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The distributions and fluxes of methane, carbon monoxide, nitrous oxide, hydrogen, and hydroxylamine were examined in Yaquina Bay, a relatively unpolluted estuary on the coast of Oregon, and Big Lagoon, a meromictic, coastal lagoon in Northern California. Special emphasis was placed on measuring hydroxylamine, a potential precursor to nitrous oxide in aquatic systems. A gas chromatographic method that is independent of pH and salinity was developed, thus allowing measurement of nanomolar concentrations of hydroxylamine in euryhaline waters for the first time. The kinetics of this reaction, involving oxidation of hydroxylamine by iron(III), were examined in detail and suggest a complex reaction sequence with a number of possible end products.

In both environments, methane reached high levels of supersaturation, its losses governed primarily by atmospheric exchange. Methane apparently was present in well oxygenated water, with extreme concentrations noted where primary production was greatest. Carbon monoxide distributions were erratic in both systems, and its turnover rates were regulated almost entirely by microbial activity. In Yaquina Bay, nitrous oxide was introduced from a variety of sources, but in situ production appeared relatively low. In Big Lagoon, nitrous oxide

concentrations were controlled by activity in the sediments, with the epilimnetic sediments differing from those of the hypolimnion. Hydrogen, studied only in Yaquina Bay, was at all times supersaturated, its erratic distributions likely influenced by base metal reduction and microbial activity.

Hydroxylamine concentrations were highest in the presence of high ammonium concentrations and oxidation rates, and often were associated with high nitrite. In Big Lagoon, hydroxylamine was present when nitrous oxide was produced and absent when it was consumed, implying that nitrification was, in part, responsible for the production of nitrous oxide. Together with high ammonium oxidation rates, these data indicate that hydroxylamine production was related to nitrification. Although ammonium oxidation rates in both systems were 10% to 50% of the apparent hydroxylamine turnover rates, the relative contribution of ammonium oxidation to total hydroxylamine production was not discernable. Laboratory measurements of hydroxylamine degradation indicated that its turnover rates, even in distilled water, were on the order of hours. This, and the lack of any apparent lag time, suggests that abiotic oxidation plays an important role in cycling hydroxylamine.

CYCLING OF REDUCED TRACE GASES AND HYDROXYLAMINE IN COASTAL WATERS

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To Sherie

for getting me started

To Kathy,

for getting me through

To Stephanie,

and the future

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PREFACE

In accordance with the most recent guidelines for manuscript preparation, the contributions of co-authors to published chapters are listed here. The studies of Yaquina Bay and Big Lagoon were collaborative efforts, hence the results are being published with a number of co-authors. The field work on Yaquina bay was done primarily in association with Jonathan Garber and Ronald Jones. In addition, Dr. Garber was responsible for some of the hydrographic analyses and Dr. Jones measured microbial activites. John Pequegnat directed the field effort on Big Lagoon and was responsible for the hydrographic analyses conducted at Humboldt State University's Marine Laboratory. Ron Jones again was responsible for the microbial analyses on the Big Lagoon samples. Lou Gordon was my major professor during the course of this work and provided technical advice and assistance, as well as valuable comments on all manuscripts.

CYCLING OF REDUCED TRACE GASES AND HYDROXYLAMINE IN COASTAL WATERS

CHAPTER 1

INTRODUCTION

Naturally occurring, reduced trace gases in the marine environment are of interest because of their roles in atmospheric chemistry and global warming (Blake et al. 1982, Logan et al. 1978, Wang et al. 1976, Khalil and Rasmussen 1984) and because they represent significant mechanisms of energy transfer across environmental boundaries (Lilley 1983, Lilley et al. 1982, Fenchel and Blackburn 1979). These gases are produced by microbes in reducing environments such as sediments (e.g. - Kuivila and Murray 1984, Seitzinger et al. 1983, Michener et al. 1985), deep oceanic oxygen minima (Cohen and Gordon 1978), anoxic basins (Cohen 1978, Lilley et al. 1982, Scranton et al. 1984), hydrothermal vents (including abiotic production - Lilley et al. 1983), and surface waters, perhaps associated with anoxic micro-environments (e.g. - Brooks et al. 1981, Oremland 1979, Traganza et al. 1979). Upon diffusion to more oxic waters, reduced trace gases can then take part in a variety of microbially mediated redox reactions, thus enhancing biological growth in aquatic systems. Evasion to the atmosphere leads to a number of destructive chemical reactions, most of which are directly or indirectly photochemically driven, and which ultimately may affect the concentrations of other atmospheric constituents (Logan et al. 1978). Particular attention has been given recently to the atmospheric effects

of some of these gases, along with the anthropogenic, low-molecular-weight chlorocarbons and chlorofluorocarbons, as introductions by man are considerably enhancing the fluxes of reduced gases, and perhaps altering the chemistry and radiative properties of the atmosphere (Ramanathan et al. 1985). However, any evaluation of anthropogenic impacts must be coupled with an understanding of the natural fluxes of these compounds and their chemistry in potential source areas, including soils, oceans, and freshwater environments.

Scientific Rationale

This thesis addresses the distributions and fluxes of the trace gases - - methane, carbon monoxide, nitrous oxide, and hydrogen - - and hydroxylamine, a potential precursor to nitrous oxide, in coastal waters. The objective of this research has been to evaluate the relative importance of in situ processes and atmospheric interactions in regulating the concentrations of the gases. These naturally occurring compounds are studied here as a group primarily because they are linked by the same biological and atmospheric cycles. Microbes cycle them in a variety of natural and artificial environments, which usually display a significant redox gradient. Further, in the atmosphere the trace gases compete for the same free radicals and, collectively, have a significant impact on atmospheric chemistry and global warming. It is therefore of considerable importance to understand the relative contributions of in situ, aquatic processes and air-sea interactions in regulating the distributions and fluxes of these compounds.

Special emphasis has been placed on understanding the fluxes of hydroxylamine. Hydroxylamine is a labile intermediate in the nitrogen cycle and its production may lead to the generation of nitrous oxide, either by nitrification or by direct chemical oxidation. The respective roles of nitrification and denitrification in producing nitrous oxide still are unresolved (e.g. - Seitzinger et al. 1983, Codispoti and Christensen 1985), partly because they operate in adjacent environments and can be linked by intermediate compounds (Knowles 1978). Since hydroxylamine is produced along the nitrification pathway, but is not involved in denitrification, an understanding of its distributions and production rates may help resolve this issue. Unfortunately, little attention has been afforded this labile compound, owing primarily to the lack of a suitable analytical technique for its measurment at natural levels (e.g. - Kolasa and Wardencki 1973). Recently, however, von Breymann et al. (1982) developed a gas chromatographic method that was capable of detecting nanomolar concentrations of hydroxylamine in seawater, thus opening new possibilities for studying the fluxes of nitrous oxide in aquatic systems. Much of the effort for this thesis has focused on improving the technique of von Breymann et al. (1982), adapting it for use in fresh and estuarine waters, and understanding the reaction kinetics, so that the method may be useful in future investigations of in situ hydroxylamine oxidation.

Organization of This Dissertation

This chapter contains a review of the literature on the environmental chemistry and cycling of methane, carbon monoxide,

hydrogen, nitrous oxide, and hydroxylamine. Chapter 2 is a report of the distributions and cycling of these compounds in Yaquina Bay, Oregon. It was during this research that problems with the von Breymann et al. (1982) technique for measuring hydroxylamine were encountered, leading to the development of an improved method. The new method is described in Chapter 3, and the kinetics and mechanism of this method are evaluated and discussed in Chapter 4. Chapter 5 deals with the cycling of nutrients, trace gases, and hydroxylamine along a redox gradient in a meromictic, coastal lagoon. Chapter 5 is the first application of the new gas chromatographic method and it presents the first complete, vertical profiles of hydroxylamine in natural waters.

Analytical Precision

The studies of Yaquina Bay and Big Lagoon required a number of analytical techniques to measure hydrographic characteristics, nutrients, gases, and microbial activities. Precision for all analyses was estimated from the measurement of duplicate samples (Table 1.1). Although the data presented in Table 1.1 were computed for Big Lagoon, the precision of the Yaquina Bay data differed only with respect to hydroxylamine, for which the errors in accuracy led to an overall error of 20% to 30%. Also, nitrite was measured by an automated technique, rather than manually, for the study of Yaquina Bay.

TABLE 1.1. ANALYTICAL PRECISION

Analysis	Error	Analysis	Error
Salinity	<0.01 o/oo	$Si(OH)_4$ (auto)	0.1 uM
Temperature	0.1 C	CH_4	0.8 %
pH	<0.01 pH	CO	1.5 %
Dissolved O_2	0.03 ml/l	N_2O	1.0 %
NH_4^+ (manual)	0.1 uM	NH_2OH	2 nM
NO_2^- (manual)	<0.01 uM	CH_4(ox)	10 %
NO_3^- (auto)	0.1 uM	CO(ox)	10 %
PO_4^{-3} (auto)	<0.01 uM	NH_4^+(ox)	14 %

Error is expressed as pooled standard deviation for a single measurement, based on laboratory replicates. The coefficient of variation is given in % for those analyses encompassing a wide range of concentrations. Variation for field replicates was slightly higher owing to random error in sampling, but never exceeded 4% for chemical analyses.

REVIEW

Trace Gases

Methane

Methane is produced microbially in anaerobic environments by fermentation (e.g. - splitting of acetate) or through the oxidation of H_2 by CO_2. Both of these processes are attributed to one group of organisms, the methanogens (Fenchel and Blackburn 1979). Methane is produced in marine sediments (e.g. - Spiker et al. 1985), hydrothermal vents (Lilley et al. 1983), lake sediments (e.g. - Woltermate et al. 1984, Kuivila and Murray 1984), rice paddies (Koyama 1963), sewage (Smith and Mah 1966), termite guts (Zimmerman et al. 1982), and cattle rumen (Rust 1981). It also is introduced into the atmosphere through biomass burning and natural gas leakage. Methane concentrations in aquatic environments can reach extreme levels of supersaturation, particularly in sewage and eutrophic freshwater lakes, where microbial turnover rates are enhanced by higher temperatures and organic loading (e.g. - Strayer and Tiedje 1978). Concentrations in the upper layers of marine sediments are limited, as methane is consumed rather than produced in the presence of sulfate (Reeburgh and Heggie 1977, Martens and Berner 1977, Devol 1983). Thus, diffusive fluxes often are greater from freshwater sediments, although ebullition from deeper sediments in both marine and freshwater systems may enhance the total fluxes (Strayer

and Tiedje 1978, Martens and Berner 1974, Martens 1976).

