14}\text{N (carrier)})}} = \frac{100R}{2 + R}$$

where R = the ratio of the peak heights.

Because of the numerous problems associated with the mass spectrometric analysis, only three experiments from 1979 were completely processed. The experiment on August 31, 1979, using the $^{15}\text{N-NO}_3^-$ dilution technique was processed with Koike and Hattori's (1978) methodology which used liquid samples for mass spectrometric analysis. A carrier for nitrate was not used. The use of liquid samples caused a considerable amount of air leakage. The degassing phase which took place before the addition of the sulfamic acid did not trap all of the O_2 or N_2 in the sample air interface. This reduced the ability to distinguish ^{15}N : ^{14}N ratios with any precision. A correction factor ($1.94 \times \frac{^{32}\text{O}_2 \text{ peak height} - ^{28}\text{N}_2 \text{ peak height}}{^{28}\text{N}_2 \text{ peak height}}$) was therefore used (Bremner, 1965). It was concluded that this method was unsatisfactory and the other two experiments (August 31, 1979, and September 14,

1979, $^{15}\text{N-NH}_4^+$ tracer experiments) were processed using Schell's (1978) methodology.

Schell's (1978) methodology was considerably better than Koike and Hattori's (1978) method for processing Toolik Lake sediment samples but also presented several problems. After numerous attempts, it was discovered that the mass spectrometer needed at least 5 μmol of N_2 to distinguish noise from the $^{28}\text{N}_2$ and $^{29}\text{N}_2$ peaks on the charts. The sediment samples had a small volume of water, at most 20 ml, with low concentrations of nitrate, approximately $0.1 \mu\text{mol N-NO}_3^- \cdot 20 \text{ ml}^{-1}$; therefore, a nitrate carrier was used. The addition of the carrier diluted the sample approximately 50X, and the conversion of the nitrate to dinitrogen diluted the sample again by a factor of two. A sample that was 30% enriched with ^{15}N would read 0.99 atom % while the natural ^{15}N -enrichment would read 0.39 atom %. Even with the addition of the carrier, the ability to measure $^{28}\text{N}_2$ and $^{29}\text{N}_2$ peaks was diminished. Due to these factors no other ^{15}N -experiments were processed.

The acetylene blockage technique (Yoshinari *et al.*, 1977) was used for measuring the rate of denitrification and N_2O production. Acetylene (C_2H_2) inhibits complete reduction of nitrate or nitrite with the subsequent accumulation of N_2O . Nitrous oxide, unlike dinitrogen, occurs in low concentrations in the atmosphere and slight increases in its concentration can be detected with a gas chromatograph.

The quantity of N_2O produced by the acetylene inhibition is a direct measure of the total gaseous N_2 produced without the acetylene inhibition. This measurement has been found to correlate well with ^{13}N -tracer studies (Smith *et al.*, 1978) and is inexpensive yet reliable. However, Walter *et al.* (1979) and Bremner and Blackmer (1978) observed that acetylene also inhibited nitrification and suggested that *in situ* studies of denitrification should be limited to short-term incubations (< 1 day) or to systems where nitrification is assumed to be complete before the onset of denitrification. The use of C_2H_2 in long-term incubations, where both processes are occurring, would limit the denitrifiers supply of nitrate, thus lower denitrification rates would be measured. In short-term assays, the accumulation of N_2O in samples without added acetylene should give a measure of the N_2O produced by both nitrification and denitrification, whereas in samples with added acetylene a measure of the N_2O produced only by denitrification should result if the amount of added acetylene is sufficient to inhibit nitrification completely. Walter *et al.* (1979) observed that a concentration of 0.01 atm of C_2H_2 completely inhibited nitrification.

Cores obtained for the denitrification experiments were sectioned in a glove bag which had been flushed four times with nitrogen gas. Sediment samples were placed in 75 ml jars and capped with lids equipped with rubber septa for easy gas sampling. A piece of tight fitting rubber was placed over the seal to assist in preventing gas

leakage. Acetylene was generated from CaC in a modified Bliss generator (Stutz and Bliss, 1973). Acetylene was added to samples at a concentration of 0.1 atm. Duplicates of sediment samples with and without C₂H₂ were prepared. Three and five replicates were used in Smith Lake water column samples. Incubations at 0, 24, and 48 h; 0, 12, and 24 h; and 0, 3, and 6 h were carried out *in situ* with jars resting on the sediment surface at Toolik Lake and jars suspended in the water column at Smith Lake. The gases in the jars were sampled with 6 ml Vacuainers®.

A Carle model 8700 gas chromatograph fitted with a 6 ft Poropak® Q column set at 200°C was used for gas analysis. Helium was used as the carrier gas at a flow rate of 26 ml·min⁻¹. A Matheson gas tank of 5.5 ppm N₂O was used to make standards. A linear regression of the standards was fitted to a line (r = 0.95), and peak heights were then used to determine μmol N₂O per sample injected. Values of N₂O concentrations ranged from 0 ppm to 33 ppm, with an average of 12.7 ppm. The lower limit of detection on the gas chromatograph being 0.36 ppm. The precision was 6.48%. A Hamilton 50 μl gas tight syringe was used for sample injections.

The concentrations of N₂O in solution were calculated from the measured headspace concentration. Solubility of N₂O was determined by a published Bunsen absorption coefficient for pure water; at 4°C it was 51.31 mol N₂O·m⁻³ (Siedell and Linke, 1940). The equation used for calculations, assuming equilibrium, states that the solubility of

a gas in solution will be directly proportional to its partial pressure in the gas phase and is as follows:

$$C = Bp$$

where C = the concentration of that gas in solution, p = the partial pressure of that gas in the gas phase, and B = the Bunsen coefficient which expresses the quantity of a gas contained in a unit quantity of water at a specific temperature (Broeker, 1974). The vapor pressure of water at the temperatures of sampling was approximately 0.8% of the total pressure. This factor was not used in the calculations as the variability due to sampling was much greater.

RESULTS

Exchangeable ammonium, interstitial ammonium, nitrate, and nitrite concentrations for sampling dates during the 1979 and 1980 field seasons are shown in Figure 2, Figure 3, and Tables 1-8. Ammonium concentrations increased with depth, while nitrate and nitrite concentrations decreased with depth. Total ammonium (exchangeable plus interstitial) was at least an order of magnitude higher than nitrate and nitrite concentrations. Any measurable amount of nitrate was found only within the top 0-6 cm of sediment. There was no significant trend in nutrient concentrations throughout the summer season.

Total nitrogen ranged from .14 to .94% of the sediment content and averaged .72%. It showed little variation with depth (Tables 1-8). Organic matter ranged from 9-26% of the sediment content and averaged 19% (Tables 1-8). There was little variation in organic matter with depth or seasonally.

Tables 1-8 also give Eh, pE, and pH measurements. The data show a decreasing trend in Eh and pE and an increasing trend in pH with sediment depth. On September 2, 1979 and May 30, 1980, pH values decreased as sediment depth increased. The Eh ranged from -7 to +484 mV and the pH ranged from 6.0 to 7.3.

The predominant reactions controlling pH and Eh in Toolik Lake sediments are most likely the iron and manganese redox reactions rather than the buffering system of CO_2 , as total CO_2 in the sediment is fairly low (J. Cornwell, personal communication). As the sediment

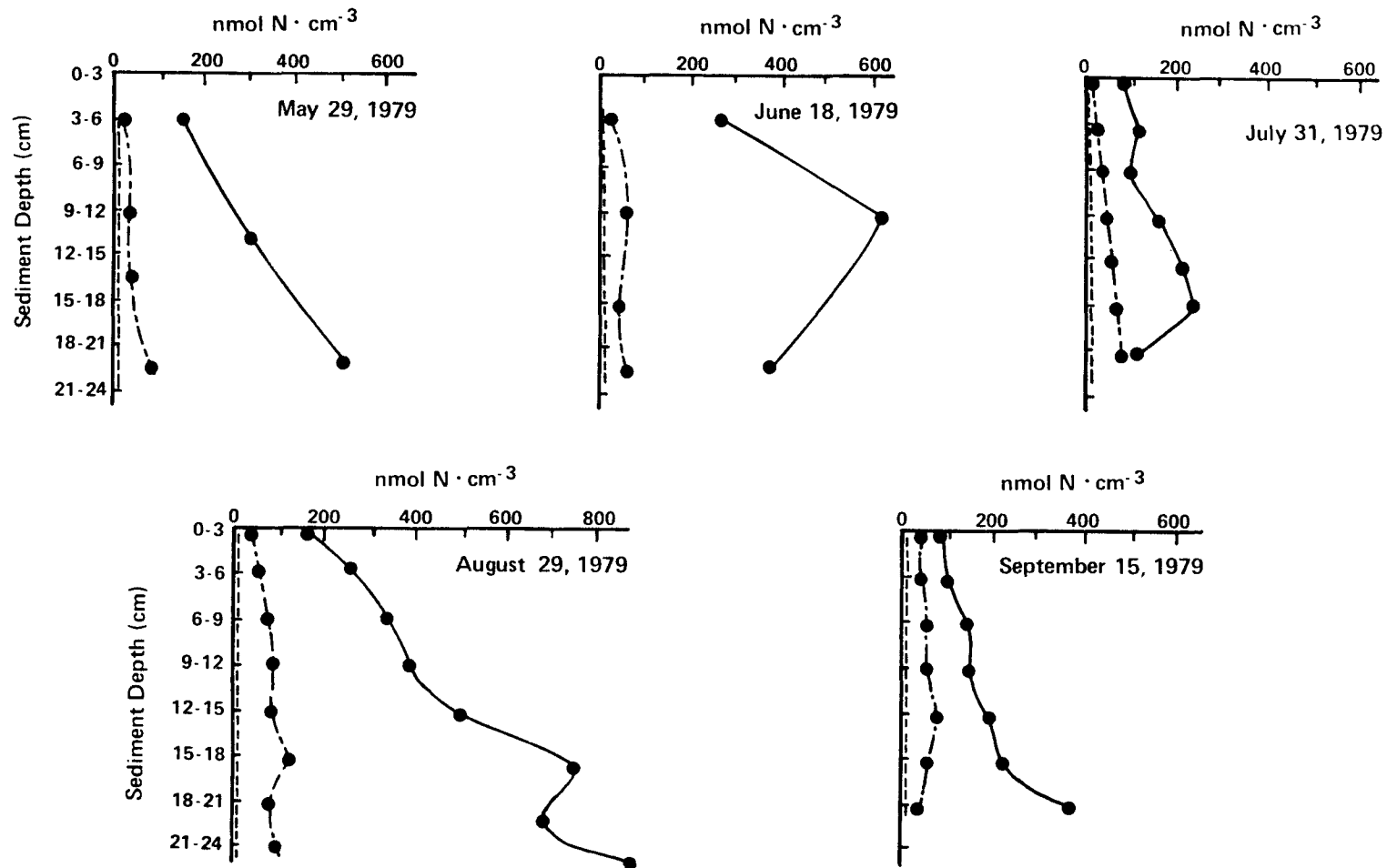


Figure 2. Toolik Lake sediment interstitial and exchangeable inorganic nitrogen during 1979. Interstitial NH_4^+ (---), exchangeable NH_4^+ (—), and interstitial $\text{NO}_3^- + \text{NO}_2^-$ (- - - -) at 10 m.

