AN ABSTRACT OF THE THESIS OF

Marie Agatha de Angelis ___ for the degree of _Master of Science_

in ____Oceanography____ presented ___January 25, 1980___

Title: _Nitrous Oxide Studies in Two Marine Environments: An Unpolluted_

Estuary and the Interstitial Water of a Deep Sea Sediment.

Abstract approved:
Dr. Louis I. Gordon

Nitrous oxide (N_2O) is a constituent of the nitrogen cycle in the marine environment. Investigations into the concentration and distribution of dissolved nitrous oxide were carried out in two diverse environments: 1) a relatively unpolluted estuary on the Oregon Coast and 2) the interstitial waters of a deep-sea sediment located near the Galapagos Spreading Center in the eastern Pacific Ocean. These studies were conducted with two basic objectives in mind. First, to determine if these environments serve as sources or sinks of dissolved N_2O to the ocean and/or atmosphere in the case of the estuary and to the ocean in the case of the deep-sea sediment. Second, to attempt, by measuring other constituents of the nitrogen cycle concurrently, to elucidate the role of nitrous oxide in the various processes involved in marine nitrogen cycles.

The results of surface water sampling in the estuary, Alsea Bay, Oregon, indicated that this environment served as a variable source of N_2O to the atmosphere during the three month sampling period in the summer of 1979. Nitrous oxide saturations ranged from 90% to 239%. Undersaturation occurred in only three out of 88 samples collected. Based on this data, an upper limit for the average annual flux of N_2O

across the air-water interface was estimated to be 1.75×10^6 moles N_2O yr^{-1} (7.7×10^7 g N_2O yr^{-1}).

The concentrations of nitrous oxide, nitrate and nitrite showed significant changes over the course of the summer. Large initial increases of all three species are attributed to nutrient-rich upwelling water being brought into the estuary with the tide. Later in the summer, the data suggest the possibility of N_2O participation in assimilatory nitrate reduction, as all of the fixed nitrogen species measured decrease in concentration. Contributions to the overlying water from processes taking place in the sediment may be significant, but could not be determined from this study.

Sampling of the Alsea River was also conducted on three occasions in late summer and early autumn of 1979. Significant N_2O variations in river samples were found before and after the rainy season began, with higher N_2O values occurring after flood conditions in the river were established. This suggests that soil runoff contributes to increased N_2O concentrations in rivers. The river samples showed N_2O saturations ranging from 94% to 166%.

In deep-sea sediments near the Galapagos Spreading Center, interstitial water profiles of nitrate plus nitrite and molecular nitrogen suggest that denitrification is occurring in the upper 25 cm of the sediment. If this is the case, then the N_2O profiles at the same locations indicate that denitrification in this marine environment results in both the production and consumption of N_2O. Consumption of nitrous oxide occurs deeper in the pore water within and below the nitrate reduction zone. However, N_2O maxima of nine to forty times ambient water column concentrations were observed in the upper pore water of

the sediment, resulting in a net diffusive flux of N_2O out of the sediments. Thus, the sediments sampled here serve as sources of nitrous oxide to the open ocean water column.

An upper limit to the total diffusive flux of N_2O out of deep-sea sediments is estimated to be 7.0×10^{11} moles N_2O yr^{-1} (3.1×10^{13} g N_2O yr^{-1}), a number comparable to the estimated flux of N_2O from open ocean surface waters to the atmosphere. The estimated flux of nitrate plus nitrite into the sediment is sufficient to support the upper pore water nitrous oxide maxima and consequent diffusive flux of N_2O out of the sediment.

Nitrous Oxide Studies in Two Marine Environments:
An Unpolluted Estuary and
The Interstitial Water of a Deep-Sea Sediment

by

Marie Agatha de Angelis

A THESIS

submitted to

Oregon State University

in partial fulfillment of
the requirements for the
degree of

Master of Science

Completed January 25, 1980

Commencement June, 1980

APPROVED

Associate Professor of Oceanography
in charge of major

Dean of the School of Oceanography

Dean of Graduate School

Date thesis is presented _____ January 25, 1980

Typed by CFS Typing Service Limited for Marie Agatha de Angelis

ACKNOWLEDGMENTS

"...This way madness lies." I think King Lear must have been a graduate student once to have come up with a line like that. If he was he didn't tell the whole story, for in the way that led to this thesis, besides the madness there was also much happiness, friendship and help. The thanks and acknowledgments given below are inadequate to express my gratitude towards all those who have helped me along the way.

I would like to thank my major advisor, Dr. Louis I. Gordon, for his help and support during my entire time here. I am especially grateful for his insistence on my participation on the Galapagos cruise.

Dr. John Baross helped with a number of constructive criticisms of many topics in this thesis.

I would also like to thank those teachers from my undergraduate years at Hofstra University who influenced the course of my life- Dr Howard Rosman and Dr. Bruce Brunschwig for instilling in me a sense of chemistry, and Dr. Edward Chalfant for his patience in teaching me not only how to write but also how to think clearly.

Many people helped in the collecting and analyzing of the samples. The Alsea Bay portion of this research would have come to grief without the efforts of those who ventured out on an open boat to help me collect samples. These brave souls were Marvin Lilley, Jenaro Acuna, Cliff Dahm, Marie de Angelis, Joseph de Angelis, Gary Hewitt, Chris Evans and Vicki Fagerness. Special thanks go to Chris Evans who survived 5 trips to Alsea Bay and whose sense of humor survived even in the face of slugs, soakings and motors powered by anemic squirrels on treadmills.

I would like to thank Jerry McNutt of the Bureau of Land Management

for showing me the source of the South Fork.

A grateful note of appreciation is given to McKinley's Marina for always renting me boats with motors that worked. Others who failed in this regard shall remain nameless.

Sandy Moore and Beth Dworetizky ran the nutrient samples from Alsea Bay. Philip Froelich analyzed the nutrients from the interstitial water samples. I would especially like to thank Dr. Ross Barnes for making the interstitial water samples available to me and for allowing me to use the nutrient and N_2 data in this thesis. Marv Lilley taught me everything I know about gas chromatography; this research wouldn't have gotten off the ground without his help in the lab.

The abovementioned people helped me directly in this research and without their help this thesis would obviously not have been written. I am exceedingly grateful to all of them. There are also those who helped me in less tangible but certainly no less important ways.

The Chicken Fried Steak Club at the Peacock- Marv Lilley, Becky McClurken, Wendy Gabriel and Eric Olson- deserve special thanks for literally convincing me I could write this thesis. Wendy Gabriel (a.k.a. H. Keller, CFS Typing Service Limited) deserves a medal for her heroic typing feats in the wee hours of the morning.

I am specially grateful to Becky McClurken and Marv Lilley for talking me into staying when I was at the point of leaving.

Wendy Gabriel provided end of the month dinners, impromptu cello lessons, friendship and much moral support.

The Top Rail pool contingent provided many hours of enjoyment and much needed relaxation.

Rich Cobler helped me get into the spirit of my thesis subject.

I have tried and I have tried to come up with the words to express Marv Lilley's contributions to this work and to my life but it's like trying to describe what it's like to see the white light- it's just not possible to bring it back and put it into words. So all I will say is this: Marv has been a true friend in every sense of the word- they don't come any better. Thanks Marv- it's been a pleasure and a privilege.

Mike Rodman helped me preserve my perspective with many hours of stimulating and enjoyable discussion on every conceivable topic except oceanography.

Dave Plath supplied enjoyment and diversion beyond the lab.

Vicki Fagerness, Wayne Dickinson, Bill Armstrong, Lisa Kaskan and Eric Olson provided encouragement and good company.

Marv Lilley, Wendy Gabriel and Rich Cobler made my years here truly memorable. I thank them for the pleasure of their company.

Al Stewart provided fitting lyrics.

Thanks to anyone who has ever raised a glass in friendship with me.

Most of all, I would like to thank my parents whose love for me and faith in me in all the years and across all the miles has never faltered. It has meant more to me than I can ever say.

TABLE OF CONTENTS

LIST OF TABLES

PREFACE

This thesis has been written in manuscript form, as recommended by the School of Oceanography in order to facilitate publication in a scientific journal. The first chapter of this thesis will be submitted to Deep-Sea Research with Marie de Angelis as first author and Louis I. Gordon as second author. The second chapter will also be submitted to a journal with Marie A. de Angelis as first author and Louis I. Gordon, Ross O. Barnes, Philip Froelich and Michael Bender as minor authors.

CHAPTER I

DISSOLVED NITROUS OXIDE IN ALSEA BAY, OREGON

ABSTRACT

Surface waters of Alsea Bay, an unpolluted estuary on the Oregon Coast, were analyzed for N_2O on a weekly or biweekly basis during the summer of 1979. The estuary was found to be a variable source of N_2O to the atmosphere with supersaturation values ranging from 104% to 239%. Systematic variations in the concentrations of N_2O, NO_3^-, and NO_2^- were observed during the course of the sampling period. Large and rapid increases in the concentrations of these nitrogen species occurred at the beginning of the sampling period and are attributed to the influx of nutrient-rich upwelling water into the estuary with the tide. The subsequent decline in concentrations of nitrate, nitrite and nitrous oxide over the remainder of the summer is attributed to assimilatory nitrate reduction taking place in the estuary and/or surface coastal waters which are subsequently transported into the estuary.

Measurements of nitrous oxide at six stations along the Alsea River were also made on three dates in September and October of 1979 both before and after the beginning of the rainy season. Samples taken after flood conditions were established were found to be systematically 50% higher than pre-flood samples. The data suggest that soil runoff results in elevated concentrations of N_2O in rivers.

DISSOLVED NITROUS OXIDE IN ALSEA BAY, OREGON

INTRODUCTION

Nitrogen is a micronutrient necessary for primary production in the marine environment. Consequently, an understanding of the marine nitrogen cycle is important. One of the constituents of this cycle is the trace gas nitrous oxide (N_2O), whose role in the aquatic nitrogen cycle has only recently been examined in detail. With molecular nitrogen (N_2), nitrous oxide represents a potential loss of fixed nitrogen from this environment.

Most studies of dissolved nitrous oxide in the aquatic environment have taken place in the open ocean (Craig and Gordon, 1963; Yoshinari, 1976; Hahn, 1974,1975; Cohen and Gordon, 1978a; Elkins, Wofsy, McElroy, Kolb and Kaplan, 1978). In all cases where the water was well-oxygenated it was found that N_2O was negatively correlated with oxygen at all depths and positively correlated with nitrate. In addition N_2O was found to be present in concentrations in excess of expected saturation values with respect to the atmosphere at the temperature and salinity conditions observed. From these observations, Yoshinari (1976) and Cohen and Gordon (1978b) concluded that nitrification, the process by which ammonium (NH_4^+) is oxidized to nitrate (NO_3^-), results in the production of N_2O in the ocean.

Evidence for the consumption of N_2O in the marine environment has been observed in the oxygen depleted waters of the Eastern Tropical North Pacific (Cohen and Gordon, 1978b), off the coast of Peru (Elkins et al.,1978) and in the intermittently anoxic waters of Saanich Inlet (Cohen,1978). In these regions, a nitrous oxide minimum in the water

column was observed to coincide with both an oxygen minimum and a nitrite maximum. The coinciding oxygen minimum and nitrite maximum are characteristic of a denitrification regime in which nitrate is reduced to molecular nitrogen (Goering, 1968; Cline and Richards, 1972). From these studies it was concluded (Cohen, 1978; Cohen and Gordon, 1978b) that the net result of denitrification is the consumption of N_2O.

The process of denitrification is believed to occur according to the sequence $NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$ (Payne, 1973). From this sequence it can be seen that although N_2O is reduced to N_2 and thus consumed, at some time in the course of denitrification it is produced as well, however transiently. The discovery that acetylene can block this final reduction of N_2O to N_2 (Fedorova, Milekhina and Il'Yukhina, 1973) has resulted in a number of studies (Yoshinari, Hynes and Knowles, 1977; Balderston, Sherr and Payne, 1976; Yoshinari and Knowles, 1976) in which it is shown that N_2O is an intermediate in denitrification.

One of the most compelling reasons for the recent interest shown in dissolved N_2O in the oceans has been the concern that N_2O dissociation in the stratosphere could result in a reduction of the ozone layer (Crutzen, 1970). Concern had arisen that increasing use of artificial fertilizers (Johnston, 1977; Liu, Cicerone, Donahue and Chameides, 1977; Crutzen, 1976) and combustion of fossil fuels (Weiss and Craig, 1976; Pierotti and Rasmussen, 1976) will result in the concurrent increase in stratospheric N_2O levels and a subsequent further depletion of the ozone layer. Recent reevaluations of photochemical reaction rates in the atmosphere (Turco, Whitten, Poppoff and Capone, 1978; Whitten, Borucki, Capone, Riegal and Turco, 1980) have lessened the importance of N_2O in this regard. Despite this, it remains of importance to

determine the major sources and sinks of N_2O for the atmosphere and biosphere, as well as their relative magnitudes, in order to evaluate the relative importance of N_2O in various nitrogen cycles and the effects of the increasing input of N_2O from anthropogenic sources on these cycles.