Methane is consumed microbially and through atmospheric reactions involving free radical mechanisms. In aquatic environments, methanotrophic bacteria are most abundant where methane and oxygen are present at optimal concentrations (Hanson 1980), and it is believed that they are responsible for oxidizing most of the methane produced in adjacent anoxic zones (Higgens et al. 1981). Anaerobic oxidation of methane in the presence of sulfate has been documented (Devol 1983), as has oxidation by nitrifying bacteria (Jones and Morita 1983a). Although methane is produced in ocean surface waters (Scranton and Brewer 1977, Burke et al. 1983) and coastal sediments (Crill and Martens 1983), it may be slowly consumed in the deep ocean (Scranton and Brewer 1978). Atmospheric methane is destroyed by free oxygen atoms, hydroxyl radicals, and free chlorine, and it undergoes photolysis to produce hydrogen gas (Logan et al. 1978). Methane absorbs electromagnetic radiation strongly in the infrared region, and its contribution to global warming may be near that of CO_2 (World Meteorological Organization 1983).

Carbon Monoxide

The production of CO in aquatic systems is directly and indirectly related to light (Conrad and Seiler 1980a,b). Aquatic CO production by photolysis alone has been demonstrated (Conrad and Seiler 1980a, Redden 1983) and its importance to CO production in the open ocean has been established (Conrad et al. 1982). However, evaluation of the contribution of this abiotic process relative to light-induced microbial responses has proved difficult in eutrophic systems (Conrad et al.

1983). Biological production of CO in the dark generally is oxidative and has been demonstrated for marine bacteria (Junge et al. 1971), a marine coelenterate (Wittenberg 1960), and for soils (Conrad and Seiler 1980b). Anaerobic production of CO in the dark has not been reported to date. In addition to these microbial sources, CO is produced in hydrothermal vents (Lilley et al. 1983), in the atmosphere through photolysis of formaldehyde (Ehhalt and Volz 1976, Calvert et al. 1972) and, anthropogenically, via fossil fuel combustion and forest clearing (Logan et al. 1981).

CO is consumed by a myriad of aerobic micro-organisms, including ammonium oxidizing nitrifiers (Jones and Morita 1983b), chemolithotrophic carboxydobacteria (Cypionka et al. 1980), fungi (Inman and Ingersoll 1971), and algae (Chapelle 1962). Anaerobic consumption has been attributed to sulfate reducers (Yagi 1958), methanogens (Daniels et al. 1977), and phototrophic bacteria (Uffen 1981). In the atmosphere, CO will react with either free oxygen or the hydroxyl radical to produce CO_2 (Logan et al. 1978). Although CO_2 absorbs infrared radiation, the consumption of hydroxyl radical by CO may be of more importance in global warming (Khalil and Rasmussen 1984); CO competes with methane at similar reaction rates for the hydroxyl radical (Davis et al. 1974).

Nitrous Oxide

Nitrous oxide production in the ocean has been the subject of considerable research over the past decade (e.g. - Cohen and Gordon 1979, Elkins et al. 1978). Although it is now accepted that the ocean

is a global source of nitrous oxide, questions concerning the relative roles of nitrification and denitrification in producing and consuming N_2O still remain (Cohen and Gordon 1978, McElroy et al. 1977, Codispoti and Christensen 1985). Nitrous oxide is produced during nitrification, but can be produced or consumed in denitrification. It generally is understood that nitrification is responsible for the net production of N_2O in the oceanic oxygen minima (Cohen and Gordon 1978, Elkins et al. 1978), but recently found high concentrations (2200% saturation) of N_2O invoke the possible involvement of processes other than just nitrification (Elkins et al. 1985). Linkage between nitrification and denitrification similar to that described by Knowles (1978) and Knowles et al (1981) for sediments was proposed by Codispoti and Christensen (1985) as a possible explanation for this phenomenon. Seitzinger et al. (1983) noted similar difficulty in evaluating the origin of N_2O from coastal sediments.

In addition to oceanic and sedimentary sources, considerable N_2O is produced in other aquatic systems (Elkins et al. 1978), as well as in soils (Hahn and Junge 1977). McElroy et al. (1977) evaluated contributions from agricultural application of fertilizers, indicating that N_2O fluxes from this source can be expected to increase dramatically in the future. Sewage also is a source of N_2O. Studies of the Potomac and Merrimack Rivers show supersaturations of up to 4600%, and associate the N_2O production in the rivers and estuaries with ammonium peaks and oxygen reductions (Wofsy et al. 1981, McElroy et al. 1978, Kaplan et al. 1978). DeAngelis and Gordon (1985) found increased concentrations of N_2O following initial fall runoff into a relatively unpolluted estuary, and attributed the elevation to leaching of soils.

The only known microbial sink for N_2O is denitrification (Payne 1981). As noted, this process also will produce N_2O, and the degree of its influence on N_2O budgets is poorly understood (e.g. - McElroy et al. 1977). Although photolysis of N_2O in the troposphere is unlikely (Johnston and Selwyn 1975), its destruction may be catalyzed by suspended particulate matter (Pierotti et al. 1978). Stratospheric photolysis of N_2O, however, is the only established atmospheric removal process at this time. This reaction gives rise to NO, which, in turn, can affect the chemistry of numerous free radicals, thereby influencing stratospheric ozone concentrations (McElroy and McConnell 1971). N_2O also absorbs infrared radiation, thus directly contributing to the global heat budget (Yung et al. 1976)

Hydrogen

Hydrogen is produced in marine and freshwater sediments primarily by microbial fermentations (Fenchel and Blackburn 1979). It is consumed by methanogens, sulfate reducers, and a variety of other chemautotrophic bacteria often before it can leave the sediments (Michener et al. 1985). These organisms probably are active in the water column, as erratic profiles of H_2 have been reported for the Atlantic Ocean (Seiler and Schmidt 1974, Herr and Barger 1978), the Norweigian Sea (Herr et al. 1981), and the tropical Pacific (Lilley 1983). Distributions are more systematic where sharp redox gradients occur, such as in Saanich Inlet (Lilley et al. 1982). Supersaturations in surface waters have been associated with a number of possible organisms, including nitrogen-fixing cyanobacteria (Herr et al. 1981), as well as denitrifier and protozoans (Lilley et al. 1982). Lilley (1983) suggested incomplete

oxidation of NH_4^+ and CH_4 by nitrifiers and methylotrophs as a possible source for hydrogen. Extreme supersaturations of hydrogen have been reported for hydrothermal vent fields (Lilley et al. 1983), and hydrogen is known to be produced by metal-catalyzed hydrolysis (e.g. - Scranton et al. 1984).

Hydrogen also is generated in the atmosphere by the photolysis of methane and by a variety of free radical mechanisms involving oxygen, methane, peroxide, water, and nitric acid (Logan et al. 1978). Atmospheric hydrogen is consumed in reactions involving the hydroxyl radical and free chlorine, hence also has an indirect role in global warming.

Hydroxylamine

Hydroxylamine is one of the least understood intermediates in the nitrogen cycle. That NH_2OH is produced and consumed along the pathway between ammonium and nitrite has been known for some time (Amarger and Alexander 1968, Verstraete and Alexander 1972), but its distribution in natural waters, particularly seawater, has been only rarely investigated. The naturally low concentrations of hydroxylamine in all but a few environments, its extreme lability, and, until recently, the lack of a sensitive method for its detection and measurement have limited the study of its chemistry in natural waters. Although NH_2OH has been detected in lakes (Tanaka 1953, Koyama and Tomino 1967, Baxter et al. 1973, Pitwell 1975, Wood et al. 1984) and some marine environments (Fiadero et al. 1967, von Breymann 1983, von Breymann et

al. 1982), detailed profiles relating processes of formation and destruction have yet to be obtained. A better understanding of the fluxes and concentrations of hydroxylamine may help answer questions concerning the relative contributions of nitrification, dentitrification, and ammonification in cycling nitrogen in natural systems. Indeed, such questions often emanate from investigations of nitrogenous gas fluxes (N_2, N_2O) (Seitzinger et al. 1983, Cohen and Gordon 1978, Sorensen 1978a) and from studies of ammonium regeneration (Koike and Hattori 1978a,b, Sorensen 1978b). An understanding of hydroxylamine fluxes would certainly aid in determining the sources and sinks of other nitrogenous compounds, particularly N_2O.

The Role of NH_2OH in the Nitrogen Cycle

The value of understanding the fluxes of hydroxylamine lies in a number of its chemical and biochemical properties. The first of these is that NH_2OH has sufficient reducing power to make it attractive to a myriad of microorganisms with enzyme systems capable of extracting this energy in an oxidizing environment (Anderson 1964b, 1965, Painter 1970, Focht and Verstraete 1977). However, NH_2OH is extremely labile; it is prone to autoxidation catalyzed by trace metals common to both freshwater and seawater (Moews and Audrieth 1959, Anderson 1964a). Thus, the mere detection of hydroxylamine in oxidative environments is indicative of high rates of production (e.g. - Tanaka 1953, Baxter et al. 1973). If the rate of autoxidation is sufficiently rapid, it may even constitute a significant sink for fixed nitrogen in natural waters.

Second, hydroxylamine is believed to be a free (non-enzyme bound) intermediate in the oxidation of ammonium to nitrite (Rajendran and

Venugopalan 1976, Focht and Verstraete 1977, Fenchel and Blackburn 1979), and, to a lesser extent, in the dissimilatory reduction of nitrate (or nitrite) to ammonium (Figure 1.1; Yoshida and Alexander 1971, Yordy and Ruoff 1981). It also is an intermediate in heterotrophic nitrification, but whether much is released to the environment as a part of this process is not certain (Verstraete and Alexander 1972, 1973). However, hydroxylamine clearly is not involved in what classically is termed denitrification, the respiratory reduction of nitrate to either dinitrogen gas or nitrous oxide (Hollocher 1978, Fenchel and Blackburn 1979, Payne 1981). Thus, together with measurements of ammonium oxidation rates, or coupled with a diffusion model, the measurement of hydroxylamine can be a potentially powerful tool.