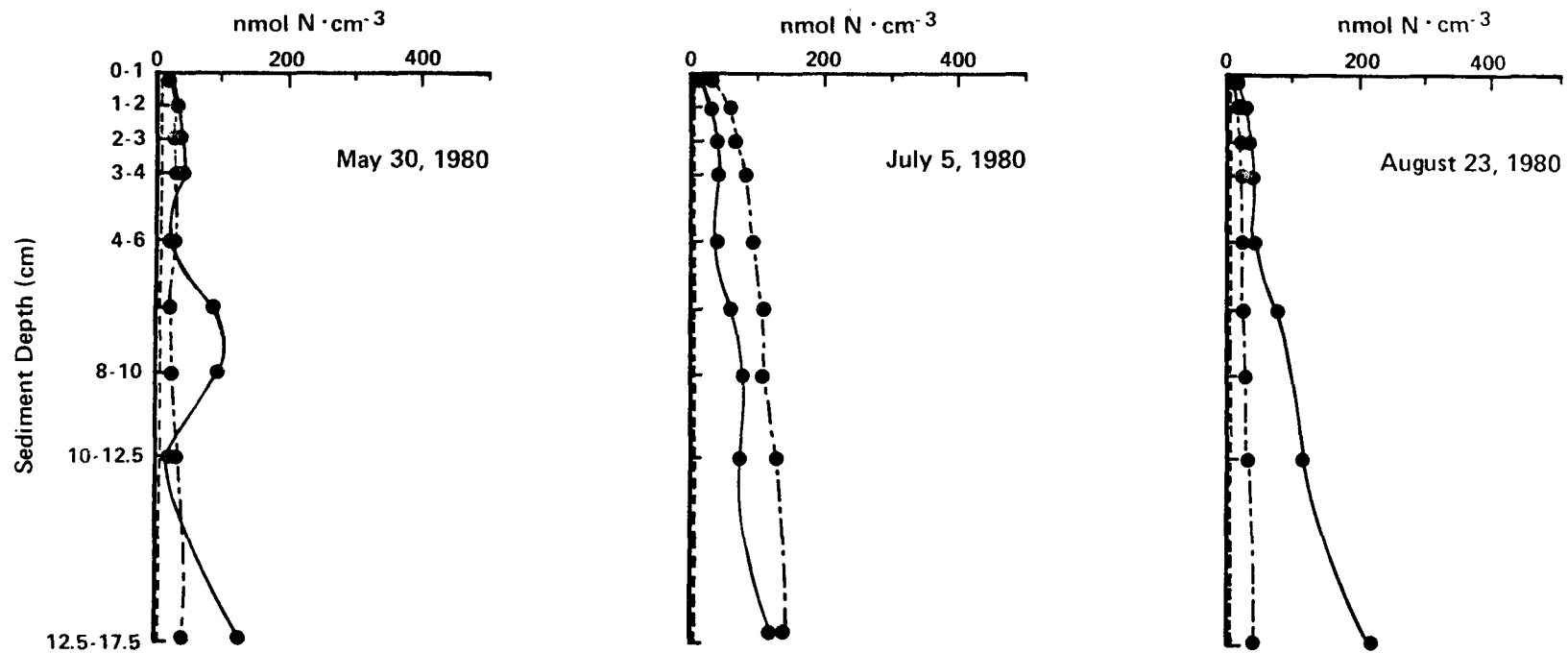


Figure 3. Toolik Lake sediment interstitial and exchangeable inorganic nitrogen during 1980. Interstitial NH_4^+ (---), exchangeable NH_4^+ (—), and interstitial $\text{NO}_3^- + \text{NO}_2^-$ (-----) at 10 m.

Table 1. Toolik Lake sediment exchangeable NH_4^+ and interstitial NH_4^+ , NO_3^- , and NO_2^- ($\text{nmol N} \cdot \text{cm}^{-3}$); total nitrogen %; and organic matter % on May 20, 1979. Sediments from 10 m. Ammonium concentrations are $\bar{x} \pm 1 \text{ s.d.}$

Sediment Depth (cm)	Inter NH_4^+	Exch NH_4^+	Inter NO_3^-	Inter NO_2^-	TN %	Org Mat %	pH	Eh (mV)	pE	pE + pH
0-6	17±6	169±22	0	0	-	15.3	-	-	-	-
6-15.5	23±2	273±99	0	0	-	13.3	-	-	-	-
15.5-28	71±22	456±16	0	0	-	11.5	-	-	-	-

- Indicate no samples taken.

Table 2. Toolik Lake sediment exchangeable NH_4^+ and interstitial NH_4^+ , NO_3^- , and NO_2^- ($\text{nmol N} \cdot \text{cm}^{-3}$) on June 18, 1979; total nitrogen % and organic matter % on July 19, 1979; and pH, Eh (mV), pE, and pE + pH on June 25, 1979. Sediments from 10 m. Ammonium concentrations are $\bar{x} \pm 1$ s.d.

Sediment Depth (cm)	Inter NH_4^+	Exch NH_4^+	Inter NO_3^-	Inter NO_2^-	TN %	Org Mat %	pH	Eh (mV)	pE	pE + pH
0-3	13±7	260±98	0	0	.89	20.8	6.2	253	4.5	10.7
3-6					.79	17.6	6.4	193	3.4	9.8
6-9	48±19	632±274	0	0	.64	-	6.4	193	3.4	9.8
9-12					.67	15.3	7.1	183	3.2	10.3
12-15	34±8	-	0	0	.61	13.8	7.2	113	2.0	9.2
15-18					.48	14.1	7.2	53	0.9	8.1
18-21	40±28	362±117	0	0	.14	16.8	7.3	3	0.0	7.3
21-24					.80	17.9	7.3	3	0.0	7.3
24-27					.71	16.4	7.3	-7	-0.1	7.2

- Not available.

Table 3. Toolik Lake sediment exchangeable NH_4^+ and interstitial NH_4^+ , NO_3^- , and NO_2^- ($\text{nmol N} \cdot \text{cm}^{-3}$); total nitrogen %; and organic matter % on July 31, 1979; and pH, Eh (mV), pE, and pE + pH on August 1, 1979. Sediments from 10 m. Ammonium and nitrate concentrations are $\bar{x} \pm 1$ s.d.

Sediment Depth (cm)	Inter NH_4^+	Exch NH_4^+	Inter NO_3^-	Inter NO_2^-	TN %	Org Mat %	pH	Eh (mV)	pE	pE + pH
0-3	5±2	83±51	4±1	2	.58	17.9	6.6	248	4.3	10.9
3-6	14±2	115±37	0±1	0	.49	15.9	6.7	218	3.8	10.5
6-9	20±3	91±50	1±0	0	.54	13.7	6.8	208	3.6	10.4
9-12	23±0	172±93	0±2	0	.50	12.5	6.6	198	3.4	10.0
12-15	30±1	201±61	0±1	0	.42	10.4	6.6	198	3.4	10.0
15-18	33±3	208±169	0±0	0	.44	-	6.6	198	3.4	10.0
18-21	38±3	72±68	0±0	0	.47	-	6.8	198	3.4	10.2

- Not available.

Table 4. Toolik Lake sediment exchangeable NH_4^+ and interstitial NH_4^+ , NO_3^- , and NO_2^- ($\text{nmol N} \cdot \text{cm}^{-3}$); total nitrogen %; and organic matter % on August 29, 1979; and pH, Eh (mV), and pE + pH on September 1, 1979. Sediments from 10 m. Ammonium and nitrate concentrations are $\bar{x} \pm 1$ s.d.

Sediment Depth (cm)	Inter NH_4^+	Exch NH_4^+	Inter NO_3^-	Inter NO_2^-	TN %	Org Mat %	pH	Eh (mV)	pE	pE + pH
0-3	30±7	172±26	3±0	0	.82	20.3	7.1	71	1.2	8.3
3-6	43±2	253±37	4±1	0	.79	23.3	6.9	51	0.9	7.8
6-9	58±1	343±168	5±2	0	.93	25.7	6.9	31	0.5	7.4
9-12	80±1	384±143	4±1	0	.88	-	6.8	31	0.5	7.3
12-15	79±8	500±83	3±1	0	.83	22.6	6.8	31	0.5	7.3
15-18	103±5	764±133	3	0	.68	19.1	6.8	26	0.4	7.2
18-21	72±4	652±213	0±1	0	.76	20.1	6.8	41	0.7	7.5
21-24	71±2	886±155	0±1	0	-	-	-	-	-	-

- Not available.