The only known sink for atmospheric N_2O is in the stratosphere through photodissociation and reaction with excited oxygen atoms (Hahn and Junge, 1977). The land is generally considered to be a major source of N_2O through bacterial denitrification and nitrification in the soil (Hahn and Junge, 1977; Bremner, 1978). Measurements of N_2O throughout the surface waters of the North Atlantic (Hahn, 1975; Yoshinari, 1976), the Northeast Pacific (Cohen and Gordon, 1978a), the Central Pacific (Elkins et al., 1978) and the Eastern Tropical North Pacific (Cohen and Gordon, 1978b; Rasmussen, Krasnec and Pierotti, 1976) indicate that the oceans are a source of N_2O to the atmosphere. An average supersaturation of 109% was estimated from these studies (Cohen and Gordon, 1978a).

Some studies of N_2O in aquatic systems other than the open ocean have been made recently. Elkins et al. (1978) reported undersaturation of N_2O in the surface waters of Chesapeake Bay during the summer, as well as in nearby tidal salt marshes, thus suggesting that estuaries and salt marshes might serve as sinks for atmospheric N_2O. McElroy, Elkins, Wofsy, Kolb, Duran and Kaplan (1978) and Kaplan, Elkins, Kolb, McElroy, Wofsy and Duran (1978) reported N_2O production and supersaturation in the Potomac River and Estuary and attributed this excess N_2O to the effects of pollution and sewage treatment plants. Kaplan et al. (1978) also examined two freshwater ponds and observed that one pond was a strong source of N_2O to the atmosphere, while the other was

a sink for N_2O. Cicerone, Shetter and Liu (1978) measured dissolved N_2O in two Michigan rivers and one lake and found that all of these systems contained excess N_2O. They also attributed these supersaturations to pollution sources. No detailed study of an unpolluted freshwater or estuarine system has been reported.

This paper presents the results of a three month study of N_2O in the surface waters of an unpolluted Oregon estuary, Alsea Bay, in the summer of 1979. The purpose of the study was twofold: the first objective was to determine if this relatively natural estuary and its associated river system serve as sources or sinks of N_2O to the atmosphere. The second object of the study was to attempt to elucidate the role of N_2O in the estuarine nitrogen cycle and determine if the processes controlling the concentration of N_2O in this environment are the same as in other marine environments, such as the open ocean.

METHODS

Experimental site

Alsea Bay (Figure 1) is a drowned river valley on the Oregon coast

located at 44° 26' N latitude and 124° 05' W longitude, approximately

130 miles south of the mouth of the Columbia River. The bay is supplied

chiefly by the Alsea River which rises on the western side of the Coast

Range. River runoff is low during the summer months. The tides are

semi-diurnal and the mean tidal range is 1.8 meters (Matson, 1972). The

tidal prism is $1.4 \times 10^7 m^3$. Tidal influence is felt to about 16 miles

from the mouth. The surface area of the bay is reported as 8.78×10^8

m^2 at mean high water and $4.73 \times 10^8 m^2$ at mean low water (Percy, Bella,

Sutterlin and Klingeman, 1974). The bay is shallow, not exceeding 2 m

in most sections. During the summer the bay is well-mixed and no

stratification takes place (Burt and McAlister, 1959).

Sampling

Sampling was conducted on six occasions during July, August and

September of 1979. On the first two sampling dates, July 13 and July

25, both surface samples and samples at one meter depth intervals were

taken. Salinity and other parameters showed the estuary to be well

mixed and on subsequent occasions only surface samples were taken.

Water samples were collected at 1 to 5 stations (Figure 1) at various

stages of the tidal cycle on each date. Sampling was conducted from a

14 foot open boat by means of either an all-plastic, battery driven

centrifugal pump or a hand operated peristaltic pump. In either

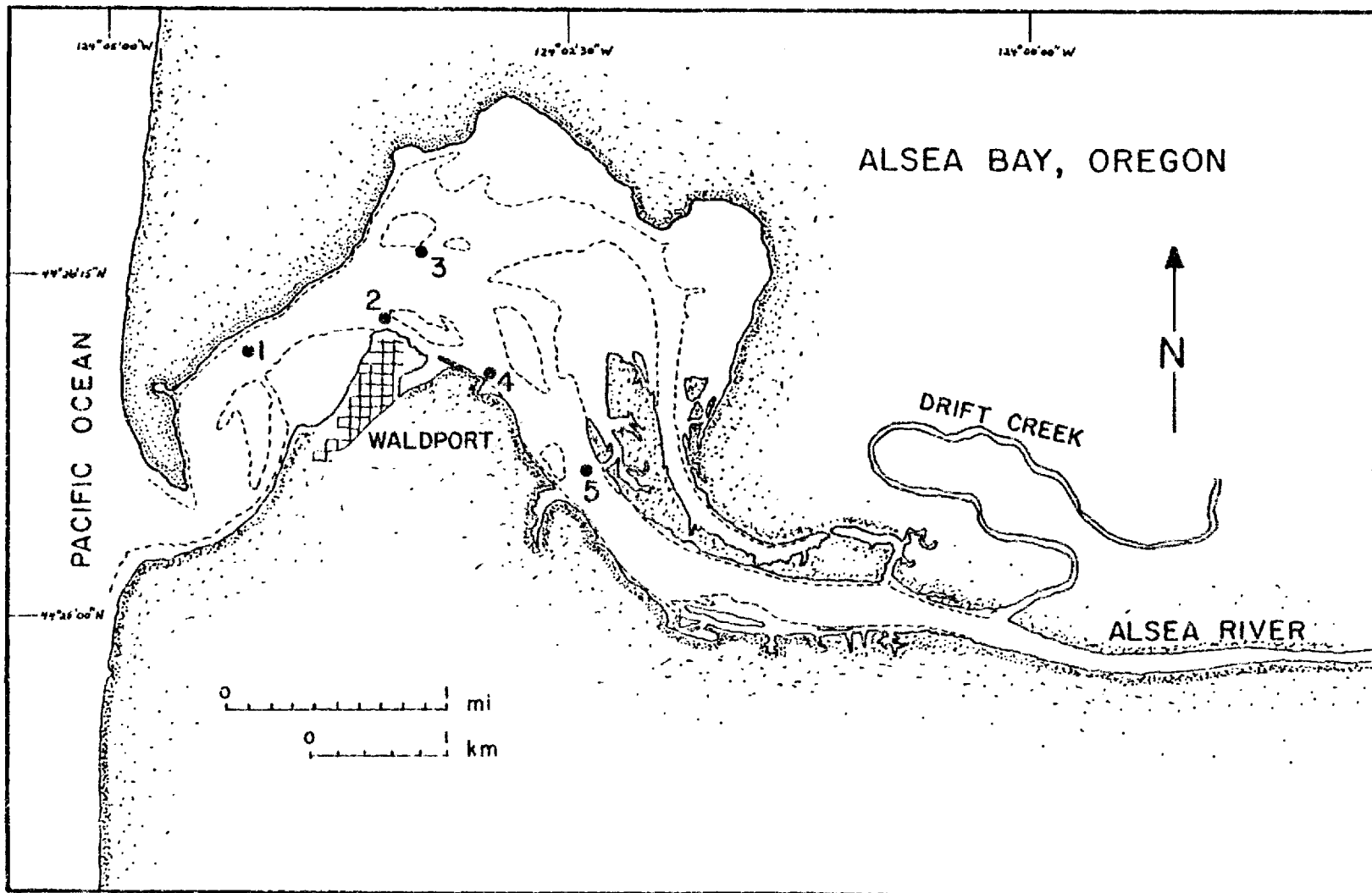sampling method, samples were not drawn until air bubbles had been

Figure 1. Alsea Bay, Oregon and station locations for summer, 1979 sampling. Dashed lines delineate tidelands exposed at mean low water.

excluded from the pump. Nitrous oxide samples were collected in either 125 cc or 25 cc Pyrex[R] gas sampling flasks with ungreased Teflon plug stopcocks, and poisoned with 100 ppm $HgCl_2$. Poisoning tests indicated that $HgCl_2$ preserved N_2O concentrations for at least 16 days. Samples were run within a week of sampling. Air samples for N_2O analysis were collected in 50 cc flasks similar to those used for N_2O water samples by means of a hand operated vacuum pump. Nutrient samples were frozen in dry ice and remained frozen in a freezer until thawed for analysis.

Analytical methods

Nitrous oxide was analyzed by means of the electron capture gas chromatographic method described by Cohen (1977). The precision of the method is ±2% and estimated accuracy is ±3%. Nutrients were measured by autoanalyzer techniques (Gordon, Dahm, Dickinson, Park and Standley, 1975). The precisions for the nitrate and nitrite analyses are ±5% and estimated accuracies are ±2% and ±5% respectively. Dissolved oxygen was measured by the Carpenter (1965) modification of the Winkler method. This method has a precision of 0.5% and an accuracy of ±0.3%. Salinity was measured on a Bissett-Berman inductive salinometer with an accuracy of ±0.003 ppt. Temperature was measured with a general laboratory thermometer with one division per degree Celcius.

Nitrous oxide values are reported in terms of % saturation throughout the text for three reasons. Primarily, there is a systematic disagreement between various laboratories measuring N_2O in air samples (Pierotti and Rasmussen, 1978). Reporting N_2O concentrations in terms of % saturation with respect to measured atmospheric values eliminates any systematic error in this variable provided both the water and air

samples are analyzed by the same method. Secondly, we were mainly
interested in the source/sink potential of the estuary with respect to
N_2O. This is directly dependent on whether the surface waters are
undersaturated or supersaturated with N_2O with respect to the atmosphere.
Hence, % saturation is the most natural form of reporting N_2O values
in this regard. Thirdly, the use of % saturation takes into account
the widely varying salinity and temperature conditions encountered in
an estuarine environment.

RESULTS

Although up to five stations were occupied throughout the estuary on any one date, only the results from station 2 will be presented and discussed in detail, although the data from all stations are used in calculations. Station 2 was the only station occupied on all six sampling occasions. The other stations, when occupied, showed similar results to those from station 2. No obvious spatial variations in N_2O concentrations throughout the estuary were observed. (See Appendix for a complete data listing).

On July 13, N_2O saturation values ranging from 104% to 143% over a five hour sampling period were observed (Figure 2, Table 1), corresponding to N_2O concentrations of 6.7 to 8.6 nM (1 nM = 10^{-9} moles 1^{-1}). All but one (143%) were in the range 104% to 115%, similar to the saturation values observed in open ocean surface waters (Cohen and Gordon, 1978a). Twelve days later on July 25, radically different dissolved nitrous oxide values were observed over the same tidal stage interval (Figure 2). Nitrous oxide saturations on this occasion ranged from 153% to 239% (10.1 to 18.6 nM) with maximal N_2O values occurring around high water.

We returned four more times in the next one and a half months and observed a systematic variation in N_2O concentrations over this time interval (Figure 2). Two observations can be made from the N_2O data presented in this figure. First, N_2O saturation values reached maxima at or near high water. Secondly, at all of the tidal stages examined, N_2O concentrations started out at near saturation levels at the beginning of July, increased sharply within the next two weeks and then
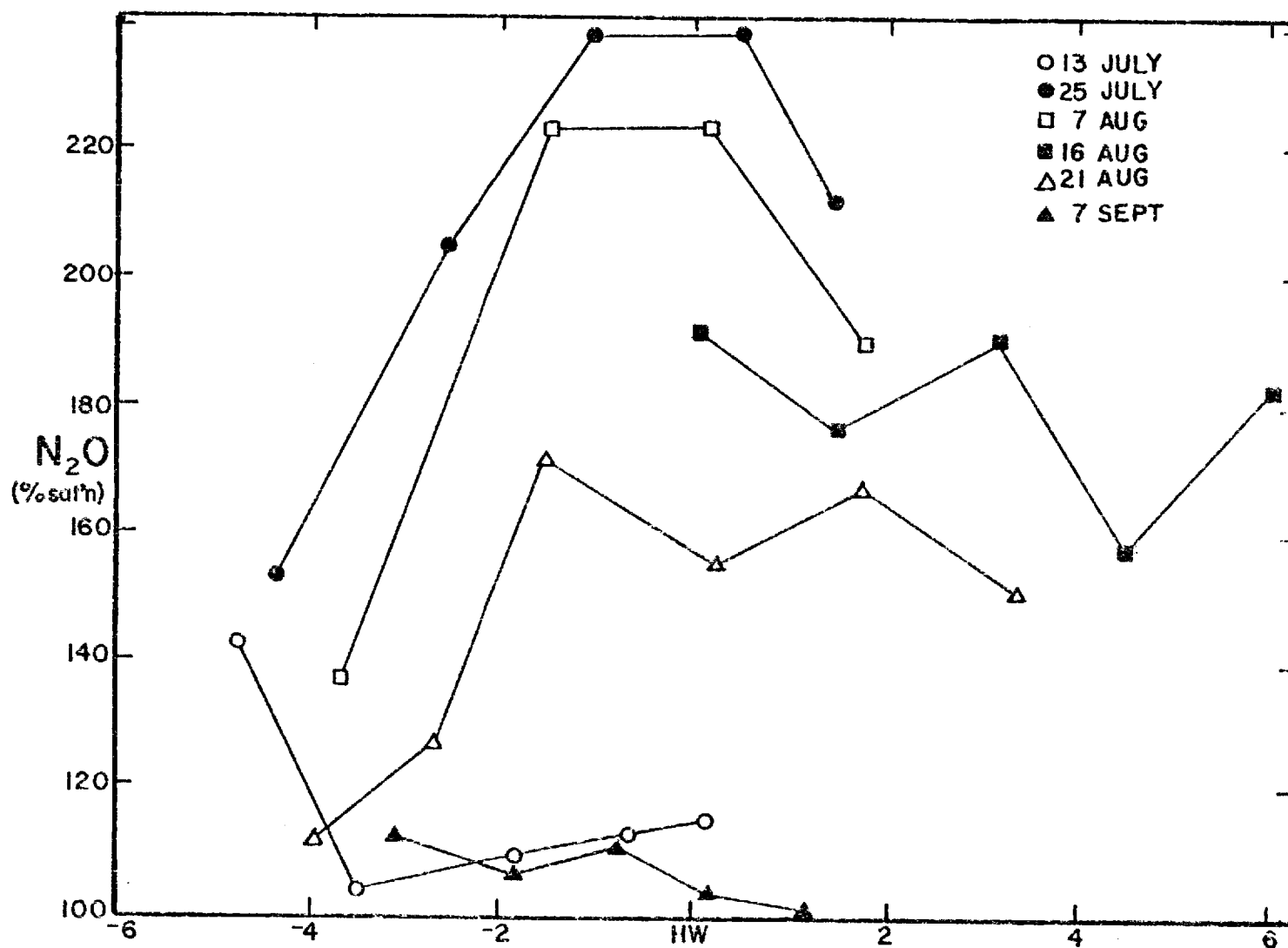
Figure 2. Nitrous oxide % saturation values vs. time (hrs) for all sampling dates at station 2 for all tidal stages sampled, summer of 1979.

decreased gradually but steadily as the summer progressed, reaching near saturation values again by early September.