Autoxidation of Hydroxylamine

Some of the earlier indications of hydroxylamine oxidation were associated with the crystalline solid, which was known to degrade rapidly in the presence of air at room temperature. This ease of oxidation gave rise to many methods for the quantitative measurement of NH_2OH (Bray et al. 1919, Kolasa and Wardenki 1974), and led to its experimental use in the photographic industry (James 1939, 1941, 1942). The oxidation of hydroxylamine is promoted or catalyzed by many metal ions, including iron (Rao and Rao 1957), copper (Anderson 1964a), cerium (Cooper and Morris 1952), vanadium (Gowda et al. 1957), and, to a lesser extent, silver and mercury (James 1942). It is strongly inhibited by the addition of metal "deactivators", or ligands (Moews and Audrieth 1959, Anderson 1964a, Hughes and Nicklin 1971). Iodine and bromate have

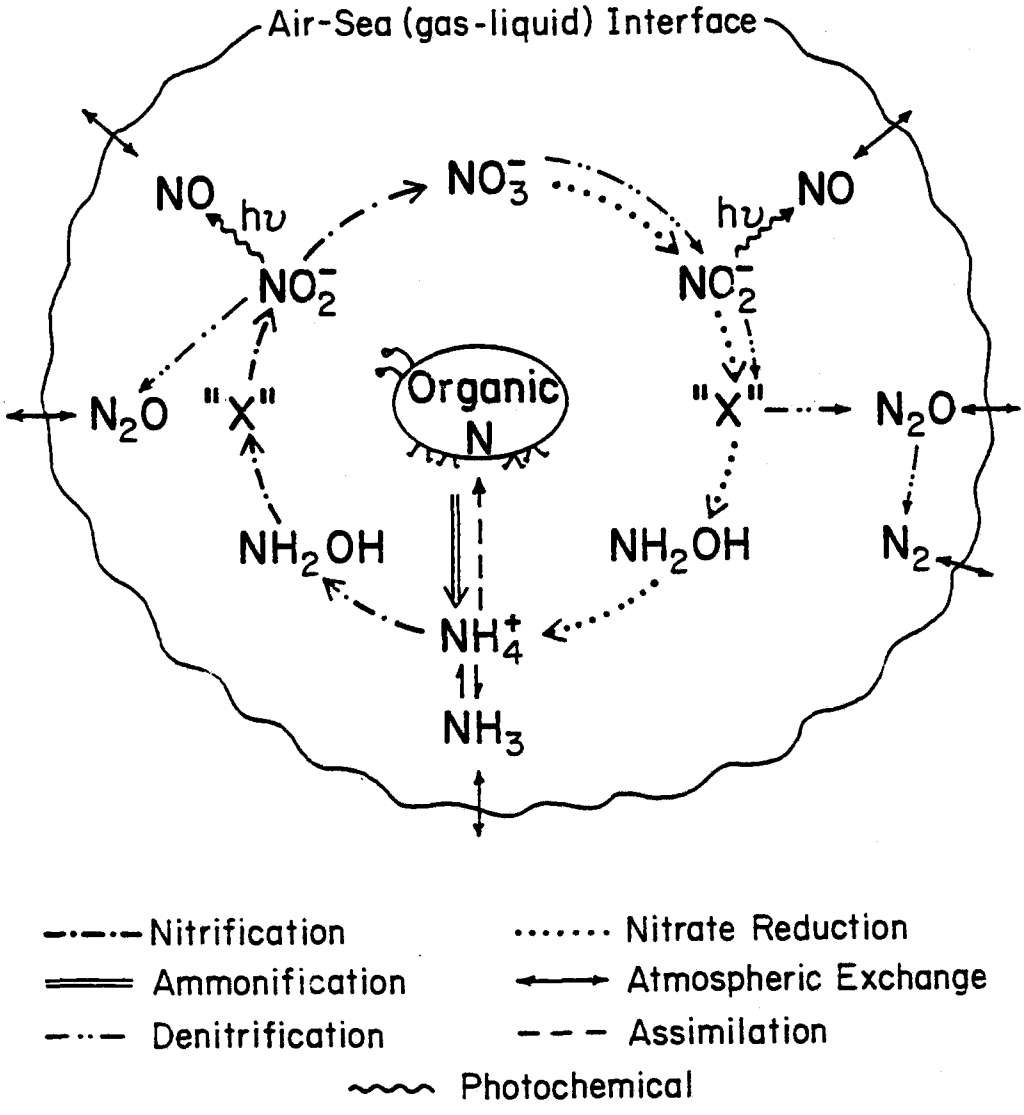

Figure 1.1. Production of gases and hydroxylamine in the nitrogen cycle

also been used in the quantitative analysis of NH_2OH by oxidation (Kolasa and Wardencki 1974). The only quantitative method for the analysis of NH_2OH which involves its reduction involves use of the titanous ion, but, as this technique requires conducting the assay under an inert atmosphere, it has not seen much use.

The products of hydroxylamine oxidation are known to vary with pH (James 1942, Hughes and Nicklin 1971) and with the oxidizing agent or catalyst (Anderson 1964a, Kolasa and Wardenki 1973). They may encompass any of a number of nitrogenous compounds including HNO_3, NO_2^-, N_2O, and N_2. At near-neutral pH and with some catalysts, a major product often detected is N_2O (e.g. - Anderson 1964a). In fact, the detection of N_2O was the method of choice for the quantitative measurement of NH_2OH at nanomolar concentrations in natural waters of neutral pH (von Breymann et al. 1982).

The mechanisms of NH_2OH oxidation are still not clear, but they are believed to involve nitroxyl as a transient intermediate, followed by either peroxonitrite or cis-hyponitrite, depending on pH. Anderson (1963) conclusively demonstrated that hyponitrite decomposed quantitatively to N_2O at neutral to slightly alkaline pH. Later, studying the copper catalyzed oxidation of NH_2OH at pH 8, he suggested that the formation of N_2O did not involve hyponitrite as an intermediate, but that a transient intermediate containing a single nitrogen atom (nitroxyl) may be involved.

Hughes and Nicklin (1971) found that peroxonitrite and nitrite were the major products of NH_2OH oxidation by molecular oxygen at pH 11-12. They proposed a mechanism whereby NH_2OH was oxidized first to NOH, then

to peroxonitrite if the pH was high, or else, at pH 7 to 8, *via* dimerization to to *cis*-hyponitrite. The peroxonitrite would react with additional NH_2OH to produce NO_2^-, and hyponitrite would rapidly convert to N_2O. Hughes and Nicklin were unable to get *trans*-hyponitrite to spontaneously generate N_2O, but the *cis* species decomposed to N_2O even at high pH.

Whatever the mechanism, it is clear that N_2O production through hydroxylamine oxidation may be significant. The lability of hydroxylamine make its measurement a particularly useful tool, although much needs to be learned about its biological modes of production and consumption. Thus, one of the major objectives of this thesis has been to evaluate the distributions and turnover rates of hydroxylamine in coastal waters, and to identify any relationships to other chemical and biological processes in the systems being studied.

CHAPTER 2

DISTRIBUTION AND FLUXES OF REDUCED TRACE GASES AND HYDROXYLAMINE IN YAQUINA BAY, OREGON

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ABSTRACT

The distributions of methane, carbon monoxide, nitrous oxide, and hydrogen along the length of the Yaquina River estuary were examined on six occasions over a year's time during 1983 and 1984. To help evaluate the fluxes of these reduced trace gases, hydroxylamine concentrations and microbial oxidation rates for methane, carbon monoxide, and ammonium were measured along with the trace gases. Methane, introduced primarily from a wastewater discharge, attained high levels of supersaturation, and was removed almost entirely by atmospheric evasion. Carbon monoxide was produced and consumed rapidly by microbes in the estuary, atmospheric evasion contributing little to its overall cycling. Nitrous oxide entered the estuary from fall runoff, upwelled seawater, and sedimentary diffusion, with little relative contribution from aquatic nitrification. Ammonium oxidation correlated with apparent hydroxylamine production, but whether these processes were one and the same is unknown. Hydrogen production rates apparently were high, as H_2 remained supersaturated at all times in the estuary.

INTRODUCTION

Over the past decade, considerable attention has been given to reduced, natural trace gases, because of their direct and indirect roles in global warming and atmospheric chemistry (Wang et al. 1976, Logan et al 1978, Khalil and Rasmussen 1984), and because they represent important mechanisms of global energy transfer (Lilley 1983). Atmospheric concentrations of CH_4 and N_2O have been increasing in recent years, owing presumably to increased anthropogenic input (Nickerson 1984, McElroy et al. 1976, Blake et al. 1982), and it is believed that their contribution to global warming could amount to as much as half that of CO_2 (World Meteorological Organization 1983). CO, although it does not absorb strongly in the infrared region, does compete with CH_4 for the hydroxyl radical and thus may indirectly affect the CH_4 budget (Khalil and Rasmussen 1984, Logan et al. 1978). Similarly, H_2 is not directly involved in global warming, but is an important component of the cycles that regulate these gases (Fenchel and Blackburn 1979).

Because significant natural fluxes exist for these gases, the assessment of man's impact on their distributions can be difficult. All are produced microbially in water and soils, and all have microbial sinks (Fenchel and Blackburn 1979). In addition, CO is produced through the photolysis of carbonyl compounds in aquatic systems (Redden 1983, Conrad et al. 1982), and H_2 is generated naturally through the hydrolysis of water. All of the gases are consumed abiotically in atmospheric reactions (Logan et al. 1978). In the marine environment trace gases are produced and consumed across oxic/anoxic boundaries such as those that

occur in sediments, fjords, enclosed seas, and the deep oceanic oxygen minima (e. g. - Lilley et al. 1982, Cohen 1978, Codispoti and Christensen 1985). Considerable attention has been given to processes regulating trace gas fluxes in the open ocean (e.g. - Cohen and Gordon 1978, 1979, Elkins et al. 1978, Bullister et al. 1982, Scranton and Brewer 1977, Burke et al. 1983) and much effort has focused on coastal sediments where burial of organic matter leads to the establishment of sharp oxygen gradients and subsequent layering of redox processes (e.g. - Seitzinger et al. 1983, 1984, Devol 1983, Crill and Martens 1983). Nevertheless, the locations and intensity of trace gas production and consumption in coastal and estuarine waters remain elusive, owing in part to the dynamics of the systems and to the complicating presence of anthropogenic sources.

We report here on the distributions and fluxes of CH_4, CO, N_2O, and H_2 in the waters of Yaquina Bay, Oregon. Yaquina Bay, although influenced measureably by some aquatic discharges, is relatively unpolluted and can be considered typical of the small estuaries of the Pacific Northwest. In Oregon, these small estuaries collectively have a tidal prism and surface area equal to about two-thirds that of the Columbia River estuary, hence they may have a considerable impact on the chemistry of coastal waters. The purpose of our investigation was to evaluate the relative contributions of atmospheric exchange and in situ processes in regulating the concentrations of trace gases in Yaquina Bay. Our plan involved the measurement of nutrient concentrations, gas concentrations, and microbial oxidation rates along the length of the estuary over a year's time. We also explored the use of hydroxylamine measurements for evaluating sources of nitrous oxide.

STUDY AREA DESCRIPTION

Yaquina Bay is one of sixteen small to medium-sized estuaries along the Oregon coast (Figure 2.1). In general, these smaller estuaries tend to be well mixed, are relatively unpolluted, and receive significant amounts of freshwater from rainfall and streamflow. This leads to a seasonal regime of freshwater input, the major contribution of nutrients from freshwater being in the winter. During the late spring and summer, when freshwater runoff is nil, these estuaries receive nutrients primarily from mixing with upwelled, coastal waters.

Yaquina Bay lies at the mouth of the Yaquina River, a coastal stream that drains 700 km^2 of watershed (Percy et al. 1974). The estuary is about 30 km long and is well-mixed for much of the year; the ratio of freshwater discharged to the tidal prism ranges from .002 to .03 and vertical salinity gradients, generally temporal in the winter, are essentially non-existent in the summer (Burt and Marriage 1957). The estuary occupies an area of 1580 hectares, 550 of which are tidelands.