Table 5. Toolik Lake sediment exchangeable NH_4^+ and interstitial NH_4^+ , NO_3^- , and NO_2^- ($\text{nmol N} \cdot \text{cm}^{-3}$); total nitrogen %; organic matter %; pH; Eh (mV); pE; and pE + pH on September 15, 1979. Sediments from 10 m. Ammonium and nitrate concentrations are $\bar{x} \pm 1$ s.d.

Sediment Depth (cm)	Inter NH_4^+	Exch NH_4^+	Inter NO_3^-	Inter NO_2^-	TN %	Org Mat %	pH	Eh (mV)	pE	pE + pH
0-3	30±1	80±52	8±1	0	.69	18.7	6.7	285	5.8	12.5
3-6	17±2	100±84	7±1	0	.85	24.6	6.8	295	6.0	12.8
6-9	31±1	159±61	6±2	0	.88	24.8	6.9	245	5.0	11.9
9-12	31±11	159±27	6±2	0	.86	26.0	6.9	145	2.9	9.8
12-15	58±1	224±105	10±2	0	.84	24.3	6.9	115	2.8	9.2
15-18	35±0	264±100	6±3	0	.71	22.0	7.0	105	2.1	9.1
18-21	67±3	392±29	4±1	0	.72	20.2	6.9	95	1.9	8.8

Table 6. Toolik Lake sediment exchangeable NH_4^+ and interstitial NH_4^+ , NO_3^- , and NO_2^- ($\text{nmol N} \cdot \text{cm}^{-3}$) on May 30, 1980; total nitrogen % and organic matter % on May 24, 1980; and pH, Eh (mV), pE, and pE + pH on May 31, 1980. Sediments from 10 m. Ammonium and nitrate concentrations are $\bar{x} \pm 1 \text{ s.d.}$

Sediment Depth (cm)	Inter NH_4^+	Exch NH_4^+	Inter NO_3^-	Inter NO_2^-	TN %	Org Mat %	pH	Eh (mV)	pE	pE + pH
0-1	23±11	14±4	4±0	1	.77	20.0	7.0	345	6.1	13.1
1-2	34±21	35±7	5±3	1	.94	19.7	7.0	205	3.6	10.6
2-3	28±15	39±41	4±1	1	.77	20.4	6.9	145	2.6	9.5
3-4	33±7	46±10	10±5	0	-	22.3	6.9	105	1.8	8.7
4-6	29±3	16±2	8±5	2	.83	22.6	6.8	105	1.8	8.6
6-8	24±19	99±1	2±3	1	.81	22.9	6.8	105	1.8	8.6
8-10	30±16	95±7	1±0	1	.78	23.2	6.7	105	1.8	8.5
10-12.5	41±6	17±4	1±0	1	.73	20.9	6.6	115	2.0	8.6
12.5-17.5	48±25	130±6	1±1	0	.80	23.7	6.6	-	-	-

- Not available.

Table 7. Toolik Lake sediment exchangeable NH_4^+ and interstitial NH_4^+ , NO_3^- , and NO_2^- ($\text{nmol N} \cdot \text{cm}^{-3}$) on July 5, 1980; total nitrogen % and organic matter % on July 3, 1980; and pH, Eh (mV), pE, and pE + pH on July 5, 1980. Sediments from 10 m. Ammonium concentrations are $\bar{x} \pm 1$ s.d.

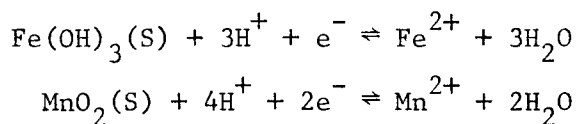
Sediment Depth (cm)	Inter NH_4^+	Exch NH_4^+	Inter NO_3^-	Inter NO_2^-	TN %	Org Mat %	pH	Eh (mV)	pE	pE + pH
0-1	36±2	1±2	1	0	.47	14.0	6.0	225	4.5	10.5
1-2	65±2	22±4	2	0	.55	16.9	6.3	195	3.5	9.8
2-3	68±19	32±1	1	1	.83	20.0	6.4	165	2.9	9.3
3-4	89±10	22±5	1	1	.85	22.5	6.5	185	3.3	9.8
4-6	98±1	32±5	1	0	.85	23.4	6.5	165	2.9	9.4
6-8	105±5	53±10	1	0	.89	-	6.6	165	2.9	9.5
8-10	103±12	84±35	1	0	.86	23.7	6.6	165	2.9	9.5
10-12.5	117	81±26	1	0	.89	-	6.6	175	3.1	9.7
12.5-17.5	145±9	122±35	1	0	.83	25.1	6.6	185	3.3	9.9

- Not available.

Table 8. Toolik Lake sediment exchangeable NH_4^+ and interstitial NH_4^+ , NO_3^- , and NO_2^- ($\text{nmol N} \cdot \text{cm}^{-3}$) on August 23, 1980; and total nitrogen %, organic matter %, pH, Eh (mV), pE, and pE + pH on August 18, 1980. Sediments from 10 m. Ammonium concentrations are $\bar{x} \pm 1$ s.d.

Sediment Depth (cm)	Inter NH_4^+	Exch NH_4^+	Inter NO_3^-	Inter NO_2^-	TN %	Org Mat %	pH	Eh (mV)	pE	pE + pH
0-1	1±2	12±4	0	0	.73	21.3	6.4	479	8.6	15.0
1-2	5±3	14±31	0	0	.74	21.9	6.3	484	8.7	15.0
2-3	14±2	20±5	0	0	.80	22.9	6.3	94	1.7	8.0
3-4	13±1	30±4	0	0	.84	23.2	6.8	64	1.1	7.9
4-6	12±1	27±7	0	0	.76	22.3	6.9	64	1.1	8.0
6-8	16±4	88±7	0	0	.76	21.7	7.0	44	0.8	7.8
8-10	23±1	57±5	0	0	.68	9.8	7.0	44	0.8	7.8
10-12.5	29±1	115±15	0	0	.64	22.2	7.0	44	0.8	7.8
12.5-17.5	35±6	218±17	0	0	.65	17.2	7.0	54	0.9	7.9

depth increases, the tendency for Eh to decrease while pH increases can be explained with the following iron and manganese redox reactions:



Protons and electrons are used when proceeding from an oxidized to a reduced zone. Nitrogen redox reactions proceed in a similar manner, as can be seen with the reactions used to plot the nitrogen species stability diagram.

Redox potentials can be expressed by either Eh (the millivolt difference in potential between a platinum electrode and the standard hydrogen electrode) or pE (-log of the electron activity). In changing Eh to pE, a useful parameter, pE + pH, can be calculated and used to describe the redox conditions of an aqueous environment in a single term. The pE + pH parameter ranges from zero on the reduced side [1 atm H₂(g) and 10^{-83.12} atm O₂(g)] to 20.78 on the oxidized side [1 atm O₂(g) and 10^{-43.56} atm H₂(g)], where pO₂(g) and pH₂(g) remain fixed for any given value of pE + pH (Lindsay, 1979). Tables 1-8 give sediment values for pE + pH. At all sampling dates, pE + pH decreased as sediment depth increased ranging from 15 at the surface, 0-1 cm and 1-2 cm, to 7.2 at 24-27 cm. Although sediment pH increased with sediment depth, the pE + pH values indicate the redox conditions become more reducing with depth.

Sediment pE and pH values are plotted on the stability diagram (Figure 4). Only two points from the surface sediment, 0-1 and 1-2 cm, fall within the NO_3^- and N_2 stability region where oxidized species of nitrogen are stable. The other Toolik Lake sediment pE and pH values fall within the NH_4^+ and N_2 stability region where reduced species of nitrogen are stable. A stability region defines what nitrogen species will predominate under a given pE and pH. The majority of Toolik Lake sediment pE and pH measurements are found in a reducing zone where other than N_2 , NH_4^+ is the predominant nitrogen species. Thermodynamically, nitrate is a stable form of nitrogen in the surficial sediments of Toolik Lake. Within the reduced zone, NO_3^- or NO_2^- are not as chemically stable as NH_4^+ and could readily be reduced to NH_4^+ . The boundary lines that define the stability limit of water are indicated on the diagram. At the $\text{O}_2/\text{H}_2\text{O}$ boundary limit, O_2 is at a pE + pH of 20.78 and at the $\text{H}_2\text{O}/\text{H}_2$ boundary limit O_2 is at a pE + pH of zero. Toolik Lake sediment pE and pH values are approximately midway between the water boundaries, suggesting an average $p\text{O}_2$ of $10^{-4.3}$ atm. The nitrogen equilibria suggests that reducing processes are more likely to be chemically feasible in Toolik Lake sediment than are oxidative processes.