This cyclic variation in N_2O over a three month period described in the second point above can most readily be seen by examining the N_2O data from each sampling date at one particular point in the tidal cycle. This has been done in Figure 3 in which the N_2O saturation values at high water for each of the six sampling dates have been plotted over the entire three month period. High water was chosen because station 2 was occupied at this tidal stage on every sampling date. Similar figures for tidal stages corresponding to two hours after high water and to one and a half, three and four hours after high water show comparable variations.

Nitrate and nitrite samples were taken at the same times and these species go through a cyclic variation similar to that undergone by N_2O. Nitrate concentrations of 0.06 µM (1 µM = 10^{-6} moles 1^{-1}) were observed at the beginning of July and increased sharply to a maximum of 21.7 µM in the same interval that N_2O undergoes its increase. Nitrate then decreases steadily, reaching a concentration of 0.015µM on the September sampling date. Nitrite followed a similar pattern with initial concentrations of 0.045 µM on July 13 and a maximum concentration of 0.22 µM on July 25. Nitrite values subsequently decreased to 0.035 µM by September 7.

Oxygen values for the same time period underwent a different pattern (Figure 3). Between July 25 and August 7, while all of the nitrogen species measured decreased slightly, O_2 also underwent a decrease from 221 µM O_2 to 191 µM O_2. However, as NO_3^-, NO_2^-, and N_2O decreased sharply by August 16, dissolved oxygen increased sharply to a
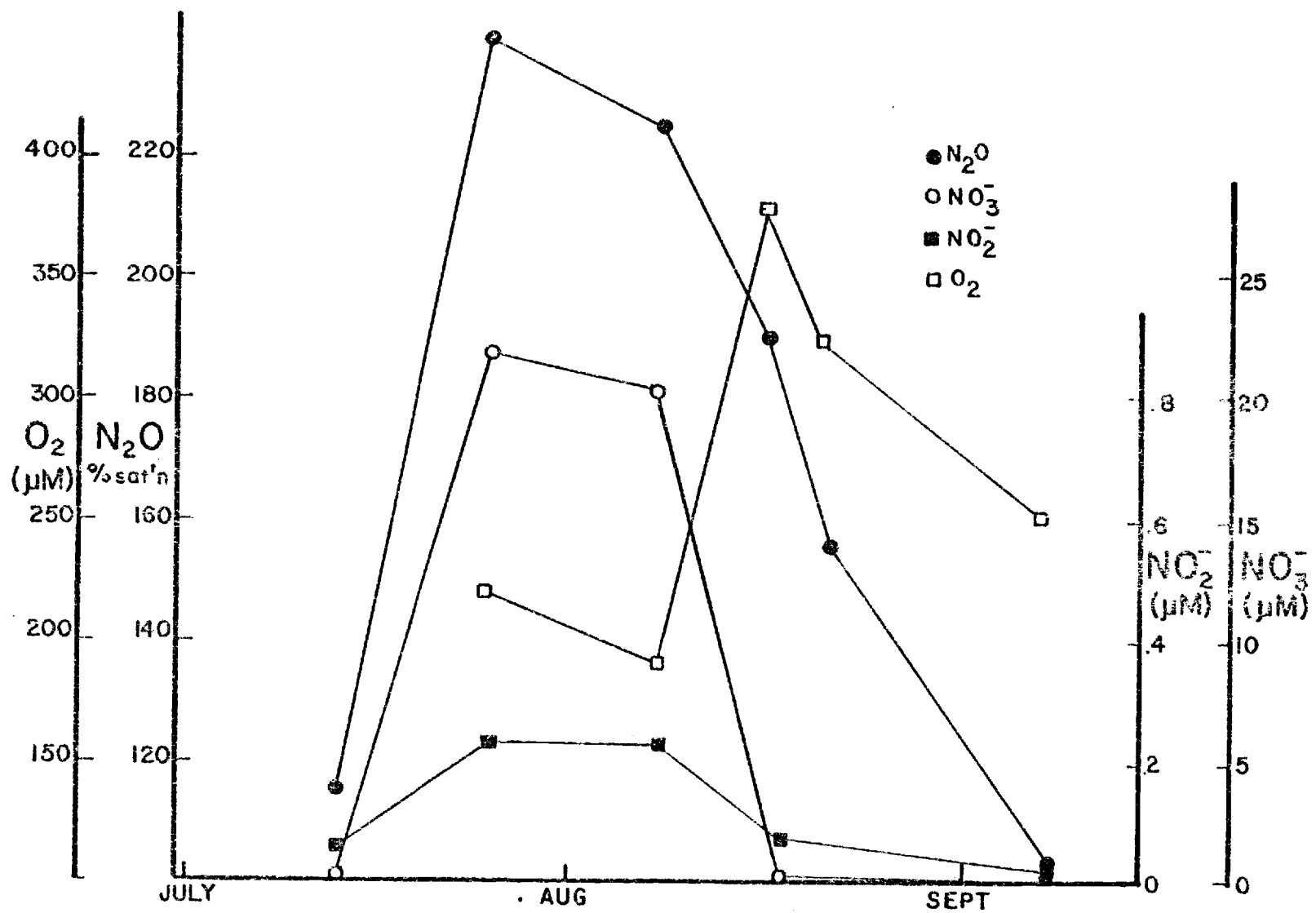
Figure 3. Nitrous oxide, nitrate, nitrite and dissolved oxygen concentration variations for summer, 1979 samples for station 2 at high water only.

maximum of 221 μM O_2. The apparent oxygen utilization (AOU), defined as O_2 saturation (T,S) $- O_2$ measured, went from positive values of 61 μM on July 25 and 93 uM on August 7 to a negative value of -110 μM on August 16. Thereafter, dissolved O_2 decreased steadily, reaching a near saturation value of 252 μM on September 7, corresponding to an AOU value of -8.9 μM. The data for the nitrogen species as well as for dissolved oxygen for station 2 at four different tidal stages are given in Table 1.

Table 1. Dissolved nitrous oxide, nitrate, nitrite, dissolved oxygen and apparent oxygen utilization (AOU) for station 2 at selected tidal stages. See Appendix for a full data listing.

THREE HOURS BEFORE HIGH WATER

Date	N_2O (nM)	N_2O (% sat'n)	NO_3^- (μM)	NO_2^- (μM)	O_2 (μM)	AOU (μM)
13 July	6.7	104	---	.18	---	---
25 July	15.9	205	24.7	.33	269	16.5
7 Aug	10.5	137	6.1	.24	215	45.0
21 Aug	8.9	127	0.22	.080	290	- 29.7
7 Sept	7.3	113	---	---	255	- 14.8

ONE AND A HALF HOURS BEFORE HIGH WATER

Date	N_2O (nM)	N_2O (% sat'n)	NO_3^- (μM)	NO_2^- (μM)	O_2 (μM)	AOU (μM)
13 July	6.9	109	0.10	.067	---	---
25 July	18.6	238	20.9	.20	219	66
7 Aug	20.7	225	24.0	.26	153	132
21 Aug	10.4	172	0.15	.080	334	- 75
7 Sept	6.8	107	0.37	.079	256	- 16.8

HIGH WATER

Date	N_2O (nM)	N_2O (% sat'n)	NO_3^- (μM)	NO_2^- (μM)	O_2 (μM)	AOU (μM)
13 July	7.6	115	0.06	.045	---	---
25 July	18.2	239	21.7	.22	221	61
7 Aug	20.6	225	20.5	.21	191	93
16 Aug	14.0	191	0.74	.067	377	-110
21 Aug	9.4	156	---	---	322	- 74
7 Sept	6.9	104	0.015	.035	252	- 8.9

ONE AND A HALF HOURS AFTER HIGH WATER

Date	N_2O (nM)	N_2O (% sat'n)	NO_3^- (μM)	NO_2^- (μM)	O_2 (μM)	AOU (μM)
25 July	15.9	212	20.9	.19	243	36
16 Aug	12.8	174	3.0	.13	342	- 75
21 Aug	10.1	167	0.27	.020	339	- 86
7 Sept	6.7	101	0.69	.14	255	- 12.1

DISCUSSION

Temporal Estuarine Nitrogen Variations

During the three month sampling period, apparent systematic variations in the concentrations of the measured nitrogen species were observed (Figure 3). The dramatic increases in all three species, NO_3^-, NO_2^-, and N_2O, between the first two sampling dates might be attributed to either of two processes. The first is that a biological process is responsible, i.e., the nitrogen species are being produced in the estuary in situ by a process such as bacterial nitrification. The sediments are the most likely site for processes of this type to be occurring. The elevated concentrations of the nitrogen species could be attributed to their production in the sediment and subsequent diffusion into the overlying water. If this were the case, maximum concentrations of these compounds would be expected to occur at periods of either slack water or low currents, such as is associated with high and low water.

A second possibility is that these elevated nutrient and nitrous oxide concentrations are being physically transported into the estuary with the tide. Coastal upwelling of cold, nutrient-rich water to the surface is well known to occur during the summer months on the Oregon coast (Huyer, 1977). This upwelled water is characterized by NO_3^- (plus NO_2^-) concentrations in excess of 8 µM as well as undersaturated dissolved oxygen values (Atlas, Gordon and Tomlinson, 1978). The nutrient and N_2O values observed on July 25 probably result primarily from the influx of upwelled seawater with the tide. In Table 2, the nutrient data from this study of Alsea Bay is compared to average nutrient levels

Table 2. Average nutrient levels in Pacific Northwest coastal waters from Atlas, Gordon and Tomlinson (1978) compared to observed Alsea Bay, summer of 1979 nutrient levels at station 2 at high water.

	$NO_3^- + NO_2^-$ (μM)	PO_4^{3-} (μM)	SiO_2 (μM)
NE Pacific surface water	5	0.7	10
Columbia River water	10	0.5	150
Upwelling water	35	2.4	45
Alsea Bay water			
13 July	0.11	0.12	6.0
25 July	21.9	1.81	39.6
7 Aug	20.7	2.12	42.9
16 Aug	0.81	0.46	4.9
7 Sept	0.05	0.53	4.0

in Pacific Northwest coastal waters taken from Atlas et al.(1978). On

July 25 and August 7 the levels of nutrient concentrations observed in

Alsea Bay are similar to those which are characteristic of upwelling

water in this area. In addition, the winds on July 25 and August 7 were

northerly, i.e. favorable for upwelling to occur. With respect to N_2O,

Elkins et al. (1978) observed "largest surface concentrations [of N_2O]

in the zone of high productivity associated with the equatorial up-

welling." Under this hypothesis the maximum effect on N_2O levels of

the influx of upwelled water into the bay would be seen at high water,

when the maximum seawater invasion of the estuary occurs. In Alsea Bay,

particularly on July 25 and August 7, maximum concentrations of NO_3^-, NO_2^-

and N_2O were observed to occur at or near high water.

Regardless of the cause, extremely high supersaturations of N_2O

are observed, resulting in a release of N_2O from the surface waters of

the estuary to the atmosphere. If the cause is biological, the estuary

provides a chemical and/or biological environment in which N_2O is pro-

duced. If the cause is the influx of upwelled water, then the shallow-

ness of the estuary provides a physically large surface area for a

consequently large diffusive flux of N_2O across the air-water interface.