The residence time of water in Yaquina Bay ranges from days to weeks (Burt and Marriage 1957, Callaway and Specht 1982). Although nutrient and gas concentrations resuting from two discharges to the bay are measureable, the impact of pollutants is minimal. At the upper end of the estuary, the City of Toledo discharges an average of 600,000 gallons per day (.025 m^3/sec) of secondarily treated, disinfected, municipal wastewater, primarily domestic in nature. This is a source of

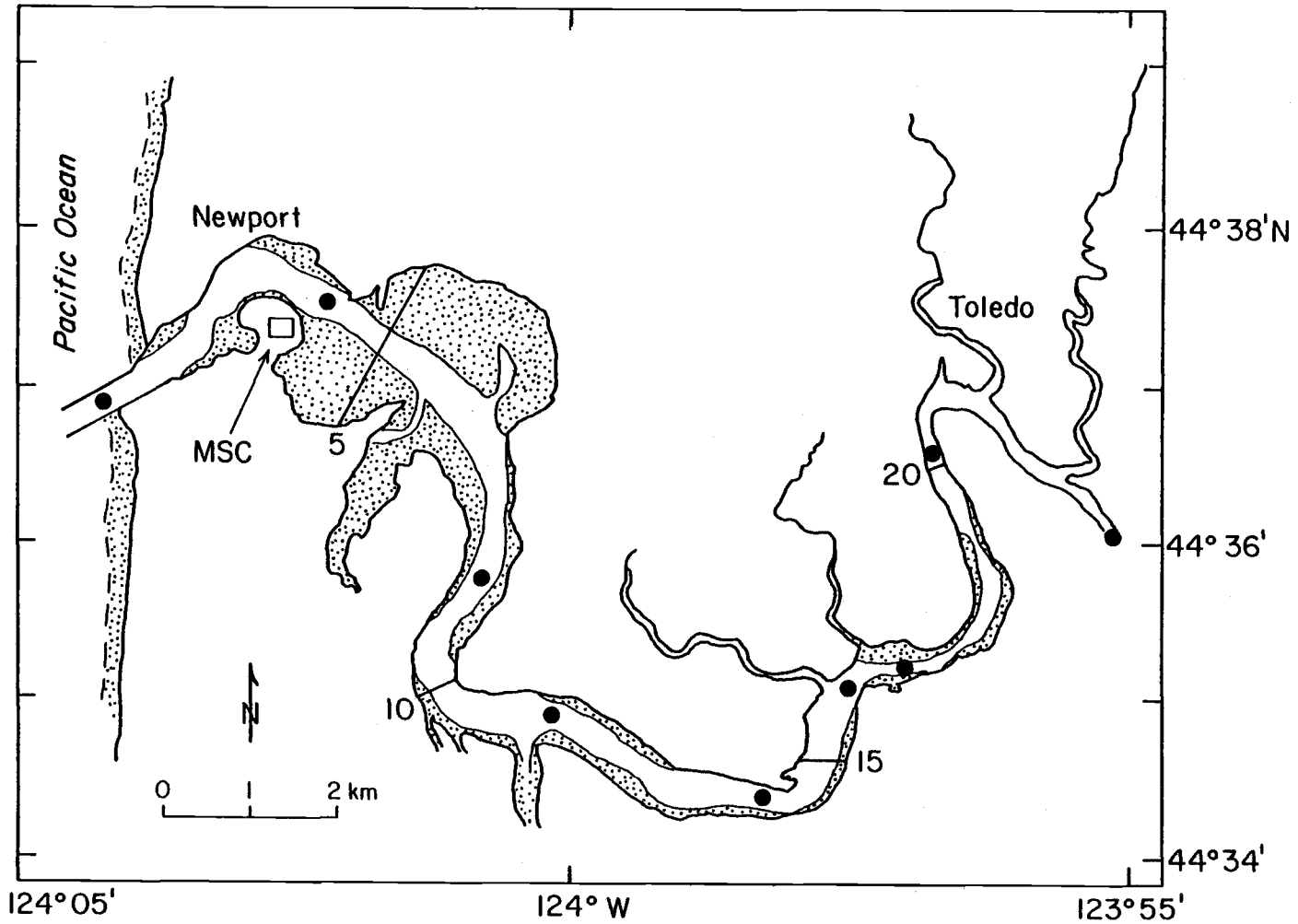

Figure 2.1. Yaquina Bay, Oregon. Intertidal zone denoted by stipling. River kilometer noted at 5 km intervals. Most frequently sampled stations are noted by (●). MSC is the Hatfield Marine Science Center.

organic material, ammonium, and, as we shall see, methane and nitrous oxide, to the bay. Downstream, near the mouth, a small fish processing industry operates in Newport, discharging liquid wastes containing dissolved organic matter into the bay. Also noteworthy is the discharge of considerable sodium tripolyphosphate during processing of shellfish. Oysters are grown commercially in the middle of the bay and a few small boat basins are located along its length.

METHODS AND MATERIALS

Field Methods and Sample Collection

As part of a comprehensive study of the nutrient dynamics of Yaquina Bay, we sampled for trace gases and related microbial activity on six occasions from October 1983 to August 1984. Samples were collected from the surface and bottom waters at six to nine locations along the length of the estuary (Figure 2.1). For consistency, we always sampled in the early morning, during a low tide. Our goal was to begin near the mouth about 1 1/2 hours before the local low tide and to collect our last upstream sample about 1 1/2 hours after the local low tide. Together with a one hour tidal delay from Newport to Toledo, this provided a four-hour sampling window. Hence, most samples were collected between the hours of 0700 and 1100 (Appendix, Table A.2). An incoming seawater sample was collected at depth, between the jetties, upon our return downstream. Although we generally sampled at fixed stations, salinities were checked on site with a hand-held refractometer to assure positioning relative to the last station. Also, because we were sampling for hydrogen, we minimized the use of metal in our collection procedures. A wooden dory was used as a platform, from which samples were collected with a five liter Niskin bottle attached to a nylon line.

Trace gas samples were siphoned into 25 ml glass flasks with Teflon^{R} stopcocks, and preserved with 0.5 ml of 5% $HgCl_2$. Hydroxylamine samples were drawn into acid washed and DDW rinsed, 125 ml, opaque bottles with greased, ground-glass stoppers, treated with ferric ammonium sulfate (FAS), and preserved with $HgCl_2$ (von Breymann et al. 1982). Dissolved oxygen samples were fixed immediately with Mn^{+2} and KI solutions. To minimize atmospheric contamination, all of the above samples were allowed to overflow the containers by about two volumes. Aliquants for pH were drawn directly into plastic, 50 ml syringes, inserted through the siphon tubing. Nutrient samples were collected into acid-cleaned, 60 ml, polypropylene bottles that had been sterilized with acetone. These, the pH samples, and the samples for microbiological analysis (drawn into 500 ml polyethylene bottles) were placed immediately into an ice bath. Last of all, the Niskin bottle was drained into a two-liter polyethylene container, to be subdivided later that day into portions for measurement of salinity and for subsequent analysis of particulate and dissolved organic matter (J.H. Garber et al. - manuscript in preparation).

Laboratory Analysis

Nutrients, dissolved oxygen, microbial activities, and pH were measured on the day of collection, whereas trace gases and hydroxylamine were analyzed within a week. Salinity samples were kept in seasoned, wire-bail citrate bottles, sometimes for months, until a sufficient number had accumulated for analysis.

Nitrite and nitrate were measured with other nutrients on a four-channel Technicon^R Autoanalyzer^R (Atlas et al. 1971), but analyses for ammonium were conducted manually by a modification of the method of Strickland and Parsons (1972). Dissolved oxygen initially was titrated according to Strickland and Parsons (1972), but later in the study we used a microburette and Carpenter's (1965) technique. pH was measured at 25 C in a temperature-controlled chamber with minimal exposure to the atmosphere. Salinity was determined with an Autosal^R for four of the six sampling dates, and with a refractometer for the other two.

Methane, carbon monoxide, nitrous oxide, and hydrogen were measured from the same sample on an automated, split-flow gas chromatograph, a complete description of which can found in Redden (1983). Briefly, however, samples were stripped with purified helium onto a liquid-nitrogen cooled trap with molecular sieve 5A. On removal of the liquid nitrogen, H_2 was allowed to flow through a room-temperature column to a helium ionization detector (HID). The trap was then heated to 250 C and the gases separated on a three foot column of MS-5A, also kept at 250 C. CH_4 and CO were further separated on a 90 C MS-5A column, combined with a stream of H_2 over a heated (320 C) nickel catalyst to reduce the CO, and subsequently sent to a flame ionization detector. N_2O was swept from the initial column with a stream of purified nitrogen gas to an electron capture detector.

Hydroxylamine was converted to nitrous oxide on collection by the addition of FAS (von Breymann et al. 1982). The samples were transferred to duplicate 25 ml gas flasks in the laboratory and analyzed for N_2O as described above. The concentration of hydroxylamine was then determined by difference from the initial N_2O. Although this method has been

demonstrated to give a quantitative recovery in seawater, we had some difficulty obtaining a constant yield of hydroxylamine for Yaquina Bay waters. (We subsequently have found that the variations in recovery as N_2O were caused by pH, alkalinity, and salt effects that arise owing to seawater dilution, and have improved the method to account for these effects - Chapters 3, 4). From the analysis of samples with standard additions, we found that the recovery by the von Breymann et al. (1982) method varied by up to 25%, thus rendering the hydroxylamine data useful only for exploratory evaluations.

Estimates of microbial oxidation rates of CH_4, CO, and NH_4^+ were based on C-14 techniques (Jones et al. 1984, Jones and Morita 1983a,b), with ammonium oxidation estimated by difference from the continued oxidation of CO after addition of NSERVE. An empirical factor of 1.5 x 10^{-3} nM CO/nM NH_4^+ was used for converting nitrifier oxidation of CO to potential oxidation of NH_4^+. In situ oxidation was estimated from in situ concentrations and potential oxidation rates.

RESULTS AND DISCUSSION

Estuarine Hydrography and Dynamics

The general hydrographic characteristics of the bay were governed primarily by streamflow, although exchange and mixing with the ocean represented a significant influence. In October of 1983, the estuary was vertically well-mixed with reasonably warm water flowing downstream, typical of late summer, low-flow conditions (Table 2.1). Oxygen was about 80% saturated throughout the estuary, owing presumably to overnight respiration, and nitrogenous nutrients were abundant, although modestly so. The November sampling was conducted about a week after the onset of fall rains (Table 2.2). The increased flow tended to stratify the estuary and leached considerable nitrate from the soils in the watershed. Dissolved oxygen was still around 80% saturated, indicating that respiration rates must have increased along with the streamflow.