Results of the $^{15}\text{N-NH}_4^+$ tracer and $^{15}\text{N-NO}_3^-$ dilution experiments are shown in Tables 9 and 10 where interstitial NH_4^+ concentrations and $^{15}\text{N-NH}_4^+$ atom % are estimated. There was an ^{15}N -enrichment of nitrate in the tracer experiments and a $^{15}\text{N-NO}_3^-$ dilution in the dilution experiment in both the 24 and 48 h incubations. These experiments

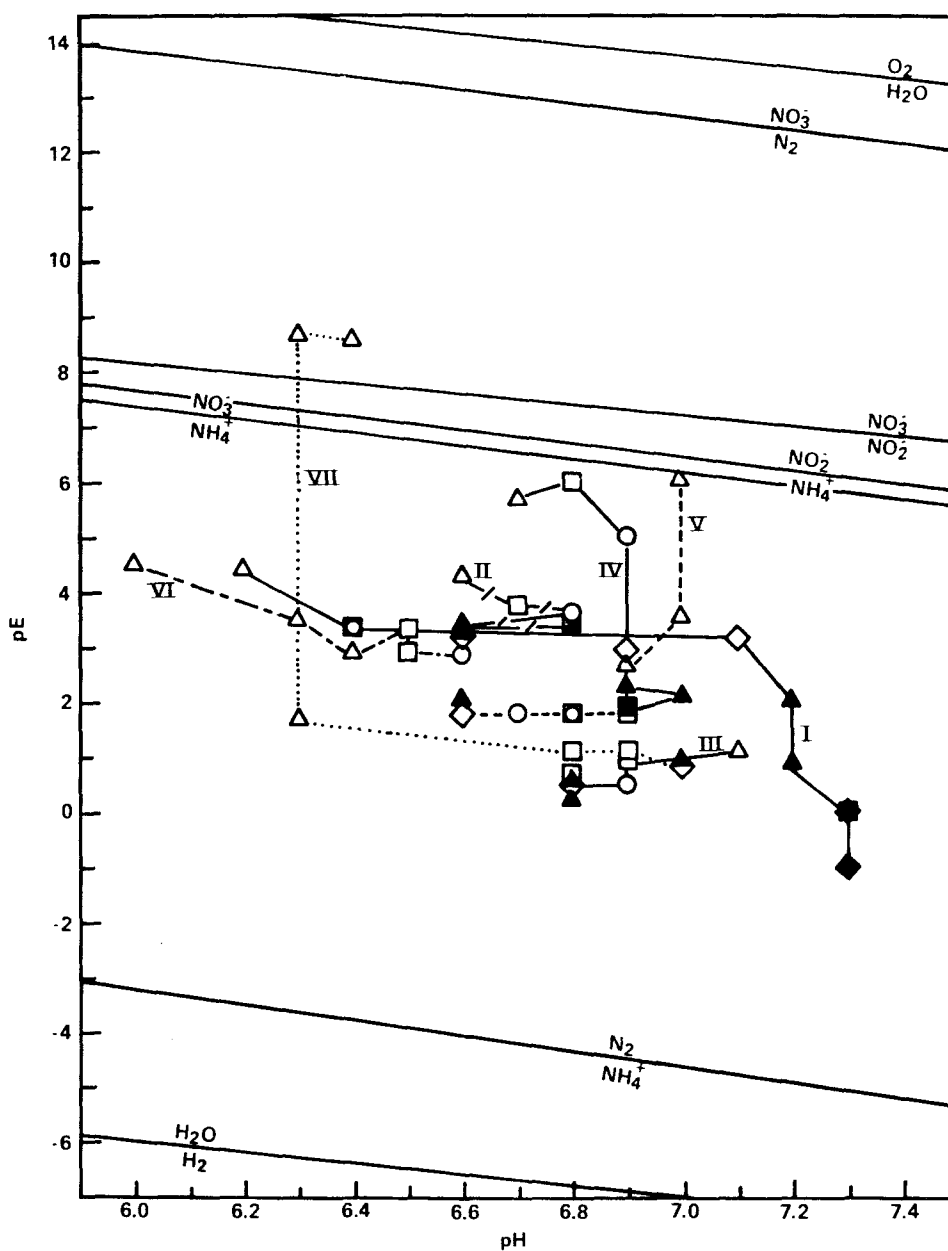


Figure 4. Stability diagram for NO_3^- , NO_2^- , N_2 , and NH_4^+ plotted with Toolik Lake sediment pE and pH measurements at 10 m. I - June 25, 1979; II - August 1, 1979; III - September 1, 1979; IV - September 15, 1979; V - May 21, 1980; VI - July 5, 1980; and VII - August 18, 1980. Sediment depth increments are as follows: (Δ) 0-3, 0-1, and 2-3 cm; (\square) 3-6, 3-4, and 4-6 cm; (\circ) 6-9, 6-8, and 8-10 cm; (\diamond) 9-12 and 10-12.5 cm; (\blacktriangle) 12-15, 15-18, and 12.5-17.5 cm; (\blacksquare) 18-21 cm; and (\blacklozenge) 21-24 cm.

Table 9. Results of Toolik Lake sediment ^{15}N - NO_3^- dilution experiments on August 31, 1979. Sediments from 10 m.

Sediment Depth (cm)	NO_3^- (nmol N·cm ⁻³) and ^{15}N (atom %)						NO_3^- Turnover rates (nmol N·cm ⁻³ ·d ⁻¹)	
	0 h		24 h		48 h		0-24 h	24-48 h
	NO_3^-	^{15}N	NO_3^-	^{15}N	NO_3^-	^{15}N		
0-3	4	3.48	4	2.86	5	1.82	6.2	5.8
3-6	3	5.88	5	2.39	8	2.45	14.2	-1.91
6-9	4	5.26	5	3.49	8	-	8.9	-
9-12	4	-	5	2.51	8	0.97	-	11.9

- Not available.

Table 10. Results of Toolik Lake sediment $^{15}\text{N-NH}_4^+$ tracer experiments on August 31, 1979. Sediments from 10 m.

Sediment Depth (cm)	NH_4^+ and NO_3^- ($\text{nmol N}\cdot\text{cm}^{-3}$) and ^{15}N (atom %)						NH_4^+ flux ($\text{nmol N}\cdot\text{cm}^{-3} \text{d}^{-1}$)	
	0 h		24 h		48 h		0-24 h	24-48 h
	NH_4^+	^{15}N	NO_3^-	^{15}N	NO_3^-	^{15}N		
August 31, 1979								
0-3	30	23.3	3.6	3.95	-	-	.61	-
3-6	27	25.8	4.1	3.53	-	-	.56	-
6-9	30	23.3	6.4	4.40	-	-	1.20	-
9-12	30	23.3	5.0	2.99	-	-	.64	-
September 14, 1979								
0-3	30	23.3	3.9	3.65	5.0	12.97	.61	2.17
3-6	32	21.9	3.8	9.75	3.6	14.38	1.69	.67
6-9	37	19.0	4.0	12.86	3.3	11.30	2.70	.74
9-12	42	16.9	4.8	16.20	8.6	14.90	4.60	2.90

- Not available.

indicate that nitrification is occurring. In some samples nitrate increased with time, but in most cases it decreased, suggesting other processes were using the NO_3^- pool.

Estimated rates of nitrification using the $^{15}\text{N-NH}_4^+$ tracer technique ranged from 0.56-4.2 $\text{nmol N}\cdot\text{cm}^{-3}\cdot\text{d}^{-1}$ for 0-12 cm, whereas using the $^{15}\text{N-NO}_3^-$ dilution technique the rates ranged from 5.8-14.2 $\text{nmol N}\cdot\text{cm}^{-3}\cdot\text{d}^{-1}$ for 0-12 cm. The September 14, 1979, tracer experiment showed an increase in nitrification rate with sediment depth in the 24 h incubation period whereas other samples showed no specific depth trend.

Tables 11 and 12 give N_2O concentrations at 0, 24, and 48 h and 0, 12, and 24 h for all denitrification experiments. The 0 h N_2O concentrations are indicative of the sediment *in situ* N_2O profiles. When the 0 h concentrations were plotted, it was apparent that some sample exposure to air had occurred during sampling or analysis, as several samples showed extremely low N_2O concentrations. The N_2O profile showed no clear depth trend, but on three sampling occasions (10 m, June 1980; 2 m, August 1980; and 10 m, August 1980) that had no apparent air contamination, a uniform depth distribution was observed. The range of N_2O concentrations on these sampling dates was 87-582 $\text{pmol N}_2\text{O}\cdot\text{cm}^{-3}$ with an average of 343 $\text{pmol N}_2\text{O}\cdot\text{cm}^{-3}$ for 0-12 cm. The ranges for the individual sampling dates are as follows: 87-358 $\text{pmol N}_2\text{O}\cdot\text{cm}^{-3}$ for 10 m, June 1979; 259-444 $\text{pmol N}_2\text{O}\cdot\text{cm}^{-3}$ for 2 m, August 1979; and 259-582 $\text{pmol N}_2\text{O}\cdot\text{cm}^{-3}$ for 10 m, August 1979. Lower N_2O concentrations occur under spring conditions (June) and at shallow depths (2 m) than occur during summer conditions and at greater depths.

Table 11. Results of Toolik Lake sediment C₂H₂ blockage experiments during June and July 1980. Sediments from 10 m. Values are $\bar{x} \pm 1$ s.d.

Experiment	C ₂ H ₂	Sediment Depth (cm)	pmol N ₂ O·cm ⁻³				
			0 h	24 h	48 h		
June 2	Absent	0-2	196	1117	737		
		2-4	196	900	575		
		4-6	0	791	1063		
		6-8	336	900	1225		
		8-10	196	900	1388		
		10-12	196	2092	1063		
	Present	0-2	195±77	710±267	696±133		
		2-4	87	737±229	331±345		
		4-6	250	981±38	724±210		
		6-8	196	900±76	954±1		
		8-10	141	899±153	818±115		
		10-12	195±77	845±229	751±363		
		July 6	Absent	0-2	190±33	223±315	199±282
				2-4	83±118	561±294	399±65
4-6	167±65			223±315	561±164		
6-8	83±118			608±164	364±16		
8-10	120±65			584±197	584±327		
Present	0-2			199±282	269±380	399±0	
	2-4		422±33	491±197	399±65		
	4-6		199±282	199±282	332±159		
	6-8		199±282	617±872	468±33		
	8-10		269±380	515±32	-		
	July 6 NO ₃ addition		Absent	0-2	561±426	561±32	492±0
				2-4	176±249	631±131	607±33
				4-6	199±282	746±163	631±196
6-8				376±32	492±0	839±491	
8-10		399±0		501±708	561±229		
Present		0-2		375±98	269±380	454±642	
		2-4	375±98	491±65	538±0		
		4-6	153±216	246±347	269±380		
		6-8	341±49	654±32	515±32		
		8-10	176±249	700±33	862±458		

- Not available.