The chemical observations for the remainder of the summer are also

subject to the same considerations. There is a systematic decrease in

all of the nitrogen species after the maximum concentrations of July 25

and August 7. A plot of N_2O versus salinity (Figure 4) for the entire

sampling period shows marked nonlinearity, particularly at high salin-

ities. If the observed concentrations of N_2O in Alsea Bay reflect simple

two point mixing between seawater and river water, Figure 4 would indi-

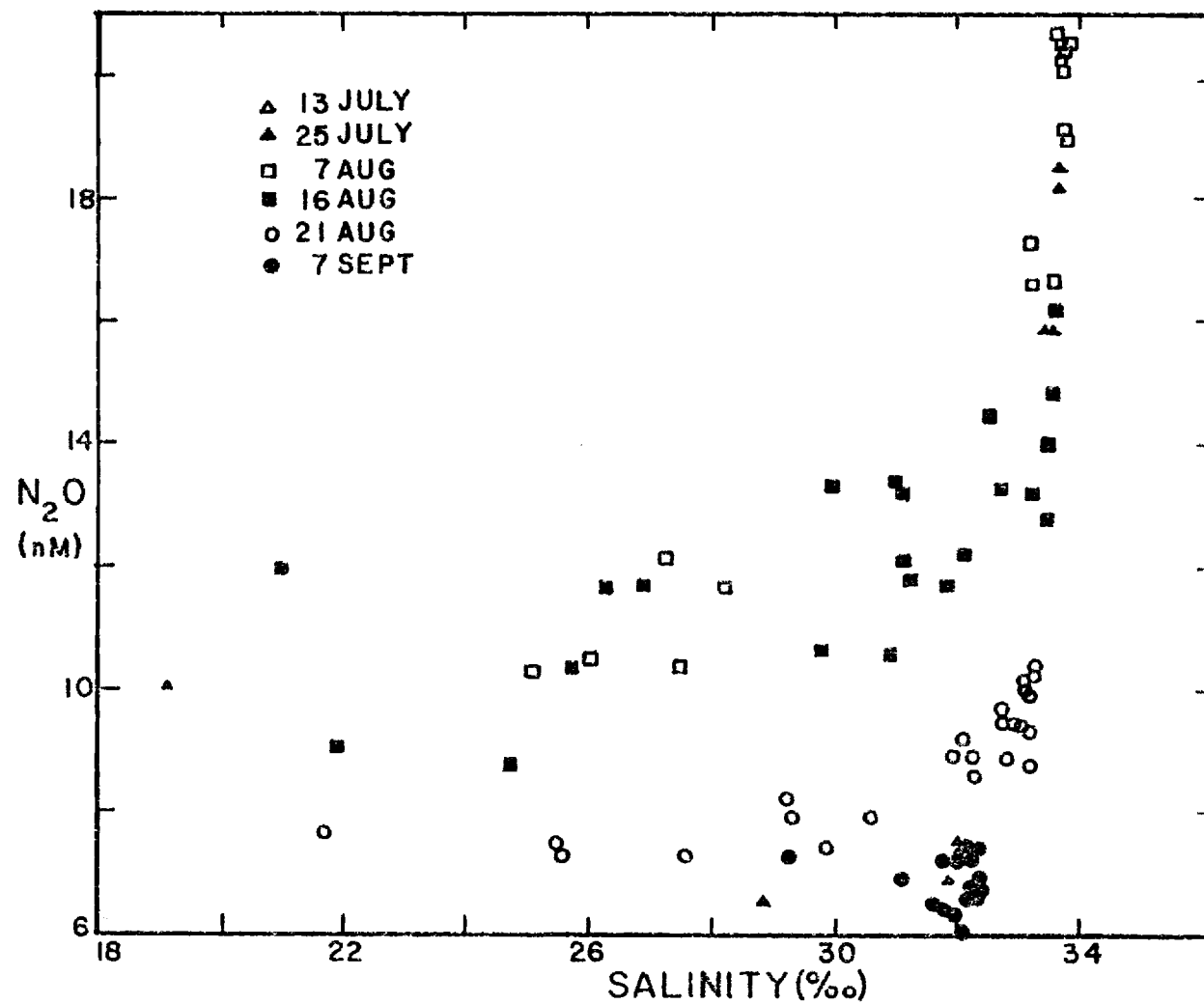cate that between July 13 and September 7, dissolved N_2O being brought

Figure 4. Nitrous oxide concentration vs. salinity for all sampling dates and stations, summer of 1979.

into the estuary with incoming seawater is being lost or consumed. An
alternate explanation is that the N_2O-S curves in Figure 4 reflect
three point mixing between near N_2O saturated river water, high salinity
coastal surface water that is slightly supersaturated with respect to
N_2O, and high salinity upwelling water that is highly supersaturated
with N_2O.

However, biological processes must be responsible for the decline
in nitrate, nitrite and nitrous oxide concentrations throughout the
latter part of the summer, whether they take place in the estuary or
in coastal waters that are subsequently transported into the estuary.
With regard to these biological processes, either denitrification or
assimilatory nitrate reduction (Painter, 1970) may be taking place,
either of which could result in the consumption of nitrate and nitrite.
However, the observed dissolved oxygen values are higher than the
threshold limit of approximately 5 μM above which denitrification in
marine systems is not believed to occur (Goering, 1968).

Assimilatory nitrate reduction, or nitrate uptake, in which NO_3^-
is used as a nitrogen source rather than as an energy source, is
carried out by phytoplankton and blue-green algae in the euphotic zone
as well as by some bacteria (Painter, 1970). This nitrate consuming
process results in the concurrent release of oxygen, consistent with
both the dissolved oxygen and nitrogen nutrient data after August 7.
Between August 7 and August 16, NO_3^- and NO_2^- concentrations decrease
sharply while dissolved oxygen concentrations undergo a sharp increase
from undersaturated O_2 values (positive AOU) to supersaturated values
(negative AOU). Nitrogen is generally considered to be the limiting
micronutrient in Pacific Northwest coastal waters. Phytoplankton blooms

with resultant nitrate depletion are common occurrences after upwelling events supply high levels of nitrate to the euphotic zone in this region (Atlas, Gordon and Tomlinson, 1978). The role of N_2O in assimilatory nitrate reduction is not known. Although the relative concentrations of nitrous oxide in the estuary decrease from July 25 onward, the observed levels of this gas are still well above saturation until early September when they approach saturation values. As a result, the estuary continues to be a source of N_2O to the atmosphere throughout the summer. This suggests that assimilatory NO_3^- reduction may result in the production of N_2O in aquatic systems. After August 21, when nitrate and nitrite have been depleted to low levels, the N_2O supersaturations may result from a process such as denitrification taking place in the sediments of the estuary. No conclusive evidence for this was found in this particular study due to the fact that sampling was limited to surface waters during the latter part of the summer.

Nitrous Oxide Exchange Across the Air-Water Interface

The dissolved nitrous oxide surface saturation values measured in the estuary varied widely over the course of the summer. Nitrous oxide per cent saturations ranged from a minimum of 90 % at station 5 on September 7 to a maximum of 239% at station 2 on July 25. Undersaturation of dissolved N_2O with respect to the atmosphere was observed on only three occasions on September 7, while supersaturations were observed with the remaining 85 samples. It can be concluded then that during the summer of 1979, Alsea Bay was a variable source of N_2O to the atmosphere.

The magnitude of the diffusive flux of N_2O across the air-water interface can be estimated using a simple stagnant film model (Bolin, 1960). This model assumes that the rate determining step for gas exchange is molecular diffusion through a liquid laminar layer at the air-water interface. The gas flux, F, of N_2O across the interface is given as:

$$F = \frac{D}{Z} \Delta N_2O \tag{1}$$

where Z is the thickness of the laminar layer, D is the diffusion coefficient for N_2O and ΔN_2O is the difference between the measured near surface N_2O concentration and the N_2O equilibrium solubility with respect to the atmosphere at the temperature and salinity conditions of the water. The diffusion coefficient is a function of temperature and values for D were extrapolated from those given for N_2O by Broecker and Peng (1974). The laminar layer thickness is a function of wind speed. Values for Z for each of the sampling dates were estimated from

the relationship between Z and wind speed given by Emerson (1975).
Laminar layer thicknesses ranged from 12μm to 480μm corresponding to
wind speeds of 11 m sec^{-1} to 1.8 m sec^{-1} respectively.

Using equation 1, average N_2O fluxes across the interface were
calculated for each sampling date in terms of both moles N_2O sec^{-1}cm^{-2}
and moles N_2O yr^{-1}, using the surface area of the estuary at mean high
tide (8.78 X 10^8 m^2, Percy et al., 1974). The results are given in
Table 3. An overall average flux for all of the samples was calculated
to be 6.3 X 10^{-11} moles N_2O sec^{-1}cm^{-2} (2.8 X 10^{-9} g N_2O sec^{-1}cm^{-2}).
This is an estimated annual flux of N_2O into the atmosphere of
1.75 X 10^6 moles N_2O yr^{-1} (7.7 X 10^7 g N_2O yr^{-1}). Due to the vari-
ability of the N_2O values observed during the summer months and the
lack of data from other seasons, this probably is an upper limit to
the source term for this estuary.

Using an average open ocean N_2O supersaturation of 109%, Cohen
and Gordon (1978b) estimated an N_2O flux into the atmosphere from the
ocean of 3.6 X 10^{11} moles N_2O yr^{-1} (2 X 10^{12} g N_2O yr^{-1}). Thus the N_2O
flux into the atmosphere across the air-water interface from Alsea Bay
is much smaller than that from the open ocean surface waters, as would
be expected from the large difference in surface area between the two
environments. On a per square centimeter basis, the estimated annual
flux for Alsea Bay is 2.0 X 10^{-7} moles N_2O yr^{-1} cm^{-2}, as compared to
1.1 X 10^{-7} moles N_2O yr^{-1}cm^{-2} for open ocean surface waters. Therefore,
on a per unit area basis, Alsea Bay is comparable to the surface waters
of the open ocean with respect to the diffusive flux of N_2O to the
atmosphere.

Table 3. Average calculated fluxes of nitrous oxide for all stations on each sampling date. The surface area of the bay at mean high tide was used to calculate the flux in terms of moles N_2O yr^{-1}.

Date	Average flux (10^{-11}) moles N_2O $sec^{-1}cm^{-2}$	Average flux (10^6) moles N_2O yr^{-1}
13 July	4.0	1.1
25 July	8.3	2.3
7 Aug	20	5.6
16 Aug	2.1	.58
21 Aug	1.3	.35
7 Sept	7.0	1.5

Riverine Nitrous Oxide Observations

On two occasions in October, 1979, surface water samples from seven stations along the Alsea River were analyzed for N_2O. A single river station was also occupied on a single date in September. Figure 5 shows the locations of these stations. River station A, 73 miles from the mouth of the estuary, is a spring fed pool which is one of the sources of the South Fork of the Alsea River. River station G corresponds to estuary station one with respect to distance from the mouth of the bay. The results of the nitrous oxide river measurements are given in Table 4 in terms of both molar concentration units and per cent saturation with respect to the atmosphere. All samples were collected at fast moving parts of the river.

The first observation that can be made from the data presented in Table 4 is the difference between the nitrous oxide values obtained on the first two sampling dates and those observed on the last date. The N_2O river values for September 12 and October 10 are close to saturation with respect to the atmosphere. The values for October 27 are systematically about 50% higher at all of the river stations. The major difference between these dates is that the first two occurred before the rainy season began or before flood conditions in the river prevailed, while the last date occurred after the rainy season had begun and river flooding had occurred. On October 27 the river was visibly swollen.

The higher N_2O values on the post flood sampling date might be attributed to increased soil runoff, which at the beginning of the rainy season would result in an increased supply of nitrogen compounds
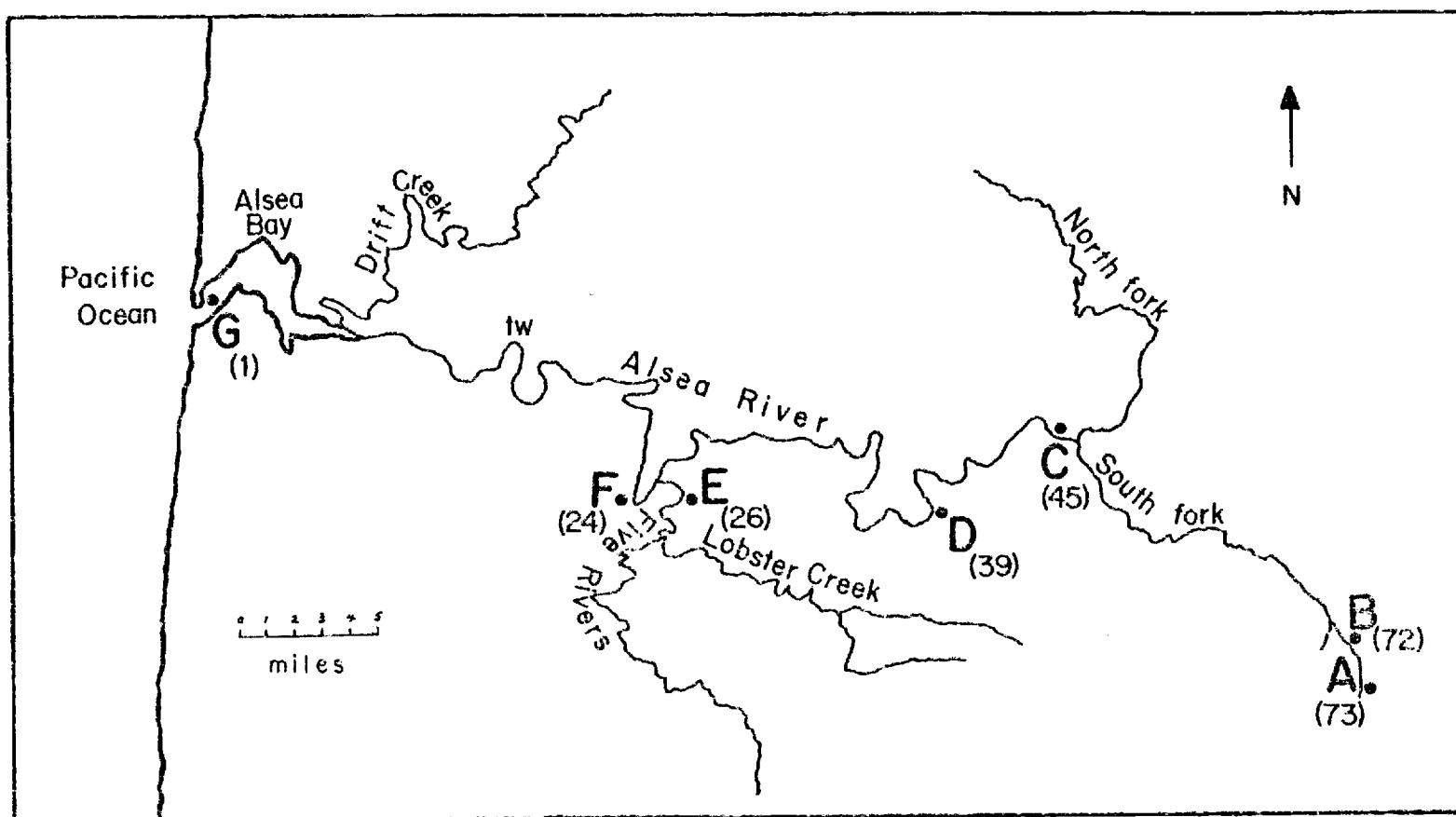
Figure 5. Map of the Alsea River system. Stations sampled for N_2O in September and October of 1979 are designated by letter. Numbers in parentheses refer to the distance in river miles from the indicated station to the mouth of the estuary.