In January and April of 1984, the estuary assumed a typical winter profile, with a strong surface freshwater signal downstream, and a saline penetration of only 20 km (Table 2.1). Higher dissolved oxygen concentrations probably were the result of a higher flow to respiration ratio in the estuary. Stratification was significant in January, particularly at the 14.2 km station, where bottom water movement was slowed by a sill just downstream. This effect also was noted in November. The trapping of saline water resulted in a chemical signal in

TABLE 2.1. HYDROGRAPHIC CHARACTERISTICS AND NITROGENOUS NUTRIENTS IN YAQUINA BAY

(10/6/83)

River Km		Sal. (o/oo)	Temp. C	pH	O_2 (%Sat)	NO_3^- (uM)	NO_2^- (uM)	NH_4^+ (uM)
1.5	b	34	10.1		92	14.6	.36	1.3
3.9	s	33	11.2		91	10.1	.36	2.7
	b	34	10.9		84	10.4	.30	2.8
8.5	s	30	13.6		85	9.5	.36	3.4
	b	30	13.4		84	9.5	.33	3.4
11.4	s	24	14.2		80	12.8	.42	4.0
	b	24	14.2		81	12.8	.38	4.0
14.2	s	23	14.5		82	14.2	.36	4.5
	b	23	14.4		79	14.2	.38	4.4
16.2	s	22	14.5		80	15.0	.36	4.7
	b	22	14.2		79	15.3	.35	4.7
17.0	s	22	14.5		80	15.2	.39	4.7
	b	22	13.5		78	15.5	.36	4.7
20.5	s	20	14.8		80	16.9	.36	5.2
	b	19	14.6		80	16.7	.36	5.1
25.0	s	11	14.4		85	22.8	.32	4.5
	b	10	14.3		82	22.9	.32	4.1
27.0	s	6	14.6		82	24.4	.21	3.2
	b	5	14.5		81	24.4	.21	3.1

(11/8/83)

River Km		Sal. (o/oo)	Temp. C	pH	O_2 (%Sat	NO_3^- (uM)	NO_2^- (uM)	NH_4^+ (uM)
1.5	b	32.26	12.9	8.17	101	2.8	.28	.9
3.9	s	27.00	12.1	8.04	93.4	16.5	.31	3.5
	b	31.58	13.0		101	4.3	.24	1.5
8.5	s	17.94	11.5	7.80	91.5	47.6	.38	4.8
	b	25.40	12.6	8.00	84.7	20.9	.34	4.1
10.5	s	11.75	11.2	7.54	83.1	77.2	.44	4.8
	b	19.34	12.1	7.84	85.6	42.4	.38	4.9
11.4	s	9.79	11.2	7.46	80.8	86.9	.49	4.5
	b	17.29	12.3	7.78	84.4	51.0	.42	4.9
14.2	s	6.25	11.1	7.27		106	.49	4.1
	b	22.18	12.2	7.92	86.0	31.2	.38	4.6
16.2	s	5.09	10.7	7.19	82.5		.47	4.1
	b	15.68	11.9	7.71	83.1	60.2	.47	4.9
18.0	s	4.63	10.7	7.18	83.0	114	.54	4.0
	b	9.23	11.3	7.38	80.9	89.1	.45	4.5
20.3	s	2.21	10.5	7.01	82.9	122	.49	3.1
	b	3.25	10.7	7.10	82.1	116	.56	3.6

TABLE 2.1. (continued)

River Km		Sal. (o/oo)	Temp. C	pH	O_2 (%Sat)	NO_3^- (uM)	NO_2^- (uM)	NH_4^+ (uM)
(1/7/83)								
1.5	b	29.60	11.2	8.16	105	5.2	.36	.6
3.9	s	23.22	11.0	8.10	92.3	27.3	.39	1.6
	b	29.90	11.0	8.16	101	6.3	.35	.9
8.5	s	12.96	10.4	7.82	94.3	61.0	.25	2.0
	b	23.83	11.0	8.10	91.7	25.4	.36	1.7
11.4	s	5.70	10.1	7.36	92.9	86.3	.18	1.8
	b	13.90	10.5	7.87	93.5	58.1	.20	2.0
14.2	s	3.19	10.1	7.19	93.1	95.0	.27	1.6
	b	18.97	10.5	8.02	93.9	40.5	.39	2.1
16.2	s	1.18	10.0	7.05	92.8	100	.18	1.3
	b	5.59	10.2	7.34	92.3	101	.20	1.8
18.0	s	1.02	10.1	6.96	92.1	101	.23	1.3
	b	5.59	10.0	7.27	91.4	86.4	.21	1.9
20.3	s	.30	10.0	6.83	92.5	102	.15	1.2
	b	.19	10.0	6.83	91.3	103	.19	1.2

River Km		Sal. (o/oo)	Temp. C	pH	O_2 (%Sat)	NO_3^- (uM)	NO_2^- (uM)	NH_4^+ (uM)
(4/5/84)								
1.5	b	32.08	11.0	8.12	105	1.2	.20	.6
3.9	s	23.21	11.0	8.11	97.7	24.1	.22	1.7
	b	29.14	11.0	8.15	101.5	7.0	.27	1.4
8.5	s	15.03	10.7	7.96	94.2	36.3	.23	1.7
	b	18.16	10.9	8.04	95.5	37.2	.21	1.8
11.4	s	8.75	10.8	7.28	94.0	60.7	.21	1.3
	b	9.20	10.4	7.71	93.2	59.4	.28	1.3
14.2	s	3.16	10.3	7.19	94.6	76.0	.19	.9
	b	6.47	10.5	7.69	92.4	67.0	.23	1.2
20.3	s	.08	10.0	7.13	97.6	83.3	.17	.7
	b	.12	10.0	7.47	97.5	82.3	.18	.8
25.0	s	.01	10.5	7.01	99.7	85.1	.17	.7
	b	.01	10.2	7.22	99.3	85.3	.15	.7

TABLE 2.1. (continued)

(6/13/84)

River Km		Sal. (o/oo)	Temp. C	pH	O_2 (%Sat)	NO_3^- (uM)	NO_2^- (uM)	NH_4^+ (uM)
1.5	b	32.96		7.89	(78.6)	18.1	.35	1.4
3.9	s	20.37	14.0	7.87	96.8	31.5	.34	1.7
	b	26.23	13.0	7.92	88.7	21.5	.41	2.1
8.5	s	11.13	14.6	7.60	94.4	49.9	.43	1.7
	b	12.29	14.8	7.66	95.3	47.1	.37	1.6
11.4	s	2.59	15.0	7.19	96.6	70.5	.53	1.5
	b	3.45	14.9	7.25	99.2	68.0	.47	1.4
14.2	s	.41	14.3	7.02	99.9	77.2	.34	.8
	b	1.95	14.7	7.13	96.3	72.1	.80	1.5
20.3	s	.04	13.7	7.00	98.8	79.6	.31	.9
	b	.05	13.3	6.94	97.7	77.1	.26	1.1
25.0	s	.01	13.0	7.12	102	82.0	.26	.9
	b	.02	13.0	7.13	104	83.8	.71	1.0

(8/15/84)

River Km		Sal. (o/oo)	Temp C	pH	O_2 (%Sat)	NO_3^- (uM)	NO_2^- (uM)	NH_4^+ (uM)
1.50	b	34.3	14.5	8.10	119	3.8	.25	1.40
3.90	s	33.0	15.3	7.89	93	5.4	.31	2.83
	b	33.8	14.8	7.83	84	4.0	.26	2.93
8.50	s	29.7	18.8	7.65	84	6.7	.31	1.30
	b	30.0	18.0	7.58	83	6.3	.32	1.94
11.40	s	25.0	21.0	7.54	81	9.4	.32	1.59
	b	25.5	20.4	7.54	78	8.5	.33	1.83
14.20	s	22.5	21.8	7.49	81	11.1	.35	2.13
	b	23.3	20.1	7.44	75	10.8	.38	2.45
17.00	s	18.7	22.0	7.32	75	14.9	.41	3.25
	b	19.8	22.4	7.44	78	14.6	.39	3.23
22.40	s	14.3		7.25	(77)	21.5	.40	3.22
27.00	s	6.3	23.0	7.28	83	32.2	.36	2.22
35.00	s	.4	22.6	7.22	78	33.1	.35	2.25

TABLE 2.2. WEATHER AND STREAMFLOW DATA FOR SAMPLING TIMES

Date	Windspeed (m/sec)	Precip (cm/5-day)	Str. Flow (m^3/sec)	WW Disch. (m^3/sec)	Ratio (%)
10/6/83	2.4	0.15	1.3	.017	1.4
11/8/83	3.3	1.85	22	.067	.3
1/7/84	2.7	0.41	53	.069	.1
4/5/84	4.0	4.95	18	.040	.2
6/13/84	2.6	0.25	25	.048	.2
8/15/84	2.7	0	1.6	.018	1.1

All values, except precipitation which is a five day total, are averages for five days before sampling. Windspeed and precipitation data are for Portland, Oregon; actual precipitation on the watershed probably was much higher. Streamflow rates were estimated from gauged flows and drainage areas. The ratio given is the percent wastewater contribution to natural streamflow.

the bottom water that was more representative of downstream properties, particularly evident in the nutrient and pH values (Table 2.1; Appendix Table A.2), and which lead to anomalies in some of the trace gas profiles. The estuary was less stratified in April as a result of a lowered flow (Table 2.2), and the effects of the sill were less pronounced.

Unusually high rainfall continued into June, allowing the stratification to persist and keeping the oxygen high. However, the water was considerably warmer than during the winter, and the incoming ocean water had a considerable upwelling component, as shown by the low oxygen and high nitrate. By August, the estuary once again had assumed its summertime profile of weak stratification, undersaturated morning oxygen, and lower nitrate concentrations.

Distributions and Fluxes of Trace Gases and Hydroxylamine

Methane

Methane was supersaturated throughout the estuary at all times, showing extremely high concentrations upstream, with downstream reductions being a function not only of mixing, but also of removal processes (Figure 2.2). The source of most of the methane in the estuary was the City of Toledo municipal wastewater discharge. Methane is generated during the digestion of sewage, and its concentrations can become very high. Observed lower methane concentrations upstream of Toledo further support this contention. Although methane is produced at considerable rates in marine and freshwater sediments, we should have