Table 12. Results of Toolik Lake sediment C₂H₂ blockage experiments on August 26, 1980. Values are $\bar{x} \pm 1$ s.d.

Experiment	C ₂ H ₂	Sediment Depth (cm)	pmol N ₂ O·cm ⁻³		
			0 h	12 h	24 h
2 m	Absent	0-3	282±32	467±97	813
		3-6	328±32	859±1	1183
		6-9	374±98	721±65	421±32
	Present	0-3	305±65	628±65	790±490
		3-6	305±65	744±97	698±32
		6-9	351±0	521±142	802±506
5 m	Absent	0-3	198±281	998±261	1229±391
		3-6	291±411	1044±195	1183±0
		6-9	536±130	1160±97	859±392
		9-12	351±0	1044±195	1090±392
	Present	0-3	351±0	975±975	813±260
		3-6	675±391	1102±82	894±376
		6-9	721±130	1364±70	1136±587
		9-12	698±424	1391±97	1598±130
10 m	Absent	0-3	327±31	582±0	905±65
		3-6	397±130	1090±130	882±163
		6-9	386±179	744±294	928±163
		9-12	513±97	1090±130	1044
	Present	0-3	467±32	398	582±65
		3-6	444±0	628±130	859±457
		6-9	444±0	581±64	975±359
		9-12	513±32	582	929±359
<u>10 m</u> NO ₃ addition	Absent	0-3	467±32	1021±163	374±163
		3-6	268±379	1021±32	351±0
		6-9	513±32	1206±97	489±195
		9-12	605±98	1321±260	398±326
	Present	0-3	152±215	917±48	37±52
		3-6	0	1067±163	351±0
		6-9	567	1160±32	397±130
		9-12	291±411	1229±195	374±33

Rates of N_2O production for June, July, and August 1980 are shown in Figures 5 and 6. During June and July in the initial 24 h incubation, more nitrous oxide was produced in the absence of acetylene. In June there was little variation in the presence or absence of acetylene with depth, but in July greater N_2O production was observed deeper in the sediment (6-12 cm) than in the surface (0-6 cm) sediment. After 24 h the rate of N_2O production decreased, and in some samples N_2O reduction was observed. The reduction pattern occurred in both the absence and presence of C_2H_2 .

In August, a sediment transect of 2 m, 5 m, and 10 m water column depth was sampled and 12 h incubations were used (Figure 6). N_2O production was greater in the absence of acetylene in the top 0-6 cm but in the 6-12 cm section, N_2O production was greater in the presence of acetylene at all sampling sites on the transect. The same pattern of initial N_2O production with subsequent reduction was also observed at all the water column depths sampled. There was no apparent variation in N_2O production between the different sampling sites of the transect. Reduction of N_2O or a decrease in N_2O production was observed in the 12-24 h period except at 10 m where an increase in N_2O production in the presence of acetylene was observed.

The average N_2O production in the top 12 cm of sediment in the absence of acetylene was $452 \text{ pmol } N_2O \cdot \text{cm}^{-3} \cdot \text{d}^{-1}$ and in the presence of acetylene was $337 \text{ pmol } N_2O \cdot \text{cm}^{-3} \cdot \text{d}^{-1}$ (the 24 h incubation period at 10 m was used to calculate N_2O production).

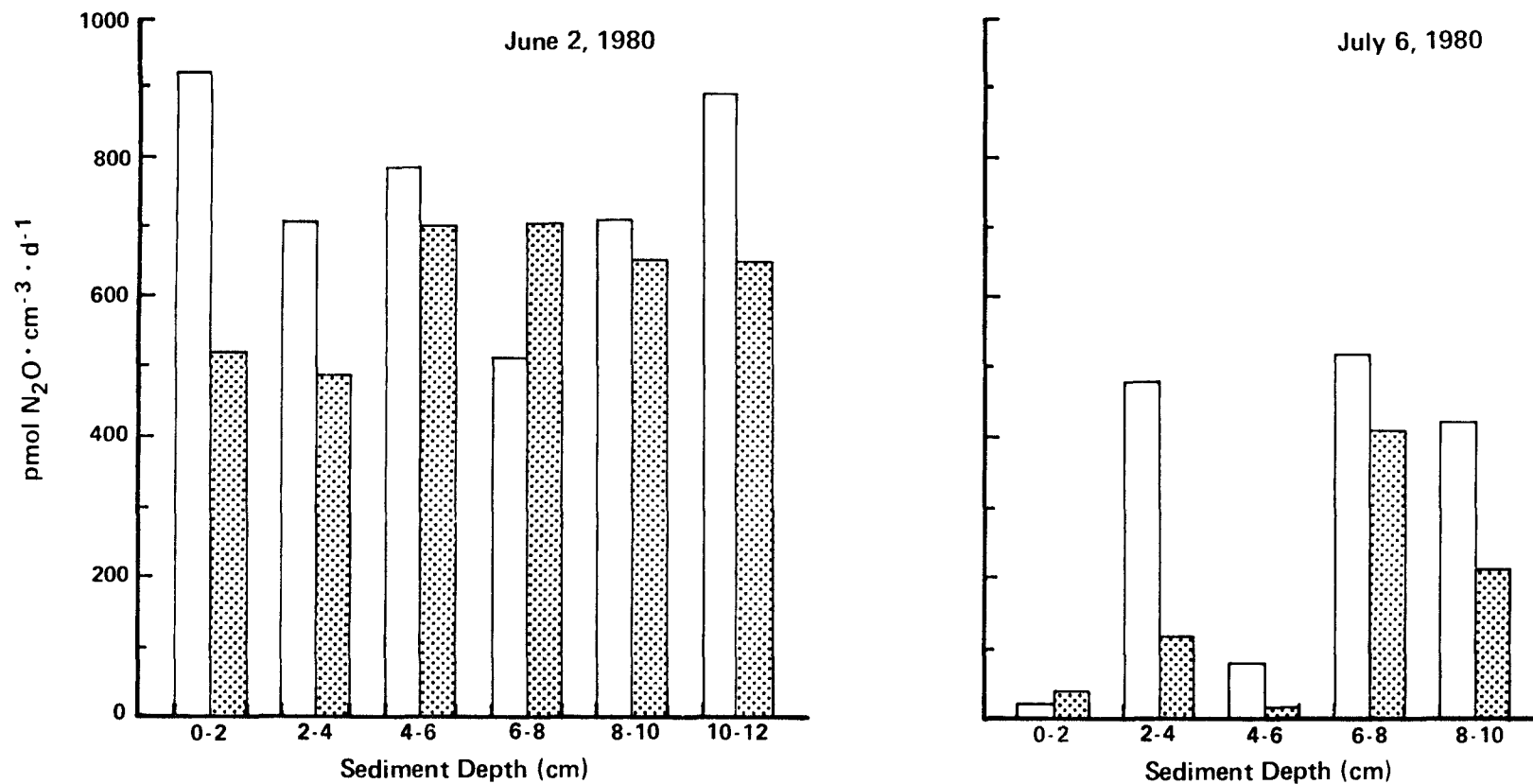


Figure 5. Toolik Lake sediment N₂O production in the presence (▨) and absence (□) of acetylene at 24 h. Sediments from 10 m.

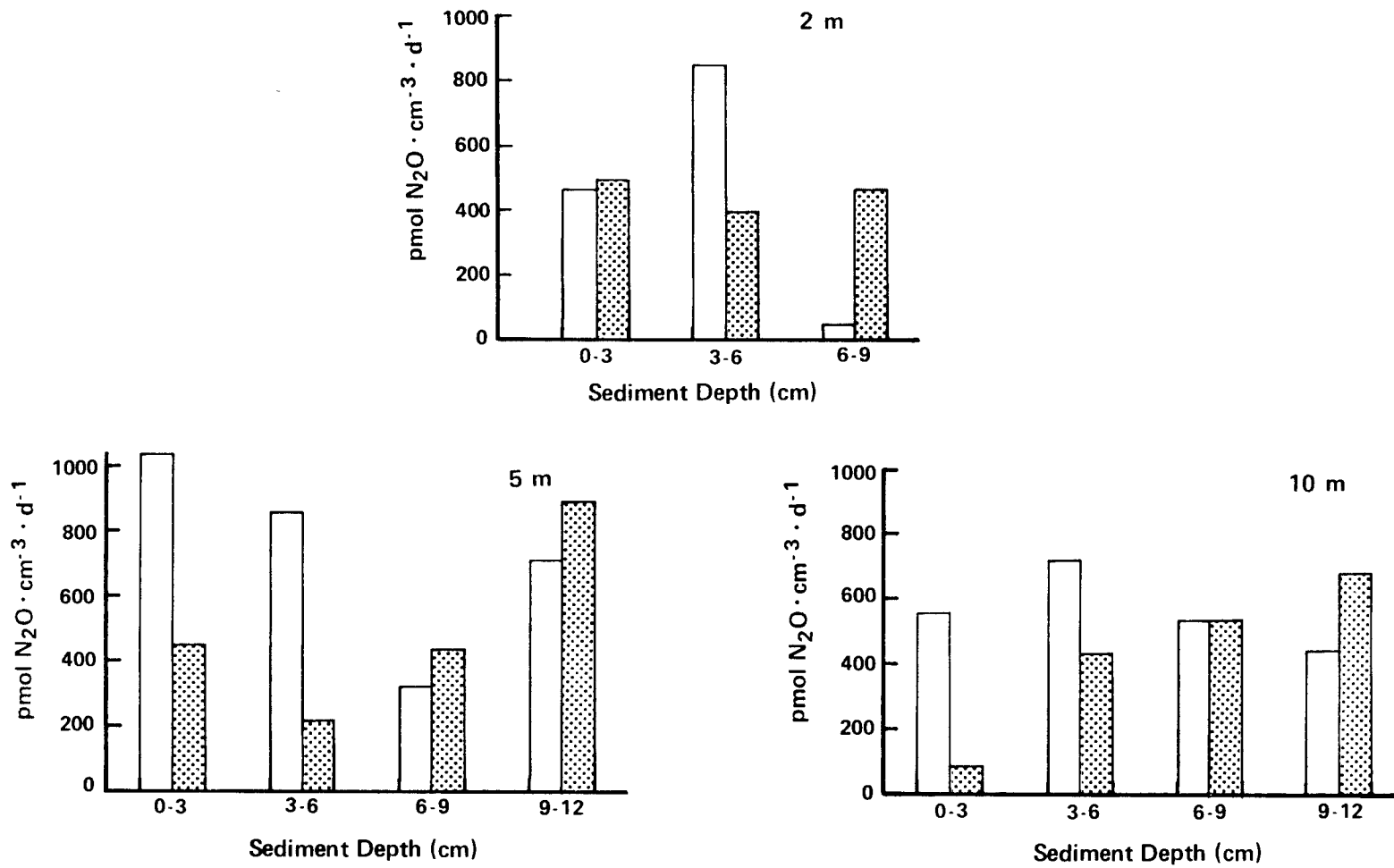


Figure 6. Toolik Lake sediment N_2O production at different depths in the presence (▨) and absence (□) of acetylene. Incubation period was 24 h.