Table 4. Dissolved nitrous oxide concentrations from the Alsea River during September and October of 1979. Numbers in the parentheses are per cent saturation with respect to the atmosphere.

River Station	N_2O nM (% saturation) 12 Sept 79	10 Oct 79	27 Oct 79
A		9.5 (99)	12.4 (125)
B		9.3 (94)	11.5 (120)
C		9.1 (106)	13.5 (146)
D	8.9 (117)	9.0 (105)	14.1 (147)
E		8.7 (104)	15.6 (166)
F		8.8 (104)	15.0 (163)
G		8.6 (119)	8.2 (115)

to the river. Dowdell, Burford and Crees (1979) reported elevated N_2O values in drainage water from cultivated land. An additional piece of evidence that tends to support this hypothesis is the differences in N_2O concentrations on October 27 at stations A and B on one hand and stations C through F on the other. Stations A and B are located in the hills and the surrounding land is forested and not cultivated at all. The N_2O values at these two river stations are lower than at the other stations that are all located in the river valley. This valley is less forested and both cultivation and grazing take place in it. There are no sources of pollution to this river that could be responsible for the high levels of N_2O.

CONCLUSIONS

In Alsea Bay, during the summer of 1979, rapid changes took place with respect to the aquatic nitrogen chemistry. The temporal variations in nitrate, nitrite and nitrous oxide concentrations in the estuary appear to reflect three point mixing between river water, coastal surface seawater and upwelling water. Processes taking place in the sediment could be important but their contributions to the effects seen in the overlying water could not be deduced from this study. The influx of upwelled water at the beginning of the sampling period resulted in high nutrient concentrations and supersaturated N_2O values. During the latter part of the sampling period, assimilatory nitrate reduction is the most probable cause of the eventual near depletion of NO_3^- and NO_2^- and the gradual decline of N_2O values to near saturation.

It was found that during the summer of 1979, the estuary served as a source of N_2O to the atmosphere. The N_2O diffusive flux to the atmosphere from Alsea Bay appears to be comparable to that from the surface waters of the open ocean on a per unit areal basis. This estuary and probably its associated surface coastal waters serve as sites for the loss of fixed nitrogen from the aquatic environment during the summer.

The river studies presented showed interesting variations. The increased concentration of N_2O after a period of heavy rainfall and subsequent runoff from land may indicate that large amounts of nitrogen from soil may be lost by this process. It appears that at least during some parts of the year, large supersaturations and consequent diffusive fluxes of N_2O to the atmosphere occur in this river system. There is no

obvious source of pollution to which these supersaturations can be
attributed. This suggests that natural freshwater systems can serve as
sources of nitrous oxide to the atmosphere and receiving estuaries on
at least a seasonal basis. Nitrous oxide may prove to be a quantita-
tively important medium for the loss of fixed nitrogen from this and
other aquatic ecosystems.

Future studies should include concurrent sampling of coastal
seawater and entering river water as well as estuary sampling embracing
a wider range of salinity conditions than that encountered in this
study. Sampling should extend to a year round basis and should include
near bottom and sediment sampling as well as surface water sampling.
In addition, microbiological studies investigating such processes as
denitrification and nitrification should be carried out. Estuaries are
extremely complex systems with which to work but may prove to be
extremely important with regard to understanding the aquatic nitrogen
cycle.

ACKNOWLEDGMENTS

BIBLIOGRAPHY

Atlas, E.L., L.I. Gordon and R.D. Tomlinson (1978) Chemical character-
istics of Pacific Northwestern coastal waters- nutrients, salin-
ities , seasonal fluctuations, p. 57-79. In R. Krauss (ed.) The
Marine Plant Biomass of the Pacific Northwest Coast. Oregon State
Univ. Press.

Balderston, W.L., B. Sherr and W.J. Payne (1976) Blockage by acetylene
of nitrous oxide reduction in Pseudomonas perfectomarinus. App.
Environ. Microbiol. 31, 504-508.

Bremner, J.M. (1978) Effects of soil processes on the atmospheric
concentration of nitrous oxide. In Nitrogen in the Environment,
Vol. 1, Academic Press. pp. 477-491.

Bolin, B. (1960) On the exchange of CO_2 between the atmosphere and the
sea. Tellus 12, 274-281.

Broecker, W.S. and T.-H. Peng (1974) Gas exchange rates between air
and sea. Tellus 26, 21-35.

Burt, W.V. and W.B. McAlister (1959) Recent studies in the hydrography
of Oregon estuaries. Oregon Fish Commission Research Briefs 7,
14-27.

Carpenter, J.H. (1965) The Chesapeake Bay Institute technique for the
Winkler dissolved oxygen method. Limnol. Oceanog. 10, 141-143.

Cicerone, R.J., J.D. Shetter and S.C. Liu (1978) Nitrous oxide in
Michigan waters and in U.S. municipal waters. Geophys. Res. Lett.
5, 173-176.

Cline, J.D. and F.A. Richards (1972) Oxygen deficient conditions and nitrate reduction in the eastern tropical North Pacific Ocean. Limnol. Oceanog. 7, 885-900.

Cohen, Y. (1977) Shipboard measurement of dissolved nitrous oxide in seawater by electron capture gas chromatography. Anal. Chem. 49, 1238-1240.

Cohen, Y. (1978) Consumption of dissolved nitrous oxide in an anoxic basin, Saanich Inlet, British Columbia. Nature 272, 235-237.

Cohen,Y. and L.I. Gordon (1978a) Nitrous oxide production in the ocean. J. Geophys. Res. 84, 347-353.

Cohen , Y. and L.I. Gordon (1978b) Nitrous oxide in the oxygen minimum of the eastern tropical North Pacific: evidence for its consumption during denitrification and possible mechanisms for its production. Deep-Sea Res. 25, 509-524.

Craig, H. and L.I. Gordon (1963) Nitrous oxide in the ocean and marine atmosphere. Geochim. Cosmochim. Acta 27, 949-955.

Crutzen, P.J. (1970) The influence of nitrogen oxides on the atmospheric ozone content. Quarterly J. Royal Meteorol. Soc. 96, 320-327.

Crutzen, P.J. (1976) Upper limits on stratospheric ozone reductions following increased application of fixed nitrogen to the soil. Geophys. Res. Lett. 3, 169-172.

Dowdell, R.J., J.R. Burford and R.Crees (1979) Losses of nitrous oxide dissolved in drainage water from agricultural land. Nature 278, 342-343.

Elkins, J.W., S.C. Wofsy, M.B. McElroy, C.E. Kolb and W.A. Kaplan (1978) Aquatic sources and sinks for nitrous oxide. Nature 275, 602-606.

Emerson, S. (1975) Gas exchange rates in small Canadian Shield lakes. Limnol. Oceanog. 20, 754-761.

Fedorova, R.I., E.I. Milekhina and N.I. Il'Yukhina (1973) Evaluation of the method of "gas metabolism" for detecting extraterrestrial life. Identification of nitrogen-fixing microorganisms. Izv. Akad. Nauk, SSSR, Ser. Biol. 6, 797-806.

Goering, J.J. (1968) Denitrification in the oxygen minimum layer of the eastern tropical Pacific Ocean. Deep-Sea Res. 15, 151-164.

Gordon, L.I., C.N. Dahm, W.H. Dickinson, P.K. Park and D.R. Standley (1975) A precision oceanographic nutrient data system. In, Proceedings of the UNOLS Working Conference on Oceanographic Data Systems, Woods Hole Oceanographic Institution, November 12-14, pp. 38-56.

Hahn, J. (1974) Nitrous oxide in air and seawater over the Atlantic Ocean, p. 53-69. In, D. Dryssen and D. Jagner (eds.) The changing chemistry of the oceans. John Wiley.

Hahn, J. (1975) N_2O measurements in the northeast Atlantic Ocean. 'Meteor' Forsch. Reihe A, 16, 1-14.

Hahn, J. and C. Junge (1977) Atmospheric nitrous oxide: a critical review. Zeitschrift für Naturforsch. 32a, 190-214.

Huyer, A. (1977) Seasonal variation in temperature, salinity and density over the continental shelf off Oregon. Limnol. Oceanog. 22, 442-453.

Johnston, H.S. (1977) Analysis of the independent variables in the perturbation of stratospheric ozone by nitrogen fertilizers. J. Geophys. Res. 82, 1767-1772

Kaplan, W.A., J.W. Elkins, C.E. Kolb, M.B. McElroy, S.C. Wofsy and A.P. Duran (1978) Nitrous oxide in fresh water systems: an estimate for the yield of atmospheric N_2O associated with disposal of human waste. Pageoph. 116, 423-438.

Liu, S.C., R.J. Cicerone, T.M. Donahue and W.L. Chameides (1977) Sources and sinks of atmospheric N_2O and the possible ozone reduction due to industrial fixed nitrogen fertilizers. Tellus, 29, 251-263.

McElroy, M.B., J.W. Elkins, S.C. Wofsy, C.E. Kolb, A.P. Duran and W.A. Kaplan (1978) Production and release of N_2O from the Potomac estuary. Limnol. Oceanog. 23, 1168-1182.

Matson, A.L. (1972) Zooplankton and hydrography of Alsea Bay, Oregon, September 1966 to September 1968. Ph.D. thesis, Oregon State Univ. 228 pp.

Painter, H.A. (1970) A review of literature on inorganic nitrogen metabolism in microorganisms. Water Res. 4, 393-450.

Payne, W.J. (1973) Reduction of nitrogenous oxides by microorganisms. Bacteriol. Rev. 37, 409-452.

Percy, K.L., D.A. Bella, C. Sutterlin and P.C. Klingeman (1974) Descriptions and information sources for Oregon estuaries. Sea Grant College Program Publication, Oregon State Univ.

Pierotti, D. and R.A. Rasmussen (1976) Combustion as a source of nitrous oxide in the atmosphere. Geophys. Res. Lett. 3, 265-267.

Pierotti, D. and R.A. Rasmussen (1978) Interlaboratory calibration of atmospheric nitrous oxide measurements. Geophys. Res. Lett. 5, 353-355.

Rasmussen, R.A., J. Krasnec and D. Pierotti (1976) Report on the cruise of the Alpha Helix Research Vessel, March 5 to 20, 1976, N.S.F. Grant No. OCE 75-04688-A03.

Turco, R.P., R.C. Whitten, I.G. Poppoff and L.A. Capone (1978) SSTs, nitrogen fertiliser and stratospheric ozone. Nature 276, 805-807.

Yoshinari, T. (1976) Nitrous oxide in the sea. Marine Chem. 4, 189-202.

Yoshinari, T., R. Hynes and R. Knowles (1977) Acetylene inhibition of nitrous oxide reduction and measurement of denitrification and nitrogen fixation in soil. Soil Biol. Biochem. 9, 177-183.

Yoshinari, T. and R. Knowles (1976) Acetylene inhibition of nitrous oxide reduction by denitrifying bacteria. Biochem. Biophys. Res. Commun. 69, 705-710.

Weiss, R.F. and H. Craig (1976) Production of atmospheric nitrous oxide by combustion. Geophys. Res. Lett. 3, 751-753.

Whitten, R.C., W.J. Borucki, L.A. Capone, C.A. Riegal and R.P. Turco (1980) Nitrogen fertiliser and stratospheric ozone: latitudinal effects. Nature 283, 191-192.