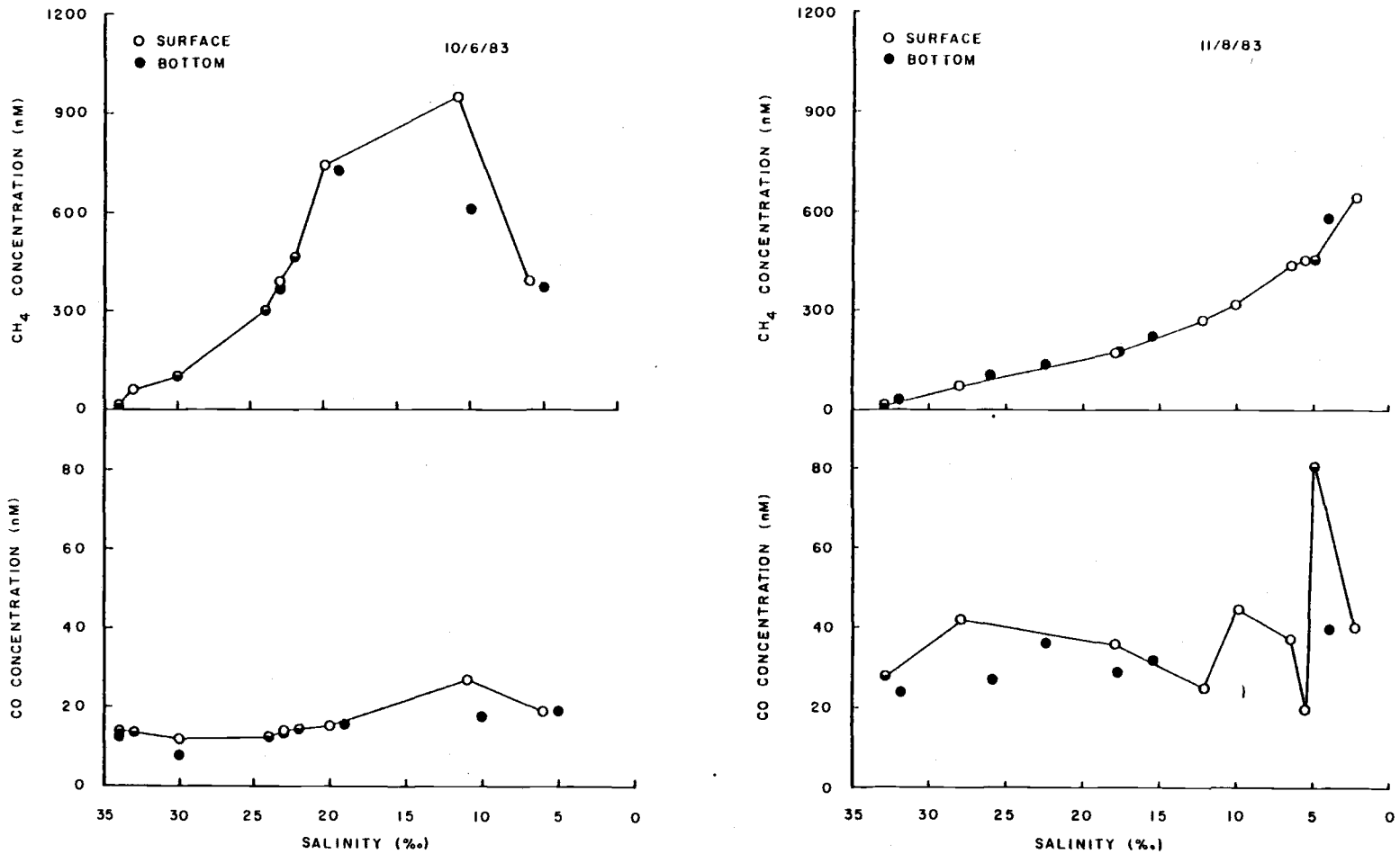

Figure 2.2a. Methane and carbon monoxide distributions in Yaquina Bay, 10/6/83, 11/8/83.

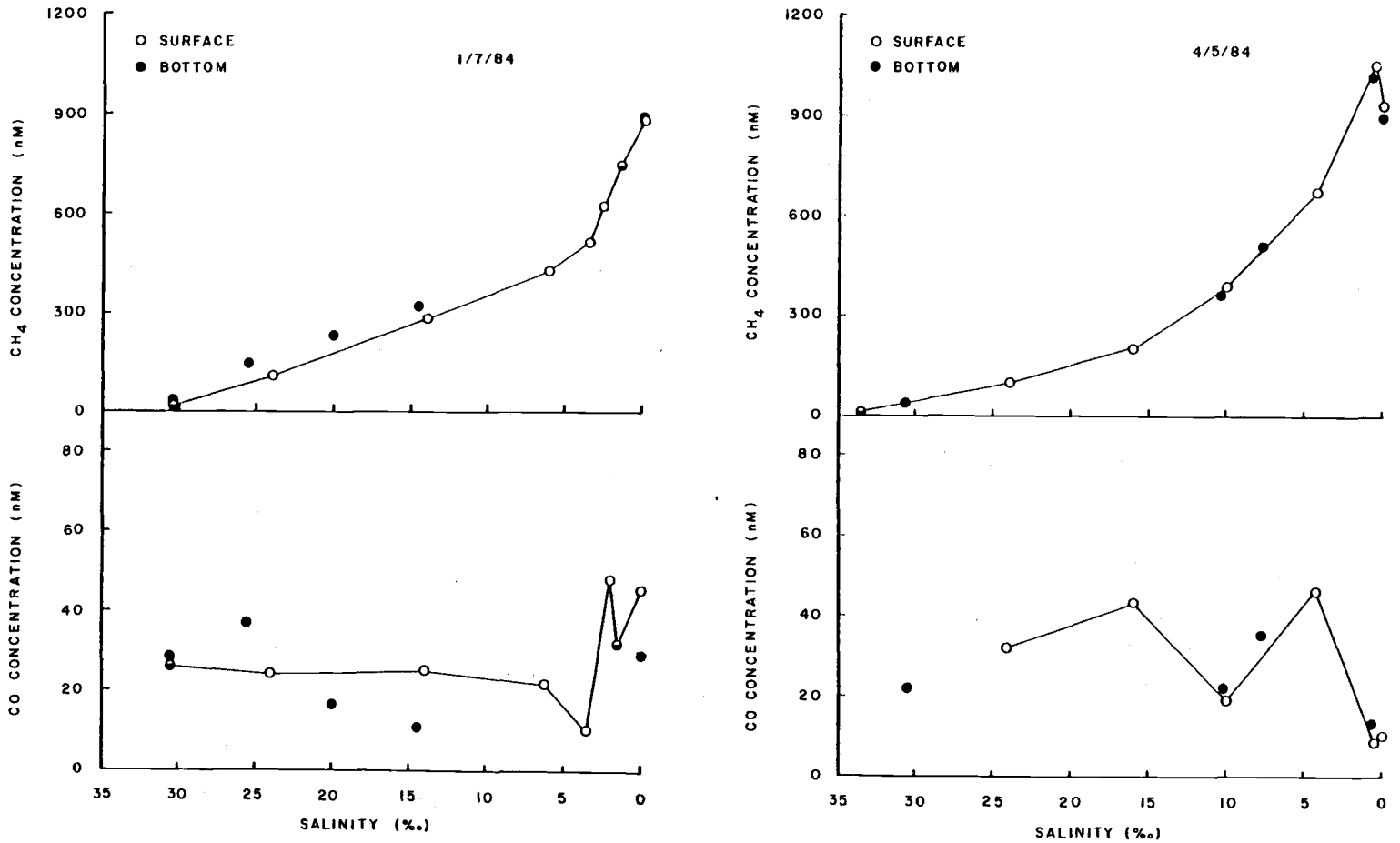

Figure 2.2b. Methane and carbon monoxide distributions in Yaquina Bay, 1/7/84, 4/5/84.

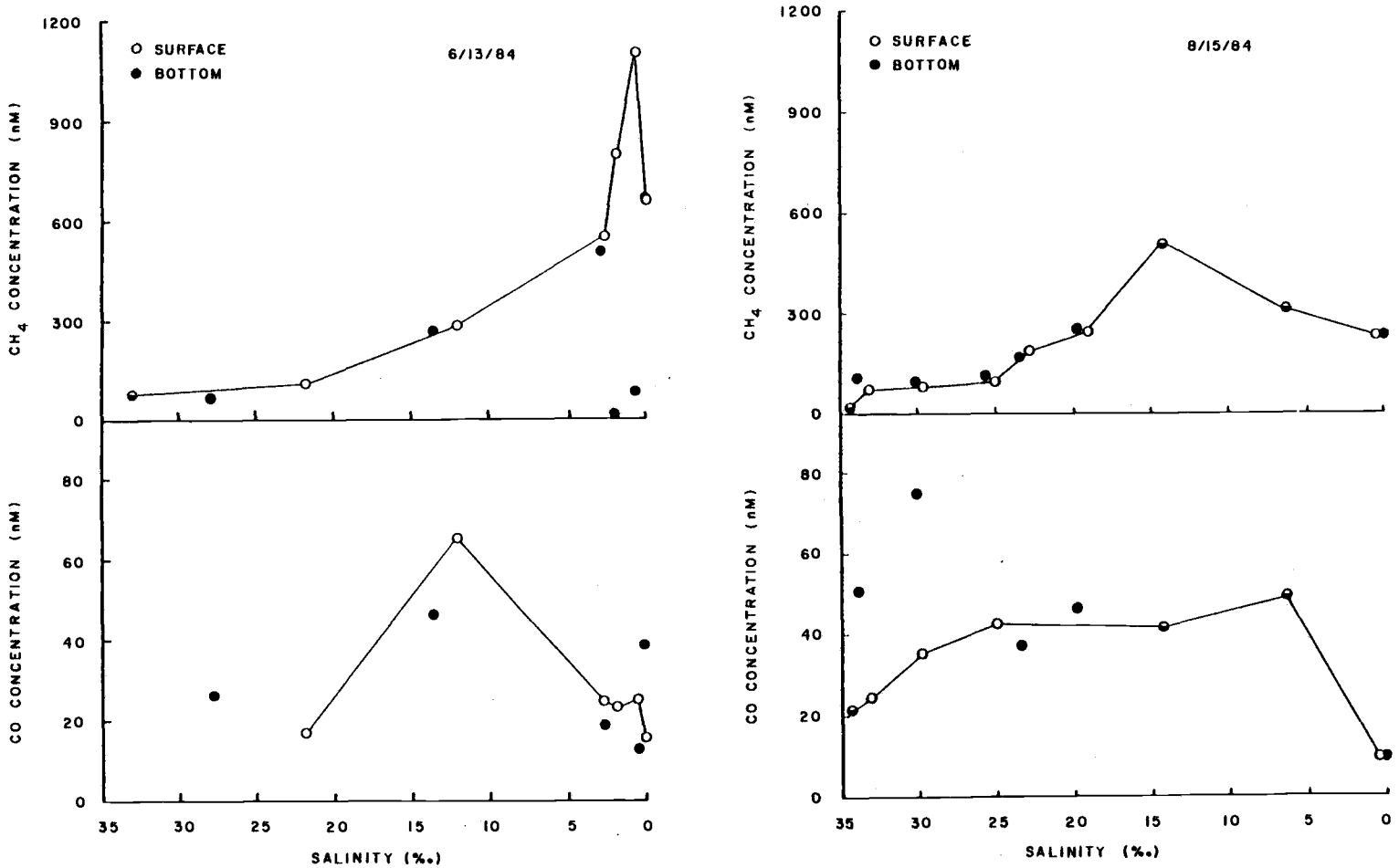

Figure 2.2c. Methane and carbon monoxide distributions in Yaquina Bay, 6/13/84, 8/15/84.

observed a stronger signal in bottom waters downstream were sediments the predominant source, as much of the lower portion of the bay is tidal flat (Figure 2.1).

Despite the high concentrations of methane in the estuary, the microbial oxidation rates were low, representing partial residence times of weeks to years (Table 2.3). Methane turnover rates were lowest in the incoming water, but the upstream rates, although much faster, were not nearly as high as would have been expected for such high concentrations of methane (Chapter 5, Rudd and Hamilton 1978, Harrits and Hanson 1980). The inability of the populations to acclimate fully to these high concentrations probably was the result of the relatively short residence time of water in the bay. Given turnover times of a few days in the winter to a few weeks in the summer for water in Yaquina Bay (Burt and Marriage 1957, Callaway and Specht 1982), it is unlikely that microbial oxidation plays a significant role in removing methane.