To determine whether nitrate limited denitrification, a 2.5 nmol N-NO₃⁻·cm⁻³ addition was made to a July 1980 experiment and a 2.5 μmol·cm⁻³ to an August 1980 experiment (Figure 7). In July, with the added nitrate, N₂O production decreased with sediment depth in the absence of acetylene and increased with depth in the presence of acetylene. Total N₂O production for 0-12 cm was greater in the absence of acetylene and little variation was observed between nitrate-treated and untreated samples.

In August, with a larger nitrate addition, N₂O production during the initial 12 h period was similar to N₂O production for a 24 h period in untreated samples. N₂O production was also greater in the presence of acetylene with the nitrate addition than without a nitrate addition. Average 0-12 cm N₂O production in the presence of acetylene was 813 pmol N₂O·cm⁻³·d⁻¹ and in the absence of acetylene was 678 pmol N₂O·cm⁻³·d⁻¹.

Higher rates of N₂O reduction were observed in the nitrate-treated samples in the 12-24 h period than those samples without a NO₃⁻ addition. Firestone and Tiedje (1979) observed N₂O reduction after an initial period of production and suggested this could be a response to anoxia or from depletion of available carbon not from NO₃⁻ concentrations.

N₂O concentrations for 0, 3, and 6 h in the Smith Lake water column are shown in Table 13. The average *in situ* N₂O concentration for February 6, 1981 was 920 pmol·N₂O·cm⁻³ ranging from 816-1013 pmol·N₂O·cm⁻³ and for February 11, 1981 was 737 pmol N₂O·cm⁻³ ranging from 549-897 pmol N₂O·cm⁻³.

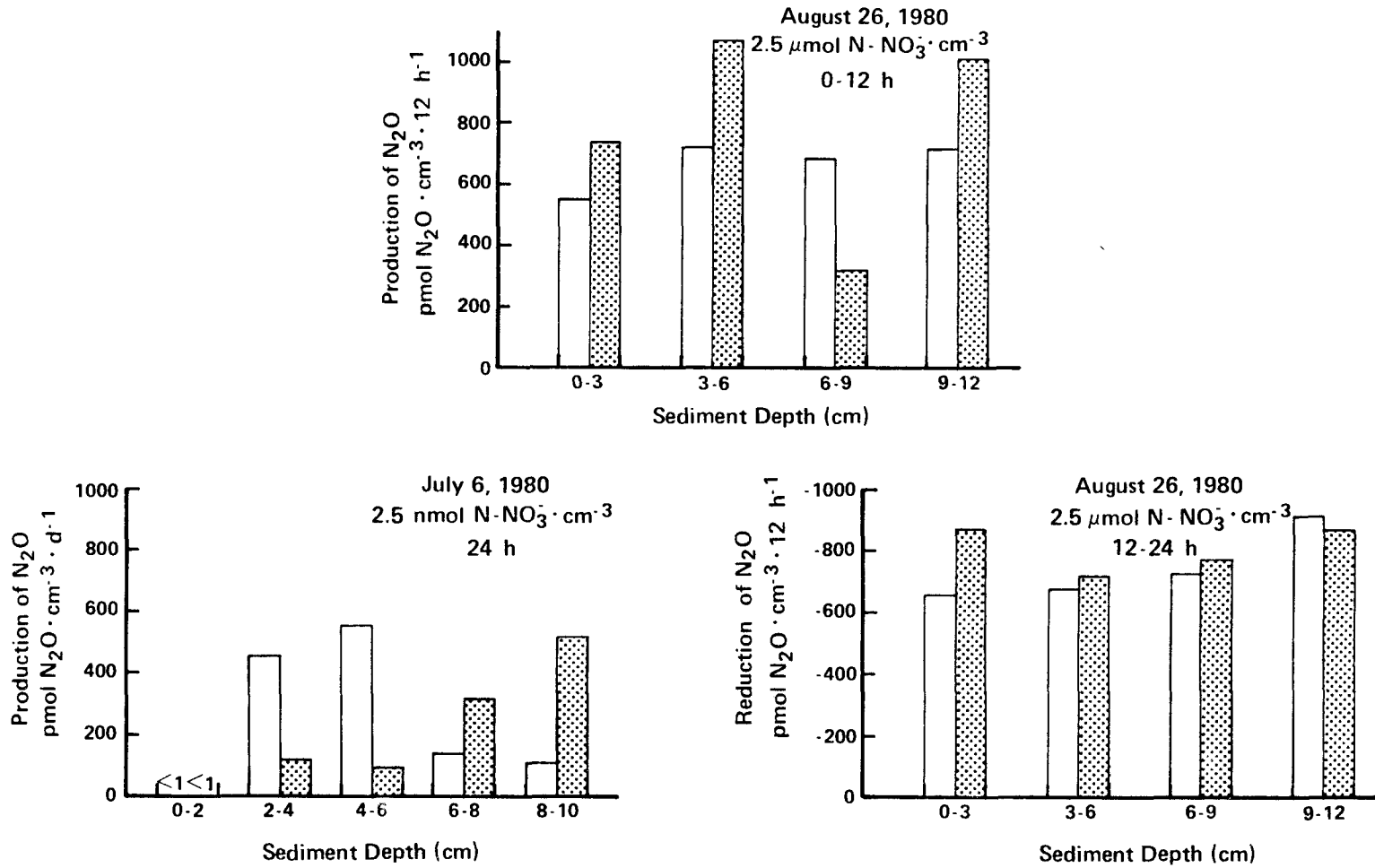


Figure 7. Toolik Lake sediment N₂O production and reduction with added nitrate in the presence (▨) and absence (□) of acetylene. Sediments from 10 m.

Table 13. Results of Smith Lake water column C_2H_2 blockage experiments during February 1981. Values are the $\bar{x} \pm 1$ s.d.

Experiment	C_2H_2	pmol $N_2O \cdot cm^{-3}$		
		0 h	3 h	6 h
February 6	Absent	980±61	1126±341	984±61
	Present	881±74	1012±128	1216±370
February 11	Absent	451±99	795±113	667±0
	Present	809±1	774±90	923±42
February 11 NO_3^- addition	Absent	781±132	688±30	1137±148
	Present	737±139	1117±70	1137±148
February 11 NH_4^+ addition	Absent	657±153	752±60	538±85
	Present	632±5	724±24	767±178

N_2O production in the Smith Lake water column is shown in Figure 8. Average N_2O production with acetylene present was $1260 \text{ pmol } N_2O \cdot \text{cm}^{-3} \cdot \text{d}^{-1}$ and in the absence of acetylene was $156 \text{ pmol } N_2O \cdot \text{cm}^{-3} \cdot \text{d}^{-1}$. A $2.5 \text{ } \mu\text{mol N-NO}_3^- \cdot \text{cm}^{-3}$ addition increased N_2O production in both acetylene-treated and untreated samples. Samples treated with a $2.5 \text{ } \mu\text{mol N-NH}_4^+ \cdot \text{cm}^{-3}$ addition did not show an increase in N_2O production. These results indicate that little if any N_2O was produced by ammonium oxidation, but that it was most likely produced by nitrate reduction. The *in situ* $N_2:N_2O$ ratio was determined to be 9 for untreated samples, and with the nitrate addition the $N_2:N_2O$ ratio decreased to approximately 1.

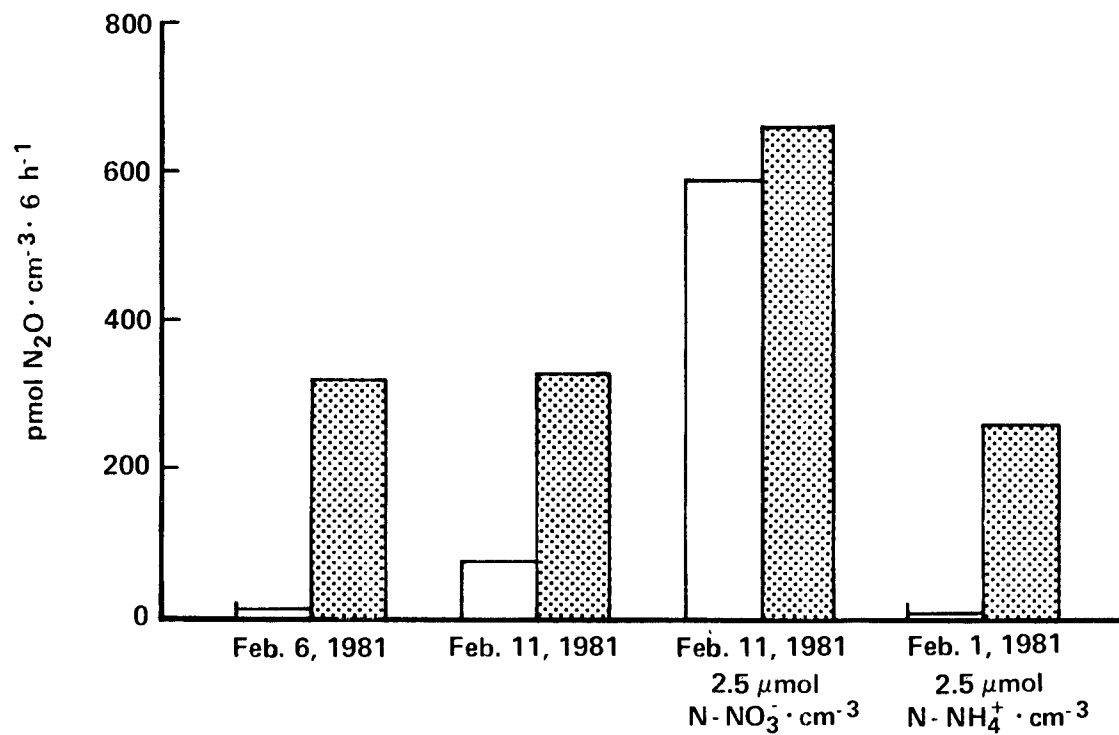


Figure 8. Smith Lake water column N_2O production in the presence (▣) and absence (□) of acetylene.