CHAPTER II

NITROUS OXIDE PRODUCTION AND CONSUMPTION

IN INTERSTITIAL WATER OF A DEEP-SEA SEDIMENT

Nitrous Oxide Production and Consumption in the Interstitial

Water of a Deep-Sea Sediment

ABSTRACT

Measurements of nitrate (plus nitrite), nitrous oxide and molecular nitrogen in deep-sea interstitial waters indicate that denitrification is taking place in the upper 25 cm. Quantitative measurements of nitrous oxide in these waters show N_2O maxima of nine to forty times ambient water column concentrations. Denitrification in the pore water results in both the production and consumption of N_2O. Although the sediments observed are an eventual sink for dissolved nitrous oxide deeper in the pore water, they are shown to serve as a source of N_2O to the overlying ocean waters. An upper limit to the possible flux of nitrous oxide out of such sediments is calculated to be 3.1×10^{13} g N_2O yr^{-1} (7.1×10^{11} moles N_2O yr^{-1}), a number comparable to the estimated flux of N_2O from the surface ocean waters to the atmosphere.

INTRODUCTION

Dissolved nitrous oxide is a constituent of the nitrogen cycle that has only recently been examined quantitatively in the ocean. All of the detailed investigations of the distribution and chemistry of this gas in the marine environment have been confined to surface waters and the water column. The role of N_2O in marine sediments has not yet been examined thoroughly.

Craig and Gordon (1963) made the first measurements of dissolved N_2O in the open ocean waters of the South Pacific. While their data gave quantitative values for N_2O in seawater, the grouping of samples from a number of locations and depths was such that no conclusions as to the processes involved in its production and consumption could be made. Yoshinari (1976) in the Northwest Atlantic, Hahn (1974, 1975) in the Northeast Atlantic, Elkins, Wofsy, McElroy, Kolb and Kaplan (1978) in the Central Pacific and Cohen and Gordon (1978a) in the Northeast Pacific measured dissolved nitrous oxide throughout the water column of well-oxygenated ocean waters. In all cases it was found that N_2O was negatively correlated with oxygen at all depths and positively correlated with nitrate. In addition, N_2O was found to be supersaturated with respect to the atmosphere throughout the water column. From these observed correlations of N_2O with dissolved oxygen and nitrate, Cohen and Gordon (1978b) concluded that nitrification, the process by which ammonium is oxidized to nitrate, results in the production of N_2O in the oceanic environment. They estimated the total marine production of N_2O by this mechanism to range from 6 to 16 X 10^{12} g N_2O yr^{-1} (1 to 4 X 10^{11} moles N_2O yr^{-1}). The observed supersaturations of N_2O in the

water column are attributed to this process.

In the eastern tropical North Pacific, Cohen and Gordon (1978b) found evidence for consumption of N_2O in the water column. Nitrous oxide minima were found at depths where the dissolved oxygen concentrations were near zero and secondary nitrite maxima were observed. This oxygen depletion and occurrence of a nitrite maximum are characteristic features of a denitrification regime which is commonly observed in this region (Goering, 1968; Cline and Richards, 1972; Cline, 1973). Denitrification occurs as dissolved oxygen is used up in the oxidative decomposition of organic matter and nitrate is used as an alternative oxygen source. Elkins et al. (1978) also observed depletion of N_2O in low oxygen waters of the Southeast Pacific.

In his investigations of Saanich Inlet, an intermittently anoxic basin, Cohen (1978) observed dissolved nitrous oxide concentrations decreasing markedly in the interface between the upper oxic waters and the deeper anoxic zone. Chemical and microbiological evidence for denitrification occurring in this interface layer was also observed. Below the interface, in the anoxic waters, the N_2O values decreased to zero. From these studies it was concluded that denitrification in marine waters results in the net consumption of nitrous oxide.

We present here quantitative measurements of nitrous oxide in the interstitial waters of deep sea sediments. Nissenbaum, Presley and Kaplan (1972) reported the presence of N_2O in two cores from the sediments of Saanich Inlet. However, these values are described as "only approximate and ... qualitative". Sorenson (1978) reported N_2O maxima of up to 5 μM (1 μM = 10^{-6} moles 1^{-1}) in the denitrification zones of coastal marine sediments. In this report, we use vertical pore water

profiles of dissolved nitrous oxide at two stations in the eastern
equatorial Pacific to help elucidate the role of N_2O in the denitri-
fication process and the mechanisms that control the production and
consumption of N_2O in marine sediments. We then discuss the sediment
as a source or sink of nitrous oxide to the ocean.

METHODS

Sediment interstitial waters were sampled at two sites near the Galapagos Spreading Center. Station 126 was located at $0°\ 36.2'$ N, $86°\ 8.8'$ W and station 130 was at $0°\ 34.6'$ N, $86°\ 7.8'$ W. Pore waters at both stations were collected to a depth of 205 cm in the sediment with the *in situ* interstitial water sampler described by Barnes (1973). By using an *in situ* pore water sampler losses of gases from the interstitial water are minimized.

The dissolved N_2 was analyzed by a gas chromatographic method (Barnes, Bertine and Goldberg, 1975). The precision of this method is about 1%. Dissolved nitrous oxide was measured in 5 cc samples by the method described by Cohen (1977). The precision of the N_2O measurements is about 2% and accuracy is approximately 3%. Nitrate plus nitrite were determined by Philip Froelich of the University of Rhode Island by autoanalyzer techniques based on the method of Wood, Armstrong and Richards (1967). The precision for this method is 0.5% and the estimated accuracy 2%. All precisions given are for deep water levels of the various measured species.

RESULTS AND DISCUSSION

The results of the analyses for dissolved molecular nitrogen, nitrous oxide and nitrate plus nitrite for the sediment interstitial water of stations 126 and 130 are presented in Table 1 and Table 2. Vertical profiles for these nitrogenous species in the upper 205 cm of the sediment are shown in Figure 1 for station 126 and in Figure 2 for station 130.

From these two figures, it can readily be seen that the greatest changes in concentration of all of the species measured occur in the uppermost 25 cm of the sediment. We designate this as the nitrate reduction zone since it is characterized by a drastic decrease of nitrate (plus nitrite) concentrations. In the pore waters sampled here, nitrate (plus nitrite) decreased from near ambient bottom water concentrations at both stations of approximately 37 μM (NO_3^- + NO_2^-) at the water-sediment interface to minimum concentrations of 0.2 μM at station 126 and 1.1 μM at station 130 at depths of 23.0 and 19.5 cm respectively.

In the same depth interval, dissolved nitrous oxide increased in concentration above bottom water values before decreasing rapidly to minimum values near the base of the nitrate reduction zone. A strong maximum immediately below the water-sediment interface is the most striking feature at both stations for this gas. At station 126, a maximum value of 1060 nM (1 nM = 10^{-9} moles 1^{-1}) at 0.25 cm depth in the pore water is observed compared to an ambient water concentration of 24.9 nM at 22 cm above the sediment. This represents an increased N_2O concentration of greater than 40 times ambient water column values. At station 130, the N_2O maximum reaches 418 nM N_2O at a depth of 2.0

Table 1. Nitrate plus nitrite, molecular nitrogen and nitrous oxide

concentrations in interstitial water, Station 126, cast 6.

Depth with respect to water-sediment interface (cm)	$NO_3^- + NO_2^-$ (μM)	N_2 (μM)	N_2O (nM)
+ 22.0	37.6	601	24.9
+ 4.25	38.9	601	205
+ 2.75	38.0	629	137
+ 1.25	37.5	629	97
- 0.25	35.6	627	1060
- 2.0	25.4	608	124
- 4.5	21.3	657	63
- 5.25	20.8	633	56
- 10.5	14.0	660	22.5
- 13.5	4.8	325	13.9
- 15.25	3.7	647	7.9
- 16.5	0.8	684	16.3
- 19.5	0.6	639	7.2
- 23.0	0.2	685	7.9
- 25.25	0.8	661	1.28
- 45.25	1.4	650	15.8
- 85.25	1.9	649	17.7
-145.25	1.6	949	18.8
-205.25	1.1	665	10.5

Table 2. Nitrate plus nitrite, molecular nitrogen and nitrous oxide

concentrations in interstitial water, Station 130, cast 7.

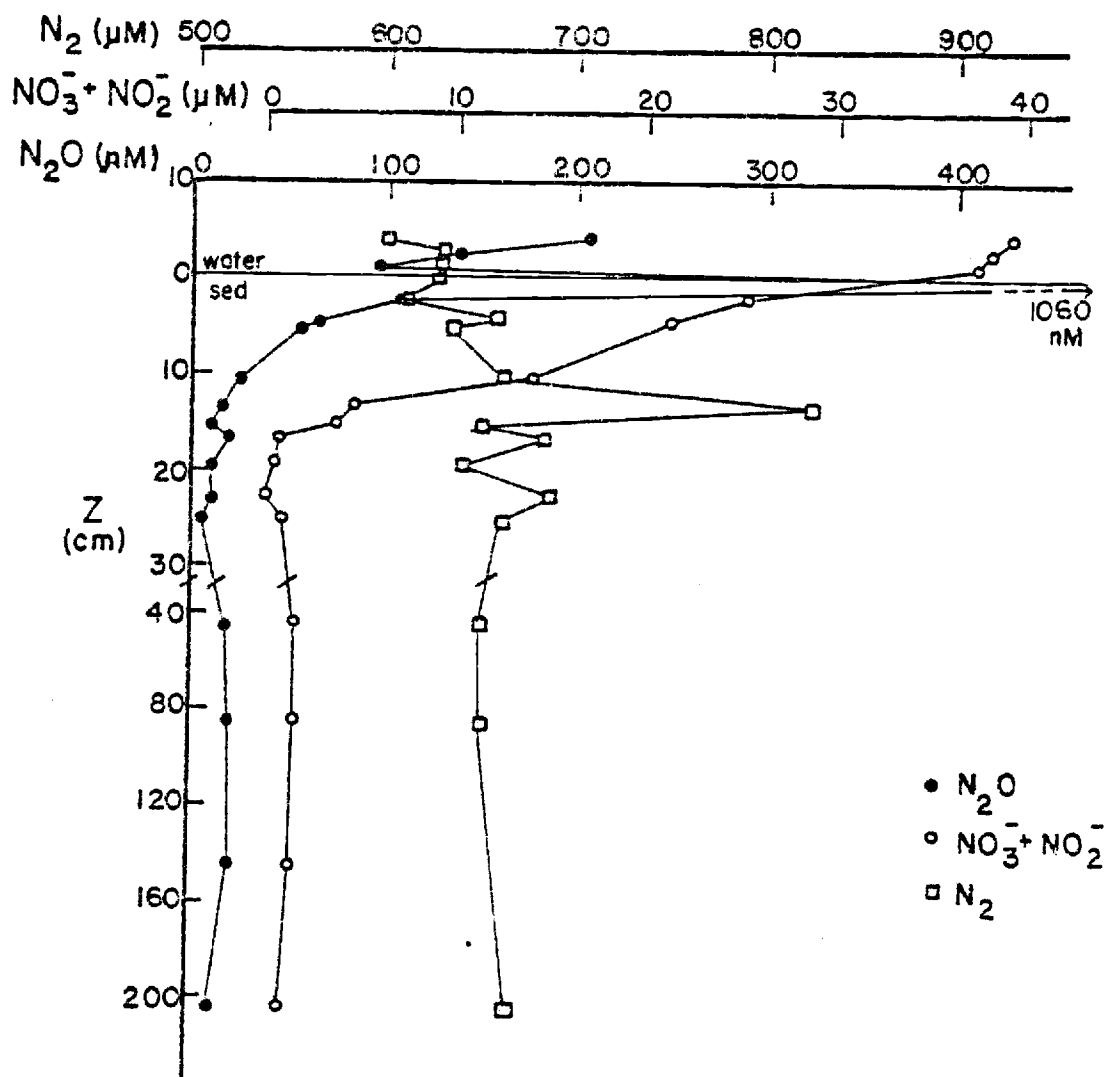| Depth with respect to water-sediment interface (cm)	$NO_3^- + NO_2^-$ (μM)	N_2 (μM)	N_2O (nM)
+ 22.0	39.2	---	45
+ 4.25	39.4	600	248
+ 2.75	38.4	606	336
+ 1.25	38.4	608	230
- 0.25	37.6	601	331
- 2.0	35.7	615	418
- 4.5	18.2	644	393
- 5.25	16.4	677	308
- 10.5	5.8	610	330
- 15.25	7.5	713	93
- 16.5	1.1	791	17.3
- 19.5	1.1	704	18.2
- 23.0	1.4	---	20.2
- 25.25	2.2	697	10.4
- 45.25	---	673	17.6
- 85.25	2.7	627	8.8
-145.25	1.9	1420	27.2
-205.25	1.1	655	144