Atmospheric losses of methane, however, were significant (Table 2.4). Atmospheric fluxes were computed from a laminar layer model with a film thickness of 200 um, corresponding to a mean windspeed of 3 m/sec (Peng and Broecker 1980). This value is near the maximum demonstrated for the laminar layer model, hence our values probably are underestimates of the atmospheric flux. Also, the laminar layer thickness decreases geometrically with increasing windspeed, so, in the presence of variable winds, the total flux would be greater than that estimated from a mean windspeed. Although our estimates of atmospheric loss could be two to three times too low, we have chosen a conservative approach to demonstrate the importance of atmospheric evasion relative to microbial oxidation. Integrated for the estuary as a whole, our data

TABLE 2.3. MICROBIAL TURNOVER TIMES* FOR CH_4, CO, and NH_4^+

Date	River Km	T(CH_4) (d)	T(CO) (h)	T(NH_4^+) (d)
10/6/83	1.5		160	55
	3.9		28	10
	8.5		8.7	2.9
	11.4		5.1	2.0
	14.2		4.4	1.4
	16.2		2.7	.9
	17.0		3.0	1.0
	20.5		2.7	1.0
	25.0		3.2	.8
	27.0		2.7	3.0
11/8/83	1.5	921	17	5.6
	3.9	2473	6.9	2.6
	8.5	137	2.9	1.1
	10.5	124	2.5	.9
	11.4	104	2.5	.9
	14.2	83	2.6	.9
	16.2	73	2.5	.9
	20.5	51	2.0	.8
1/7/84	1.5	9942	90	23.
	3.9	843	15	5.2
	8.5	571	12	4.4
	11.4	377	11	3.9
	14.2	296	14	5.3
	16.2	230	9.6	3.7
	20.5	184	17	7.3
4/5/84	1.5	4142		26
	3.9	497	16	6.5
	8.5	366	10	5.9
	11.4	262	7.0	3.7
	14.2	118	4.3	2.0
	20.3	124	7.8	3.1
	25.0	125	8.5	4.2
6/13/84	1.5	2161		12
	3.9	194	3.6	1.4
	8.5	127	2.9	1.4
	11.4	49	2.1	1.2
	14.2	74	1.8	.8
	20.3	66	4.0	2.7
	25.0	67	4.6	3.0
8/15/84	1.5	3551	109	29
	3.9	802	8.4	2.9
	8.5	321	3.6	1.2
	11.4	350	5.0	1.7
	14.2	237	3.4	1.2
	17.0	132	3.3	1.1
	22.4	103	1.9	.7
	27.0	45	1.7	.6
	35.0	18	3.9	1.2

*Turnover time is defined as the inverse of the first-order rate constant

TABLE 2.4. ATMOSPHERIC FLUXES AND MICROBIAL OXIDATION IN YAQUINA BAY

Date	CH_4			CO			N_2O		NH_4^+		H_2	
	Mass (mol)	Atm (mol/h)	Ox	Mass (mol)	Atm (mol/h)	Ox	Mass (mol)	Atm (mol/h)	Mass (mol)	Ox (mol/h)	Mass (mol)	Atm (mol/h) ($x10^{-3}$)
10/6/83	8110	111	-	492	6	92	490	1.7	133	2.7	124	1.3
11/8/83	9510	114	4.3	1460	14	440	957	7.2	161	5.7	549	6.0
1/7/84	12500	160	1.6	965	11	75	692	4.3	63	0.6	390	4.0
4/5/84	13400	175	3.4	1197	12	136	585	2.9	53	0.5	206	2.0
6/13/84	15200	186	8.4	1240	13	436	631	6.8	54	1.7	222	2.3
8/15/84	4970	80	1.1	1755	24	463	505	2.3	83	2.3	-	-

Values given are integrated for the estuary from Newport to Toledo at low tide. Atmospheric fluxes are based on a laminar layer model with a film thickness of 200 μm.

show that 30% to 40% of the methane in the estuary below Toledo would have been removed to the atmosphere each day. Methane lost owing to microbial oxidation, on the other hand, was at all times less than 1.5% of the total methane in the bay. Thus, if we consider that the methane in Yaquina Bay was in pseudo-steady state, and if we assume that all of it originating near Toledo came from the wastewater discharge, the concentration of methane in the wastewater would have to be around 1 mM, a value that, although representing immense supersaturation, is not atypical for municipal wastewater.

Carbon Monoxide

Like methane, carbon monoxide was highly supersaturated throughout the estuary (Figure 2.2). However, unlike methane, its distributions were erratic. Other than a generally sharp peak and greater variability upstream, there was no consistent pattern along the length of the estuary. Similarly, CO concentrations for bottom samples seldom agreed with those for surface samples of the same salinity. Such a distribution would be expected were the concentrations of CO regulated by rapid, localized production and consumption throughout the estuary.

Our measurements of microbial oxidation rates indeed showed that CO consumption in Yaquina Bay was rapid, with turnover times on the order of a few hours (Table 2.3). When these rates were compared to those for atmospheric loss for each sampling period (Table 2.4), it became clear that the fate of CO was governed primarily by microbial activity; atmospheric loss, although significant with a daily export of 23% to 33% of the total CO present, amounted to only 3% to 15% of the CO lost

through microbial oxidation. Even if we consider that our estimates of atmospheric loss were low, the role of microbial CO oxidation remains significant. Such high total loss rates for CO indicated that it also must have been produced throughout the estuary at similarly high rates. CO is produced by microbes (Seiler and Schmidt 1976, Swinnerton et al. 1976), but it also is produced through the photolysis of carbonyl compounds (Redden 1983, Conrad and Seiler 1980a). Although photolysis is a significant mode of production in surface ocean and lake waters (Conrad et al. 1982, 1983), its contribution to our measured values is not certain. We always began our sampling in the morning, sometimes before sunrise, but always finished about mid-day. Also, the water was somewhat high in sediments, which would result in rapid extinction of the shorter wavelengths necessary for CO production (Redden 1983). Hence, if photoysis predominated, we would have found a systematic increase in CO in the surface waters going up the estuary, and little or no CO in the bottom waters throughout. Other than the sharp peak near Toledo, probably a direct or indirect result of the sewage treatment plant, neither of these trends was apparent at any time. We must conclude, therefore, that CO was produced primarily by microbes in Yaquina Bay, and that the rates of production were on the same order as our measured rates of consumption.

Nitrous Oxide

Nitrous oxide distributions showed some similarity to those for methane, in that there was an upstream maximum near Toledo and, from November through April, a systematic decrease in concentration downstream (Figure 2.3). However, N_2O concentrations were elevated

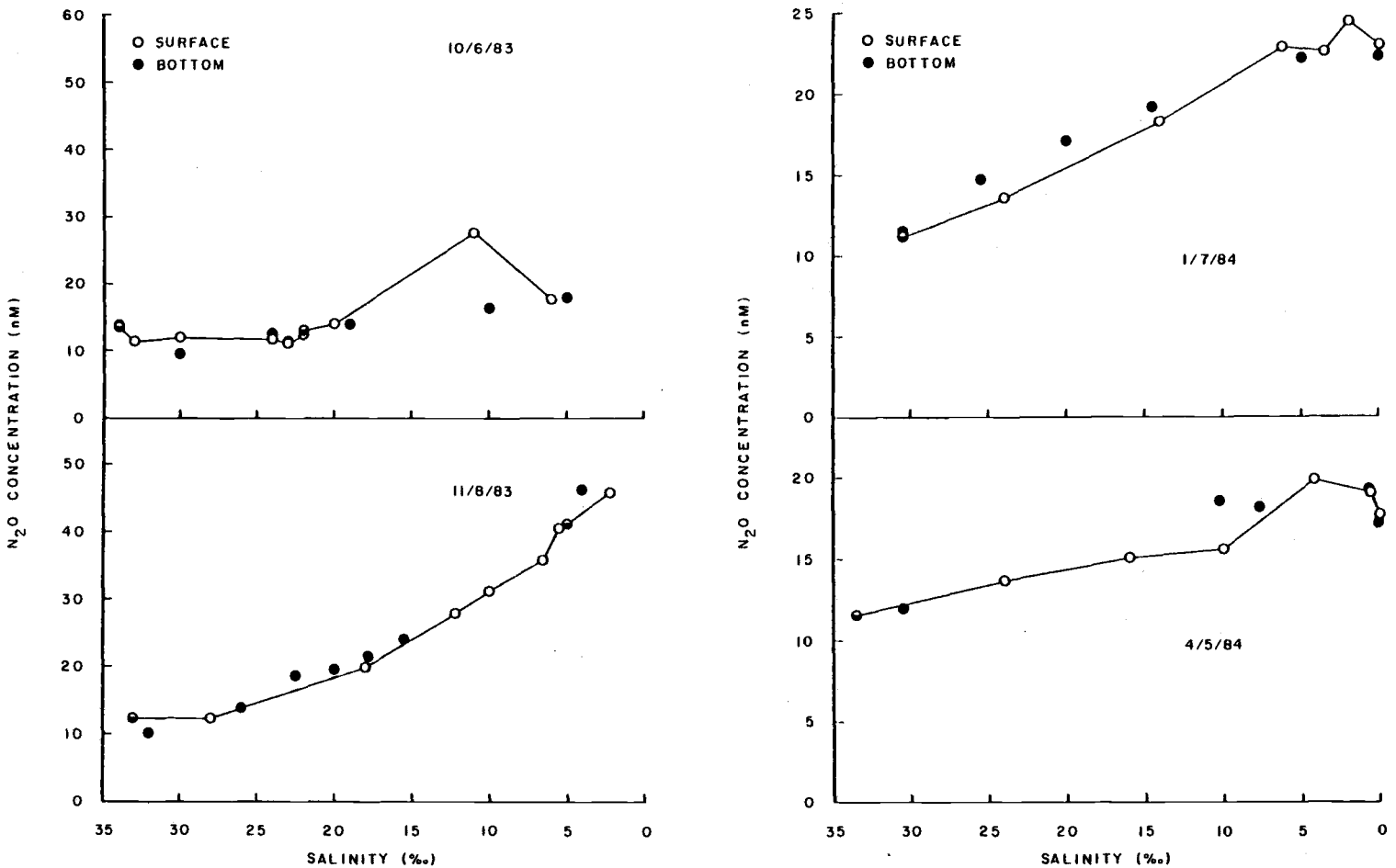

Figure 2.3a. Nitrous oxide distributions in Yaquina Bay, 10/6/83-4/5/84.