DISCUSSION

Using pure cultures of *Nitrosomonas*, ZoBell (1935) found ammonium oxidation occurring at a low Eh of 250 mV and an optimum Eh range for nitrifiers at 300-500 mV. Keeney (1973) found O₂ disappearance from sediments at 500-350 mV and NO₃⁻ disappearance from sediments at 350 mV to 100 mV. In marine sediment, low levels of nitrate and denitrification were found at Eh values of 0-225 mV (Sorensen, 1978; Oren and Blackburn, 1979). These observations indicate that the nitrification and the denitrification ranges are extended to lower Eh values than those Eh values suggested by the nitrogen equilibria.

Toolik Lake surface sediment measurements (0-3, 0-1, and 0-2 cm) showed Eh was slightly below or above 250 mV (248-484 mV) with the exception of one sampling date (September 1, 1979) that had an Eh of 71 mV. On most occasions Eh values were greater than 100 mV down to at least 12 cm in the sediment. Although in Toolik Lake sediments nitrification is thermodynamically an unfavored process, the above observations suggest that it is favorable in the more oxidized surface sediments. Denitrification is thermodynamically favored in the deeper, more reduced zones to a sediment depth of at least 12 cm.

The estimated rates of nitrification are potential rates rather than *in situ* as the experiments used to determine the rate of nitrification were incubated under normal atmospheric conditions. This would cause the samples to become more oxygenated than the *in situ* sediment conditions, and an increase in nitrification would be expected. The

measured rates of nitrification could be used as a reasonable estimate of nitrification in the surface layer (0-3, 0-1, and 1-2 cm), where sediment Eh values show a more oxidized zone than the deeper, reduced layer. The rate of nitrification was shown as increasing on September 14, 1979, which is unlikely to occur at the *in situ* conditions but in the more oxygenated assay conditions, one would expect nitrification to increase with an increase of available substrates. Results of the inorganic ammonium assays show that ammonium concentrations increase with increasing sediment depth.

Nitrification rates calculated using the $^{15}\text{N-NH}_4^+$ tracer technique were lower than those calculated using the $^{15}\text{N-NO}_3^-$ dilution technique. The former technique measures the flux of $^{15}\text{N-NH}_4^+$ to the NO_3^- pool through ammonium oxidation which has several intermediate pools, whereas the latter technique measures only the NO_3^- pool turnover rate. The lower rates observed using the $^{15}\text{N-NH}_4^+$ tracer technique could be due to an increased time necessary for equilibration of the ^{15}N -isotope among the intermediate pools.

The measured rate of denitrification in the Smith Lake water column using the C_2H_2 blockage technique was $35 \text{ ng N}\cdot\text{cm}^{-3}\cdot\text{d}^{-1}$ at 5°C during February 1981. Goering and Dugdale (1966) in an earlier study at Smith Lake estimated the winter water column denitrification at $15 \text{ ng N}\cdot\text{cm}^{-3}\cdot\text{d}^{-1}$ using nitrate concentration changes with time and a ^{15}N -labeling technique. Both this study and Goering and Dugdale's (1966) techniques produced similar rates of denitrification in Smith Lake.

Goering and Dugdale's (1966) rate of denitrification did not take into account N_2O production and assumed that N_2O was not a major endproduct of denitrification. The acetylene blockage technique confirms this, as N_2O measured in untreated samples accounted for 10% of the $N_2 + N_2O$ endproducts. The similarity of the denitrification results using different techniques for measurements indicates that the acetylene blockage technique can measure denitrification with adequate results and, therefore, can be used as an alternative method in measuring denitrification.

The Smith Lake water column samples showed a 2X increase in denitrification with added nitrate. With the ammonium addition, N_2O production rates were similar to samples without nutrient additions. These experiments suggest that denitrification is a major process in the Smith Lake water column. The nitrate addition also altered the endproduct ratio of $N_2:N_2O$. Untreated Smith Lake samples had a ratio of 9, whereas in those treated with nitrate the ratio decreased to approximately 1. Firestone *et al.* (1980) found the proportion of N_2O produced increased with increasing nitrate concentrations.

The acetylene blockage technique was used to measure denitrification in Toolik Lake sediments, and the results were quite different from the Smith Lake water column results where denitrification is a predominant process. In Toolik Lake sediments, it is apparent that both nitrification and denitrification are occurring. In a system where both bacterial processes occur, the use of the acetylene blockage technique to measure denitrification is limited.

Toolik Lake sediment samples that were not treated with acetylene gave an *in situ* rate of N_2O accumulation. The concentration of acetylene added to sediment samples (0.1 atm) was sufficient to completely inhibit ammonium oxidation; therefore, acetylene-treated samples gave a rate of denitrification. The sediment samples treated with acetylene showed less N_2O production than those without C_2H_2 treatment. The results suggest a denitrification rate lower than the *in situ* rate of N_2O production. There are two possible mechanisms for the lower denitrification rate; there is substantial N_2O production from nitrification or the denitrification rate was lower due to acetylene's inhibitory effect on the NO_3^- production from ammonium oxidation.

If nitrification was responsible for a large accumulation of the *in situ* N_2O , then N_2O production is approximately 25% of the estimated nitrification rate. Knowles *et al.* (1981) indicated that N_2O production by nitrifiers is generally less than 0.3% (sometimes as high as 10%) of the total ammonium oxidation rate. The potential nitrification rates calculated in this study are probably higher than the *in situ* rate because of oxygenated conditions during sample incubations. Yoshida and Alexander (1970) observed increases in N_2O accumulation from nitrification with increases in nitrate concentrations. Although July's small nitrate addition did not stimulate great variability, a pattern similar to that of August's large nitrate addition (if samples having apparent gas leakage are disregarded), of greater N_2O production in the presence of acetylene, was observed. The nitrate did not

stimulate greater N_2O production in July's acetylene untreated samples, but in August a 1.5X increase in acetylene untreated samples was observed.

If the denitrification rate was dependent on the nitrate supply rate, a decrease in the denitrification rate would be expected with the addition of acetylene. Since there is no nitrate accumulation in the sediments or strong gradients, which would suggest a flux of nitrate to the water column, the ^{15}N -labelling experiments indicate a continuous supply of nitrate is important for denitrification to proceed. Disregarding samples with apparent gas leakage, there was greater N_2O production in the presence of acetylene in July's nitrate addition. This was more noticeable in the deeper 6-10 cm sections. In August with the larger nitrate addition, greater N_2O production (a 9X increase) in the presence of C_2H_2 than without C_2H_2 (a 1.5X increase) was observed. This nitrate addition not only compensated for the inhibitory effects of acetylene on nitrification, because it was much larger than the nitrification rate, but also would have supplied enough nitrate if nitrate was limiting to *in situ* denitrification. In acetylene-treated samples without a nitrate addition, there was a further decrease and/or reduction of N_2O in the 24-48 or 12-24 h period. This would also support the observation of the lower denitrification rate because of the acetylene inhibition of nitrification.

Even with the large nitrate addition, the calculated denitrification rates were within the lower range of the estimated nitrification range. The average rates of both processes were similar. Assuming the

estimated nitrification rate is a reasonable estimate of the *in situ* rate, the above observations suggest Toolik Lake sediments are not necessarily sensitive to large increases in nitrate concentrations but more sensitive to lower nitrate concentration changes, such as perturbations to the *in situ* nitrate supply rate. Other possible limiting factors for Toolik Lake sediment denitrification could be available organic matter, low phosphorus, low temperature, or lower bacterial activity.

An average denitrification rate of $44 \text{ ng N} \cdot \text{cm}^{-3} \cdot \text{d}^{-1}$ ranging from 20-64 $\text{ng N} \cdot \text{cm}^{-3} \cdot \text{d}^{-1}$ was calculated using the denitrification rates with the large nitrate addition, whereas without the nitrate addition a denitrification rate ranging from 0-22 $\text{ng N} \cdot \text{cm}^{-3} \cdot \text{d}^{-1}$ and averaging 9 $\text{ng N} \cdot \text{cm}^{-3} \cdot \text{d}^{-1}$ was calculated (N_2O data from June, July, and August 1980 at 10 m was used).

Information on the N_2O produced by denitrification in the presence and absence of acetylene is needed to determine the $\text{N}_2:\text{N}_2\text{O}$ ratio. A portion of the N_2O accumulated in the absence of acetylene is from nitrification. The amount of N_2O contributed by ammonium oxidation is unknown; therefore, a $\text{N}_2:\text{N}_2\text{O}$ ratio for denitrification cannot be determined in Toolik Lake sediments.