Figure 1. Interstitial water profiles of N_2O, $(NO_3^- + NO_2^-)$ and N_2 for station 126, cast 6.
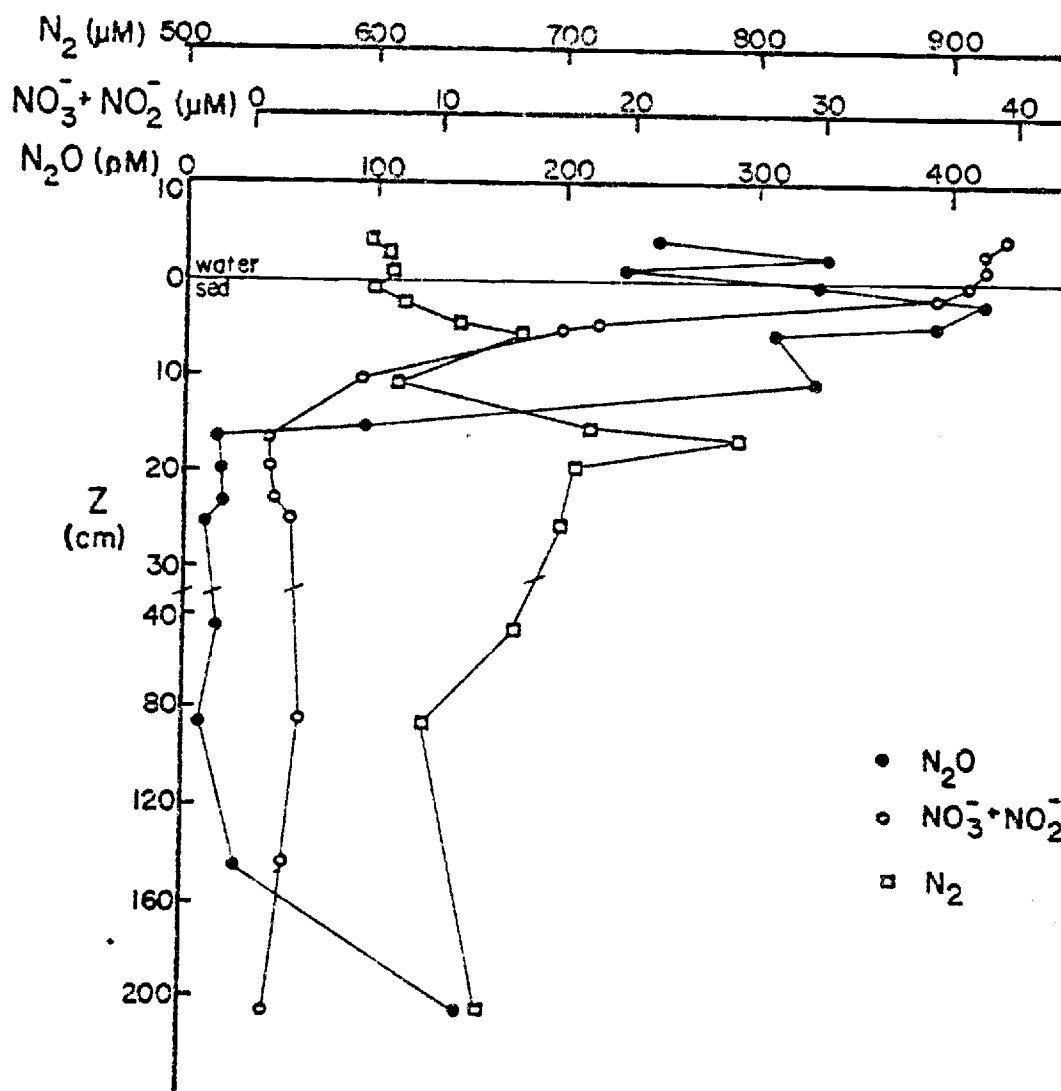
Figure 2. Interstitial water profiles of N_2O, $(NO_3^- + NO_2^-)$, and N_2 for station 130, cast 7.

cm in the sediment compared to an ambient bottom water value of 45 nM, a ninefold increase in concentration in the interstitial water. At both stations this nitrous oxide maximum decreases sharply to below ambient water column values at the base of the nitrate reduction zone, reaching 1.28 nM N_2O at 25 cm at station 126 and 10.4 nM at the same depth at station 130.

At or near the base of the nitrate reduction zone, a maximum for molecular nitrogen occurs at both stations. At station 126 a maximum value of 825 μM N_2 is observed at 13.5 cm depth in the sediment. At station 130 the N_2 maximum of 791 μM occurs at 16.5 cm depth. At both stations the ambient water values for N_2 are around 600 μM.

These upper pore water profiles of nitrogenous compounds of varying oxygen content are consistent with the process of denitrification, which is frequently observed to occur in marine sediments (Grundmanis and Murray, 1977; Vanderborght and Billen, 1975; Barnes, Bertine and Goldberg, 1975, Bender, Fanning, Froelich, Heath and Maynard, 1977; Sorenson, 1978). Denitrification is a microbiological process in which nitrate is reduced to nitrite which in turn is reduced to N_2O. As NO_3^- and NO_2^- are depleted or reach low levels, N_2O is further reduced to molecular nitrogen (Goering, 1978). This process is represented below in which the numbers in parentheses are the oxidation numbers for the nitrogen atom of each respective species (Payne, 1973).

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$$
$$(+5) \quad (+3) \quad (+2) \quad (+1) \; (0)$$
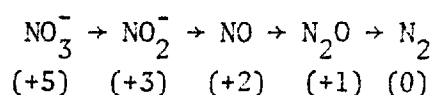
Doubt has been expressed in the past as to whether or not nitrous

oxide is an obligatory intermediate in this process (Delwiche, 1956; Fewson and Nicholas, 1961). However, recent studies by Yoshinari and Knowles (1976) and Balderston, Sherr and Payne (1976) using the acetylene inhibition method and St. John and Hollocher (1977) using nitrogen 15 tracer techniques have demonstrated that N_2O is an intermediate between nitrite and molecular nitrogen during denitrification for a number of denitrifying species.

According to the denitrification scheme given above, nitrous oxide is both produced and consumed in the course of this process. In the parts of the open ocean water column where denitrification is going on only an N_2O minimum is observed (Cohen and Gordon, 1978a; Elkins et al., 1978), i.e., only the net consumption of N_2O is evident. In the interstitial water profiles presented here, both the N_2O production and consumption steps are seen. The strong nitrous oxide maximum in the upper portion of the nitrate reduction zone is evidence of its production while the sharp decrease of N_2O to sub water column values that immediately underlies this maximum is consistent with N_2O reduction to N_2. This strong maximum is probably supported by a continual diffusion of nitrate (plus nitrite) across the water-sediment interface into the sediment caused by the strong NO_3^- (plus NO_2^-) gradient observed in the upper 25 cm.

Although it has been shown above that the reducing sediments of both stations are sinks for nitrous oxide deeper (>25 cm) in the sediment, the shallow sediment layers are a source of N_2O to the water column. As a result of nitrous oxide production taking place in the pore water, there is a net diffusive flux of nitrous oxide out of the sediments into the overlying water due to the steep concentration

gradient of N_2O in the upper sediment profile. The influence of N_2O production in the interstitial water can be seen to at least four cm above the sediment. Nitrous oxide concentrations of 248 nM and 208 nM at stations 130 and 126 respectively are seen at this depth. These values represent factors of five and ten times increase over ambient water column N_2O values. The highest open ocean water column N_2O concentration reported previously is 47.5 nM N_2O (Cohen and Gordon, 1978a) in the eastern tropical North Pacific.

The flux, F, of N_2O across the interface can be calculated from:

$$F = D \frac{\Delta C}{\Delta Z} \qquad (1)$$

where D is the diffusion coefficient and ΔC is the difference in N_2O concentration over the depth interval ΔZ. A diffusion coefficient for N_2O of 1.2×10^{-5} cm^2 sec^{-1} is obtained by extrapolating from D values given in Broecker and Peng (1974) for N_2O. Using this value of D and the N_2O data from Tables 1 and 2, an upper limit for the injection of N_2O into the deep water from the sediment can be calculated. For station 126, taking $\Delta Z = 1.5$ cm and $\Delta C = 963$ nM, we calculate a flux of 7.7×10^{-6} nmoles N_2O sec^{-1} cm^{-2}. For station 130, a flux of 6.9×10^{-7} nmoles N_2O sec^{-1} cm^{-2} is calculated from a ΔZ of 3.25 cm and a $\Delta C = 188$ nM. Taking an average flux from these two stations of 8.4×10^{-6} nmoles N_2O sec^{-1} cm^{-2}, we calculate an annual flux of 3.1×10^{13} g N_2O yr^{-1} (7.1×10^{11} moles N_2O yr^{-1}) from the world's deep sea sediments. This is a number comparable to the estimated flux of 1.3×10^{13} g N_2O yr^{-1} (Cohen and Gordon, 1978a) from the ocean to the atmosphere. This calculated flux from the sediments is an order of magnitude estimate. Not all deep sea sediments are reducing

sediments in their upper portions and in those that are, the strength
of the N_2O maximum will vary. In spite of this, N_2O flux from denitri-
fication in the sediments is substantial and should not be neglected
in computing oceanic N_2O budgets or global oceanic models of N_2O cycling.

Using a diffusion coefficient of 10^{-5} cm^2 sec^{-1} (Vanderborght and
Billen, 1975) for NO_3^- (plus NO_2^-) we calculate a flux of 1.5 X 10^{-5}
nmoles sec^{-1} cm^{-2} into the sediment for station 126 and 1.8 X 10^{-5}
nmoles sec^{-1} cm^{-2} for station 130. If we assume steady state conditions
prevail in the interstitial water with respect to the nitrogen species,
then the flux of NO_3^- plus NO_2^- into the sediment should be equal to
twice the N_2O flux out of the sediment since it takes two moles of
NO_3^- to produce one mole of N_2O. For station 126, twice the N_2O flux
out equals 1.5 X 10^{-5} nmoles sec^{-1} cm^{-2}, the identical number ob-
tained for the NO_3^- plus NO_2^- flux into the sediment. At station 130
twice the calculated flux of N_2O is 1.4 X 10^{-6} nmoles sec^{-1} cm^{-2} as
compared to 1.8 X 10^{-5} nmoles sec^{-1} cm^{-2} for NO_3^- + NO_2^-. These cal-
culations show that the N_2O values observed in the sediment can be
supported by the amount of NO_3^- and NO_2^- diffusing across the water-
sediment interface. From these calculations it also appears that
surprisingly little N_2O is being reduced to N_2, especially at station
126. The N_2O flux out of the sediments may represent a large fraction
of the nitrogen budget in these sediments. In order to determine this,
concurrent measurements of all the major nitrogen species, including
ammonium and organic nitrogen need to be made.

CONCLUSIONS

(1) The sediment interstitial water profiles measured at two sites near the Galapagos Spreading Center indicate that a denitrification regime is operating in the upper 25 cm of the sediment. The profiles of $(NO_3^- + NO_2^-)$, N_2O and N_2 at these two stations are consistent with such a regime.

(2) Denitrification in interstitial water results in the production of nitrous oxide followed by its eventual consumption.

(3) Although reducing sediments are sinks for nitrous oxide at depth, they serve as sources of nitrous oxide to the overlying ocean waters where the N_2O maximum caused by denitrification is close to the water-sediment interface.

(4) The steep concentration gradient of nitrate plus nitrite results in a continuous diffusive flux of these nitrogen species into the sediment across the water-sediment interface. This flux into the sediment maintains the upper pore water N_2O maximum which results in a diffusive flux of N_2O out of the sediment. The estimated annual flux of N_2O from the world's deep sea sediments to the water column, based on the two stations observed in this study, is comparable to the N_2O flux from the ocean surface waters to the atmosphere.

ACKNOWLEDGMENTS

BIBLIOGRAPHY

Barnes, R.O. (1973) An in-situ interstitial water sampler for use in unconsolidated sediments. Deep Sea Res. 20, 1125-1128.

Barnes, R.O., K.K. Bertine and E.D. Goldberg (1975) N_2:Ar, nitrification and denitrification in southern California borderland basin sediments. Limnol. Oceanog. 20, 962-970.

Balderston, W.L., B. Sherr and W.J. Payne (1976) Blockage by acetylene of nitrous oxide reduction in Pseudomonas perfectomarinus. App. Environ. Microbiol. 31, 504-508.

Bender, M.L., K.A. Fanning, P.N. Froelich, G.R. Heath and V. Maynard (1977) Interstitial nitrate profiles and oxidation of sedimentary organic matter in the Eastern Equatorial Atlantic. Science 198, 605-609.

Broecker, W.S. and T.H. Peng (1974) Gas exchange rates between air and sea. Tellus 26, 21-35.

Cline, J.D. (1973) Denitrification and isotopic fractionation in two contrasting marine environments: the eastern tropical North Pacific and the Cariaco Trench. Ph.D. thesis, University of California, Los Angeles, 270 pp.

Cline, J.D. and F.A. Richards (1972) Oxygen deficient conditions and nitrate reduction in the eastern tropical North Pacific Ocean. Limnol. Oceanog. 7, 885-900.

Cohen, Y. (1977) Shipboard measurement of dissolved nitrous oxide in seawater by electron capture gas chromatography. Anal. Chem. 49, 1238-1240.

Cohen, Y. (1978) Consumption of dissolved nitrous oxide in an anoxic

   basin, Saanich Inlet, British Columbia. Nature 272, 235-237.

Cohen, Y. and L.I. Gordon (1978a) Nitrous oxide production in the

   ocean. J. Geophys. Res. 84, 347-353.

Cohen, Y. and L.I. Gordon (1978b) Nitrous oxide in the oxygen minimum

   of the eastern tropical North Pacific: evidence for its consump-

   tion during denitrification and possible mechanisms for its

   production. Deep Sea Res. 25, 509-524.

Craig, H. and L.I. Gordon (1963) Nitrous oxide in the ocean and marine

   atmosphere. Geochim. Cosmochim. Acta 27, 949-955.

Delwiche, C.C. (1956) Denitrification in McElroy, W.D. and B. Glass,

   eds., Inorganic Nitrogen Metabolism. Johns Hopkins, Baltimore,

   pp. 233-256.

Elkins, J.W., S.C. Wofsy, M.B. McElroy, C.E. Kolb and W.A. Kaplan

   (1978) Aquatic sources and sinks for nitrous oxide. Nature 275,

   602-606.

Fewson, C.A. and D.J.D. Nicholas (1961) Utilisation of nitrate by

   microorganisms. Nature 190, 2-7.

Goering, J.J. (1968) Denitrification in the oxygen minimum layer of

   the eastern tropical Pacific Ocean. Deep Sea Res. 15, 151-164.

Goering, J.J. (1978) Denitrification in marine systems. In Micro-

   biology, 1978. D. Schlessinger, ed. Amer. Soc. Microbiol., Wash.

   D.C.,pp. 357-361.

Grundmanis, V. and J.W. Murray (1977) Nitrification and denitrification

   in marine sediments from Puget Sound. Limnol. Oceanog. 22, 804-813.

Hahn, J. (1974) Nitrous oxide in air and seawater over the Atlantic Ocean. In Dryssen, D and D. Jagner (eds), The changing chemistry of the oceans. John Wiley, pp. 53-69.

Hahn, J. (1975) N_2O measurements in the northeast Atlantic Ocean. 'Meteor' Forsch. Reihe A, 16, 1-14.

Nissenbaum, A., B.J. Presley and I.R. Kaplan (1972) Early diagenesis in a reducing fjord, Saanich Inlet, British Columbia- I. Chemical and isotopic changes in major components of interstitial water. Geochim. Cosmochim. Acta 36, 1007-1027.

Payne, W.J. (1973) Reduction of nitrogenous oxides by microorganisms. Bacteriol. Rev. 37, 409-452.

Sorenson, J. (1978) Occurrence of nitric and nitrous oxides in a coastal marine sediment. App. Environ. Microbiol. 36, 809-813.

St. John, R.T. and T.C. Hollocher (1977) Nitrogen 15 tracer studies on the pathway of denitrification in Pseudomonas aeroginosa. J. Biol. Chem. 252, 212-218.

Vanderborght, J.-P. and G. Billen (1975) Vertical distribution of nitrate concentration in interstitial water of marine sediments with nitrification and denitrification. Limnol. Oceanog. 20, 953-961.

Wood, E.D., F.A.J. Armstrong and F.A. Richards (1967) Determination of nitrate in seawater by cadmium-copper reduction to nitrite. J. Mar. Biol. Assoc. U.K. 47, 23-31.

Yoshinari, T. (1976) Nitrous oxide in the sea. Marine Chem. 4, 189-202.

Yoshinari, T. and R. Knowles (1976) Acetylene inhibition of nitrous oxide reduction by denitrifying bacteria. Biochem Biophys. Res. Commun. 69, 705-710.

APPENDIX

DATA FROM ALSEA BAY, OREGON, SURFACE SAMPLING, SUMMER OF 1979

The following notations are used in the data listing:

Stn #	Station number. See Figure 1 for station locations.
T	Temperature in degrees Celcius.
S	Salinity in parts per thousand.
O_2	Dissolved oxygen in micromoles per liter.
AOU	Apparent oxygen utilization in micromoles O_2 per liter.
N_2O	Dissolved nitrous oxide in nannomoles per liter.
N_2O sat	Dissolved nitrous oxide saturation in per cent.
ΔN_2O	$(N_2O_{observed} - N_2O_{saturation\ (T,S)})$ in nannomoles per liter
NO_3^-	Nitrate in micromoles per liter.
NO_2^-	Nitrite in micromoles per liter.

For analytical methods employed, see methods section of Chapter I.

Missing data points in the cases of O_2 and AOU represent samples not taken. In the case of other quantities, missing data points represent samples lost during analysis.

All high water times are corrected for Waldport, Alsea Bay (station 2) and are taken from predictions from National Ocean Survey, NOAA.

Alsea Bay, Oregon   13 July 1979   High water at 1655

Time	Stn #	T (^{o}C)	S (ppt)	O_2 (µM)	AOU (µM)	N_2O (nM)	N_2O sat (%)	ΔN_2O (nM)	NO_3^- (µM)	NO_2^- (µM)
1205	2	20.3	16.428			8.6	143	2.6	0.18	.21
1325	2	18.0	28.822			6.7	104	0.2		.18
1505	2	18.0	31.817			6.8	109	0.5	0.090	.067
1615	2	17.0	31.958			7.4	113	0.8	0.10	.062
1700	2	17.0	31.982			7.6	115	1.0	0.060	.045

Alsea Bay, Oregon   25 July 1979   High water at 1506

Time	Stn #	T ($^\circ$C)	S (ppt)	O_2 (µM)	AOU (µM)	N_2O (nM)	N_2O sat (%)	ΔN_2O (nM)	NO_3^- (µM)	NO_2^- (µM)
1040	2	17.0	19.040	292	− 21.0	10.1	153	3.5	0.48	.20
1230	2	10.0	33.400	269	15.1	15.9	205	8.1	24.7	.33
1350	2	9.8	33.660	219	56	18.6	238	10.8	20.9	.20
1545	2	10.5	33.653	221	61	18.2	239	10.6	21.7	.22
1630	2	11.0	33.519	243	32.6	15.9	212	8.4	20.9	.19

Alsea Bay, Oregon   7 Aug 1979   High water at 1327

Time	Stn #	T (°C)	S (ppt)	O_2 (µM)	AOU (µM)	N_2O (nM)	N_2O sat (%)	ΔN_2O (nM)	NO_3^- (µM)	NO_2^- (µM)
0930	1	16.0	27.240	212	49.2	12.2	157	4.5	7.0	.18
0950	2	16.5	26.050	215	45.0	10.5	137	2.8	6.1	.24
1010	3	16.0	27.515	213	47.5	10.4	134	2.7		
1040	4	17.5	28.261	234	18.0	11.7	159	4.4	10.2	.23
1100	5	17.0	25.105	220	39.4	10.3	136	2.7	5.0	.20
1140	1	10.0	33.729	157	128	20.4	222	11.2	19.2	.24
1200	2	10.0	33.709	153	132	20.7	225	11.5	24.0	.26
1215	3	10.0	33.733	179	105	19.1	208	9.9	27.0	.30
1235	4	10.0	33.706	155	129	20.3	221	11.1	20.2	.30
1250	5	10.2	33.656	151	133	20.5	225	11.4	19.6	.30
1320	1	10.5	33.739	170	111	20.1	223	11.1	17.6	.23
1340	2	10.0	33.740	191	93	20.6	225	11.4	20.5	.21
1350	3	10.0	33.747	167	118	19.0	207	9.8	16.4	.22
1430	4	11.0	33.656	175	103	16.6	187	7.7	20.2	.27
1450	5	12.0	33.231	214	59	17.3	201	8.7	19.3	.27

Alsea Bay, Oregon   16 Aug 1979   High water at 0915

Time	Stn #	T (°C)	S (ppt)	O_2 (µM)	AOU (µM)	N_2O (nM)	N_2O sat (%)	ΔN_2O (nM)	NO_3^- (µM)	NO_2^- (µM)
0900	1	13.0	33.587	410	-143	14.9	203	7.6	0.74	.045
0920	2	13.0	33.571	377	-110	14.0	191	6.7	0.74	.067
0935	4	13.0	33.243	320	- 52	13.2	180	5.9	1.9	.11
0950	5	14.5	31.169	210	53	12.1	171	5.0	3.2	.22
1030	1	13.0	33.580	391	-124	16.2	221	8.9	0.78	.063
1045	2	13.0	33.431	342	- 75	12.8	174	5.5	3.0	.13
1100	4	14.0	32.557	278	- 15.0	14.5	203	7.4	3.2	.18
1115	5	15.0	29.926	233	28.4	13.3	190	6.3	3.5	.25
1200	1	16.0	31.268	263	- 8.4	11.8	176	5.1	0.73	.058
1215	2	14.5	32.723	286	- 26.0	13.3	190	6.3	4.4	.11
1230	4	15.5	30.963	235	23.0	13.4	196	6.6	4.9	.21
1240	5	18.0	26.244	253	- 0.4	11.7	181	5.2		
1330	1	16.0	31.104	253	2.0	13.2	196	6.5	2.9	.16
1345	2	16.0	29.833	234	23.0	10.7	158	3.9	5.5	.22
1400	4	18.0	25.726	285	- 32.2	10.4	161	3.9	2.7	.10
1415	5	19.5	20.901	361	-108	12.0	190	5.7	1.2	.13
1500	1	16.0	30.914	254	1.4	10.6	158	3.9	5.0	.26
1515	2	18.0	26.881	265	- 13.0	11.7	182	5.3	3.3	.18
1530	4	18.5	24.757			8.8	138	2.4	2.4	.14
1545	5	19.5	21.867			9.1	144	2.8	0.96	.12
1605	1	15.0	32.083			12.2	177	5.3	3.0	.15
1620	2	15.5	31.838			11.7	172	4.9		

Alsea Bay, Oregon   21 Aug 1979   High water at 1327

Time	Stn #	T (^{o}C)	S (ppt)	O_2 (µM)	AOU (µM)	N_2O (nM)	N_2O sat (%)	ΔN_2O (nM)	NO_3^- (µM)	NO_2^- (µM)
0910	1	17.5	27.591	247	5.8	7.4	113	0.8	0.61	.15
0930	2	18.0	25.547	242	11.0	7.3	112	0.8	0.36	.14
0940	4	18.0	25.504	178	76	7.5	115	1.0	0.26	.12
0955	5	18.5	21.782	265	- 7.9	7.7	118	2.2		
1030	1	14.5	33.139	254	5.2	10.2	146	3.2	0.12	.094
1045	2	14.5	32.849	290	- 29.7	8.9	127	1.9	0.22	.080
1055	4	15.0	32.292	278	- 19.6	8.9	129	2.0	0.23	.076
1105	5	17.0	29.894	261	- 9.3	7.4	121	1.3	0.37	.13
1200	1	14.5	33.253	326	- 67	10.3	171	4.3		.049
1215	2	14.5	33.282	334	- 75	10.4	172	4.4	0.15	.080
1225	4	16.0	33.146	316	- 64	9.4	156	3.4	0.38	.095
1235	5	19.0	29.258	319	- 76	8.3	135	2.1	0.66	.015
1330	1	15.2	33.206	321	- 65	8.8	146	2.8		.046
1345	2	16.8	33.129	322	- 74	9.4	156	3.4		
1355	4	15.0	33.176	322	- 65	9.9	163	3.8	0.31	.016
1410	5	16.0	32.295	303	- 50	8.6	142	2.6	0.40	.015
1500	1	15.5	33.171	278	- 23.4	10.1	167	4.1	0.31	.13
1515	2	15.8	33.179	339	- 86	10.1	167	4.1	0.27	.020
1530	4	16.0	32.742	293	- 41	9.4	156	3.4		
1545	5	17.0	32.101			9.2	151	3.1	0.60	.15
1605	1	16.3	32.764			9.7	160	3.6	0.71	.10
1620	2	16.5	32.925			9.9	156	3.4	0.56	.050
1630	4	17.0	31.932			8.9	147	2.9	0.63	.094
1645	5	17.5	30.577			8.0	131	1.9	0.24	.048

Alsea Bay, Oregon   7 Sept 1979   High water at 1419

Time	Stn #	T (°C)	S (ppt)	O_2 (µM)	AOU (µM)	N_2O (nM)	N_2O sat (%)	ΔN_2O (nM)	NO_3^- (µM)	NO_2^- (µM)
1055	1	18.5	31.847	255	− 13.4	6.5	100	0.0	0.95	.079
1115	2	19.0	31.773	255	− 14.8	7.3	113	0.9		
1130	4	19.0	31.119	252	− 11.5	7.0	109	0.6		
1140	5	19.5	29.250	242	− 1.0	7.4	115	1.0	2.1	.097
1220	1	19.0	32.267	256	− 16.7	7.3	113	0.9	0.09	.095
1230	2	19.0	32.237	256	− 16.8	6.8	107	0.4	0.37	.079
1240	4	19.0	32.048	254	− 14.7	7.3	114	0.9	0.76	.056
1255	5	19.0	32.017	253	− 12.9	7.5	117	1.1	0.67	.12
1330	2	18.0	32.310	255	− 11.7	7.4	112	0.8	0.51	.096
1345	4	18.0	32.294	256	− 12.7	6.7	101	0.1	0.36	.074
1400	5	18.0	32.084	250	− 5.7	7.3	110	0.7	0.55	.052
1430	2	18.2	32.303	252	− 8.8	6.9	104	0.3	0.015	.035
1445	4	18.2	32.273	237	5.9	6.8	104	0.3	0.23	.053
1455	5	18.2	32.080	246	− 2.9	5.9	90	−0.7	0.85	.087
1530	2	18.2	32.271	255	− 12.1	6.7	101	0.1	0.69	.14
1540	4	18.5	31.956	235	6.6	6.4	98	−0.1	0.82	.28
1555	5	18.2	31.797	250	− 6.1	6.6	100	−0.01	0.85	.13