The pattern of initial N_2O production with a subsequent reduction was observed in the Smith Lake water column and in Toolik Lake sediment samples. Firestone and Tiedje (1979) described this pattern as occurring in response to anoxia and suggested it was a result of the

staggered synthesis of denitrifying enzymes, not from changes in nitrate concentrations. They found this pattern did not occur in the presence of chloramphenicol, a known inhibitor of protein synthesis, indicating that the increase in N_2O reducing activity resulted from *de novo* protein synthesis.

The Toolik Lake sediment denitrification rate ranged from 20-64 $ng\ N \cdot cm^{-3} \cdot d^{-1}$ (12-40 $ng\ N \cdot g^{-1} \cdot d^{-1}$, gram wet weight) with an average rate of 44 $ng\ N \cdot cm^{-3} \cdot d^{-1}$. The Toolik Lake sediment nitrification rate ranged from 7-199 $ng\ N \cdot cm^{-3} \cdot d^{-1}$ (5-131 $ng\ N \cdot g^{-1} \cdot d^{-1}$, gram wet weight) with an average of 49 $ng\ N \cdot cm^{-3} \cdot d^{-1}$. Iizumi *et al.* (1980) measured denitrification and nitrification using NO_3^- concentration changes and a ^{15}N -labeling technique in a highly reduced eelgrass bed at Izembek Lagoon, Alaska. Their sample incubations were conducted under aerobic conditions and an estimated rate of denitrification and nitrification was calculated as being of the same order 16.4-403.2 $ng\ N \cdot g^{-1} \cdot d^{-1}$ (gram wet weight). It was demonstrated that O_2 was being transported from the leaves of the eelgrass to the rhizomes and roots of the eelgrass and also being released to the anoxic sediments, thus providing a necessary oxic microzone for nitrification. Koike and Hattori (1978) measured nitrification and denitrification simultaneously, using a $^{15}N-NO_3^-$ dilution technique in three types of marine sediment: muddy, rich in organics; sandy; and sandy with eelgrass. They found denitrification predominated in the muddy sediments, nitrification predominated in the sandy, and in the eelgrass found both processes occurring at similar

rates. Their measurements were made under normal atmospheric conditions. Koike and Hattori's (1978) estimated rates of denitrification and nitrification are as follows: muddy sediment, $420 \text{ ng N} \cdot \text{g}^{-1} \cdot \text{d}^{-1}$ (gram dry weight) for denitrification and $56 \text{ ng N} \cdot \text{g}^{-1} \cdot \text{d}^{-1}$ for nitrification; sandy sediment, $14 \text{ ng N} \cdot \text{g}^{-1} \cdot \text{d}^{-1}$ for nitrification and $1.4 \text{ ng N} \cdot \text{g}^{-1} \cdot \text{d}^{-1}$ for denitrification; and sandy sediment with eelgrass, both nitrification and denitrification as $140 \text{ ng N} \cdot \text{g}^{-1} \cdot \text{d}^{-1}$. Using the C_2H_2 blockage technique and samples that were purged with N_2 , Sorensen (1978) estimated a denitrification rate of $490 \text{ ng N} \cdot \text{cm}^{-3} \cdot \text{d}^{-1}$ in marine sediment. The estimated rates of nitrification and denitrification in Toolik Lake sediments are on the lower end of the scale when compared to other reported rates, although Prentki *et al.* (1980) observed even lower denitrification rates, $0.17\text{-}0.19 \text{ ng N} \cdot \text{cm}^{-3} \cdot \text{d}^{-1}$, in a pond in Barrow, Alaska.

The rate of *in situ* N_2O production ranged from $0\text{-}25 \text{ ng N} \cdot \text{cm}^{-3} \cdot \text{d}^{-1}$. It is most likely produced from both nitrification and denitrification. The proportion of N_2O accumulated by either process cannot be determined. The N_2O concentrations at 0 h ranged from $87\text{-}582 \text{ pmol N}_2\text{O} \cdot \text{cm}^{-3}$ and averaged $343 \text{ pmol N}_2\text{O} \cdot \text{cm}^{-3}$. Using 400 ppb as the atmospheric N_2O concentration, the Toolik Lake sediment ranged from 435-2910% saturated with N_2O (at 5°C). McElroy *et al.* (1978), in a study of the production and release of N_2O in the Potomac Estuary, measured N_2O concentrations in the river sediment ranging from $20\text{-}1100 \text{ pmol N}_2\text{O} \cdot \text{cm}^{-3}$ in the upper 40 cm of sediment. Their observations indicated that N_2O may be

produced primarily near the sediment-water interface, and suggested a large release of N_2O may occur in shallow embayments, < 1 m, in response to turbulence associated with tidal currents. Since Toolik Lake sediment samples showed a reduction of N_2O after the initial N_2O production, uncertainty exists as to whether much of the N_2O produced is being released to the water column.

The Toolik Lake sediment inorganic nitrogen pool consists of 99.65% ammonium, where 80.07% is exchangeable ammonium and 19.57% is interstitial ammonium; 0.06% nitrate plus nitrite; and 0.28% nitrous oxide. Although the average nitrification rate is slightly higher than the average denitrification rate, both rates are similar. Therefore, high concentrations of nitrate or nitrite are not expected. Nitrification and denitrification contribute to the N_2O pool and the estimated rates for both of these processes were low. Denitrification is known to further reduce N_2O to N_2 . Therefore, high concentrations of N_2O are not expected.

Inherent in these experiments are errors associated with sampling and processing techniques. The sampling site was chosen for its depth and convenience and was located in close proximity to an inlet. The inlet could be a significant source of organic matter and inorganic nutrients which could result in higher denitrification and nitrification rates than those found in other parts of the lake sediment. The error from core variability is probably great, particularly if the bacterial populations have a patchy distribution.

The techniques employed in this study also have their limitations. The ^{15}N -methodology used for measuring the rate of nitrification alters the *in situ* rates and measures a potential rate by the addition of substrates in higher concentrations than those found in the sediment and by oxygenated incubation conditions. The C_2H_2 blockage technique, where sediment cores were processed in an N_2 environment, provides an *in situ* rate of denitrification without a substrate addition, but the effect on microorganisms of sample manipulation is unknown. Smith *et al.* (1978) found no adverse effects of C_2H_2 on denitrifiers within a 12 h assay period. However, there is conclusive evidence of its inhibitory effect on nitrifiers (Bremner and Blackmer, 1978; Walter *et al.*, 1978; Blackmer *et al.*, 1980) and on organisms whose growth is supported by methane or methanol (Knowles, 1979). Nitrogen-fixers are also affected by C_2H_2 , as they will readily reduce C_2H_2 to C_2H_4 (Stewart *et al.*, 1967).

Incubation periods could also affect rates of denitrification and nitrification. Long incubation periods tend to cause substrate availability to become limiting, and in some instances shorter incubations may not have allowed enough time for gases or ^{15}N -isotope to equilibrate with all intermediate pools necessary to measure nitrification.

In retrospect, there are several changes in sampling and experimental design that would have enhanced this study. A concentrated effort to study the surficial sediments, 0-3 cm, rather than the larger sediment increment, 0-12 cm, in defining finite zones of oxidative

processes and reducing processes would have been useful. All sediment cores should have been processed within a glove bag so as to minimize sediment contact with the atmosphere. With larger samples, sample processing would have been easier, and greater precision may have been attained. The addition of N-serve (2-chloro-6-trichloromethylpyridine), a known inhibitor of ammonia oxidation, in conjunction with the C_2H_2 blockage technique, would block out ammonium oxidation, and thus a measure of the $N_2:N_2O$ ratio from denitrifiers and the amount of N_2O produced by nitrifiers could have been calculated. Finally, had a profile of the N_2O concentrations within the Toolik Lake water column been made, a flux of N_2O from the sediment to the atmosphere could have been calculated, and an estimate of the impact this N_2O production has on the N_2O cycle could have been made.

CONCLUSIONS

1) Toolik Lake sediments contained low levels of inorganic nitrogen. Interstitial and exchangeable nitrogen increased with sediment depth, whereas nitrate and nitrite decreased with sediment depth. Ammonium was the predominant inorganic nitrogen species throughout the sediment column. Nitrous oxide concentrations were low in comparison with the total inorganic nitrogen pool; however, the interstitial water was oversaturated (435-2910% saturated) with respect to the N_2O concentration in the air (400 ppb).

2) Toolik Lake sediments were in a mixed equilibrium rather than in complete equilibrium with respect to nitrogen. Eh measurements increased with increasing sediment depth, whereas pH measurements decreased. The pE + pH values indicated a surface (0-3 cm) oxidized layer with deeper sediment becoming more reduced with depth.

3) The ^{15}N -labeling techniques and the C_2H_2 blockage technique confirm the occurrence of nitrification and denitrification and also indicated that both processes contribute to the *in situ* production of nitrous oxide. The measured potential rates of nitrification are a first attempt at estimating the rates of nitrification in the surface oxidized layer. Although the estimated rates of nitrification (ranging from 7-199 $ng\ N \cdot cm^{-3} \cdot d^{-1}$, with an average of 49 $ng\ N \cdot cm^{-3} \cdot d^{-1}$) were higher than the denitrification rates (ranging from 20-64 $ng\ N \cdot cm^{-3} \cdot d^{-1}$, with an average of 44 $ng\ N \cdot cm^{-3} \cdot d^{-1}$), both average rates are similar. The overall rates of nitrification and denitrification are low when

compared to other sediment-water systems. The *in situ* nitrous oxide production ($0-25 \text{ ng N}\cdot\text{cm}^{-3}\cdot\text{d}^{-1}$) was similar to the denitrification rate, although the contribution from either nitrification or denitrification was not discernable. A large nitrate addition did stimulate denitrification activity. The calculated rate was lower but of the same order as the estimated nitrification rate, suggesting that other factors may limit denitrification in this arctic lake system.

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