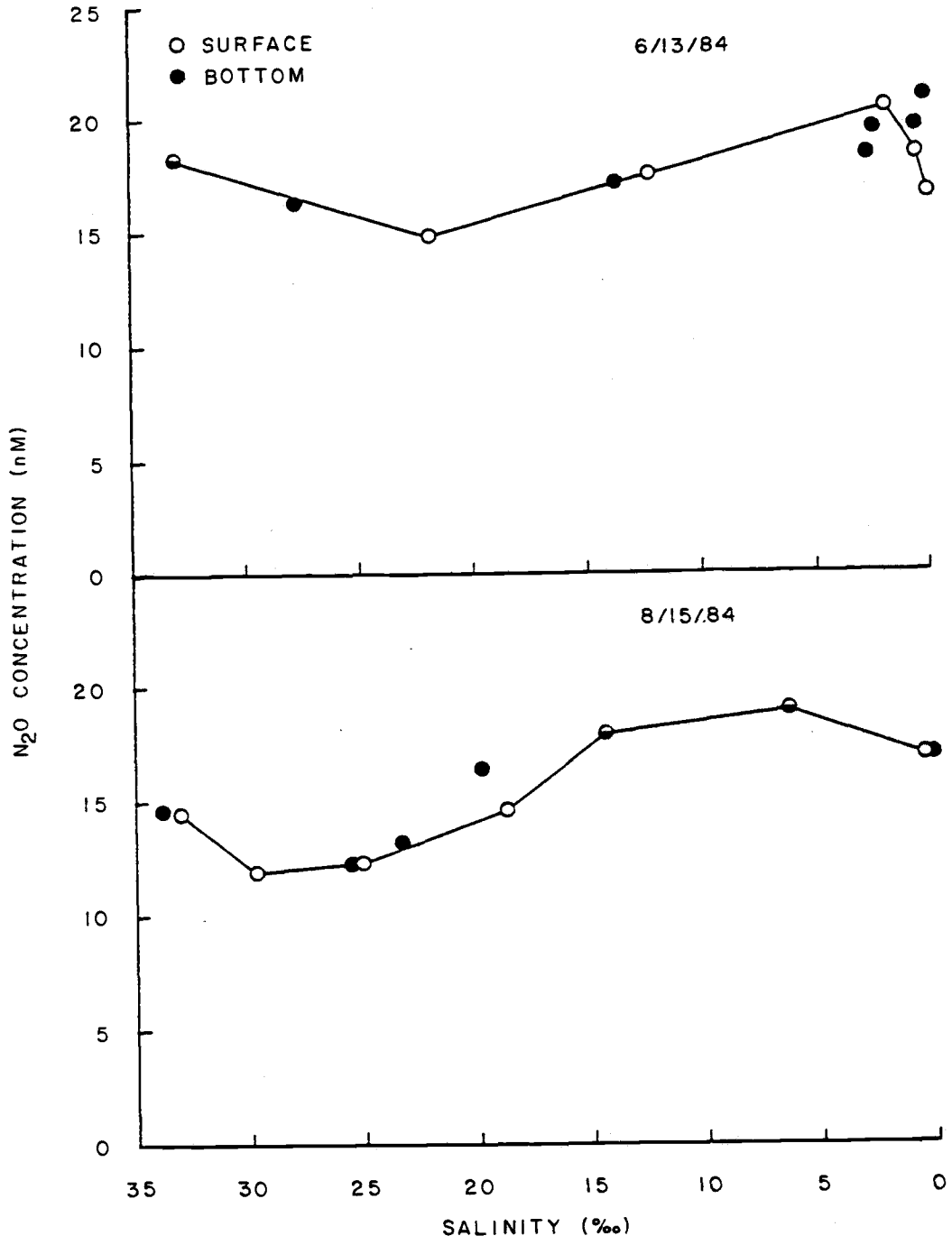

Figure 2.3b. Nitrous oxide distributions in Yaquina Bay, 6/13/84, 8/15/84.

substantially after the onset of fall rains, whereas methane concentrations had been reduced, and no similarities with methane distributions were apparent during the summer and early fall samplings (October 1983, June 1984, August 1984), when N_2O introduction from the ocean was significant. N_2O was saturated or supersaturated in all samples (100% sat = 8 to 12 nM), the highest contributions coming from upstream, especially during the late fall and winter.

De Angelis and Gordon (1985) reported elevated N_2O concentrations in the Alsea river and estuary following fall rains, but only up to 150% saturation, and attributed this increase primarily to leaching of soils in the watershed. We observed much higher supersaturations (200% to nearly 400%) in the waters of the Yaquina estuary. It is likely that runoff from the watershed contributed to the observed increases in N_2O, but wastewater and septic tank leachate also may have played a part (Kaplan et al. 1978, Wofsy et al. 1981, McElroy et al. 1978). Lemon and Lemon (1981) downplayed streamflow contributions to N_2O in the Great Lakes Basin; however, they were evaluating average summer flows, not the massive pulses associated with initial fall runoff. Our observed high concentrations in the incoming seawater are similar to those reported by DeAngelis and Gordon (1985) for the Alsea during the summer, and likewise, our highest seawater values were associated with recently upwelled waters (June 1984).

Although nitrous oxide likely was produced in the waters of Yaquina Bay, the contribution of this process to total N_2O probably was insignificant. Unless denitrification was occurring in aquatic microenvironments, the only aquatic source for N_2O was nitrification by ammonium oxidizers. Ammonium in the estuary was oxidized at a rate of

less than 6 mol/h (Table 2.4). Reports from Elkins et al. (1978), Goreau et al. (1980), and Seitzinger et al. (1983) indicate that 0.1 to 0.3% of the ammonium oxidized by nitrifiers in the presence of oxygen is converted to N_2O. Thus, the maximum rate for N_2O production in Yaquina Bay would be 0.02 mol/h, about two orders of magnitude lower than the atmospheric evasion rate.

Contributions from the sediments, however, could maintain this balance of N_2O in the estuary. A sedimentary production rate of 10 u-mol/m^2/h for the bottom sediments at low tide would account for the atmospheric losses from January through June 1984, when the system appeared in a pseudo-steady state. This number is in the middle of the range of 0.5 to 44 u-mol/m^2/d reported by Sietzinger et al. (1983) for sediments of Narragansett Bay, and is probably an overestimate, as we did not include potential contributions from the tidal flats which were exposed during low tide. Thus, nitrous oxide in Yaquina Bay probably derived mainly from three sources - watershed runoff, wastewater effluent, and sedimentary production.

Hydroxylamine

Hydroxylamine is a potential precusor to N_2O, as well as to NO_2^-, N_2, NO, and perhaps other nitrogenous compounds (e.g. - Chapter 3, Anderson 1964, Gowda et al. 1957). Hydroxylamine is produced via oxidative and reductive microbial processes, but it is consumed both by microbes (Anderson 1964a,b, Amarger and Alexander 1968, Yoshida and Alexander 1971) and by abiotic oxidation (e.g. - Kolasa and Wardencki 1973). Production processes include ammonium oxidation (Anderson 1965,

Yoshida and Alexander 1964), heterotrophic nitrification (Verstraete and Alexander 1972, 1973), and fermentative dissimilatory nitrogen reduction (Yordy and Ruoff 1981), but they do not include the membrane-bound, respiratory reduction of nitrogen known commonly as denitrification (Payne 1981). As N_2O is produced by both nitrification and denitrification, a strong association with hydroxylamine would suggest the work of nitrifiers. Unfortunately, the relationship is not clear cut, since the other biotic and abiotic processes interfere with such an interpretation, and denitrification and nitrification probably operate concomitantly across strong oxygen gradients (Grundimanis and Murray 1977, Knowles 1978, Knowles et al. 1981, Codispoti and Christensen 1985).

Nevertheless, because hydroxylamine is labile in oxygenated water, its mere presence implies a rapid rate of production. In some of our recent kinetics work in the laboratory, we found a mean degradation time of about five hours for hydroxylamine in oxygenated water at near neutral pH (Chapter 5). This number can vary considerably depending on pH, temperature, and the concentrations of trace metals, dissolved organics, and microbial populations, but it is not likely to be much longer unless the pH or temperature were lowered to unnatural levels, as one of the solutions we tested was deionized, distilled water (Chapters 4, 5).

Hydroxylamine concentrations were particularly high in Yaquina Bay in the fall (Table 2.5). During the winter, the concentrations dropped and remained much lower well into summer. As would be expected for a labile substance, and as we observed for CO, the NH_2OH concentrations bore little or no resemblance to salinity or depth. The highest

TABLE 2.5. HYDROXYLAMINE AND DISSOLVED H_2 CONCENTRATIONS

10/6/83

River Km		H_2 (nM)	NH_2OH (nM)
1.5	b		18
3.9	s	2.3	49
	b	.5	38
8.5	s		19
	b	3.4	
11.4	s		58
	b		35
14.2	s	3.2	109
	b	3.6	59
16.2	s	3.5	40
	b		
17.0	s		50
	b	5.6	25
20.5	s	5.3	188
	b	5.0	
25.0	s	.6	141
	b	3.0	63
27.0	s	6.2	42
	b	.3	40

11/8/83

River Km		H_2 (nM)	NH_2OH (nM)
1.5	b	17.7	48
3.9	s	7.1	244
	b	24.8	184
8.5	s	26.6	59
	b	10.1	362
10.5	s	20.9	214
	b		226
11.4	s	7.0	130
	b	12.9	172
14.2	s	7.1	102
	b	21.9	58
16.2	s	16.2	155
	b	9.9	118
18.0	s	14.5	141
	b	11.2	218
20.3	s	16.4	102
	b	16.8	39

1/7/84

River Km		H_2 (nM)	NH_2OH (nM)
1.5	s	7.3	5
3.9	s	14.7	5
	b	13.6	4
8.5	s	5.5	7
	b	19.7	0
11.4	s	11.5	1
	b	7.8	7
14.2	s	2.1	20
	b	1.8	7
16.2	s	17.5	17
	b		8
18.0	s		16
	b		0
20.5	s	15.4	7
	b	19.8	17

4/5/84

River Km		H_2 (nM)	NH_2OH (nM)
1.5	b	7.9	
3.9	s	5.9	10
	b	6.5	18
8.5	s	4.2	24
	b		
11.4	s	5.7	21
	b	6.8	16
14.2	s	5.7	18
	b	4.5	
20.3	s	9.0	12
	b	5.9	5
25.0	s	4.6	25
	b	4.2	7

6/13/84

River Km		H_2 (nM)	NH_2OH (nM)
1.5	b	3.8	
3.9	s	2.9	
	b	7.0	
8.5	s	5.5	
	b	5.7	
11.4	s	6.7	
	b	7.0	
14.2	s	11.1	
	b	> 40	
20.3	s	11.5	
	b	4.0	
25.0	s	6.2	
	b	28.8	

8/15/84

River Km		H_2 (nM)	NH_2OH (nM)
1.5	b		
3.9	s		9
	b		8
8.5	s		12
	b		
11.4	s		11
	b		7
14.2	s		
	b		1
17.0	s		16
	b		8
22.4	s		53
27.0	s		100
35.0	s		65

concentrations of NH_2OH were observed in November 1983, immediately after the initial heavy rains, and are indicative of significant microbial activity. Indeed, both the ammonium oxidation rates and the concentrations of ammonium were highest on this sampling date (Tables 2.1, 2.3). A turnover time of 0.9 d for ammonium and an ammonium concentration of 4 uM together represent a first-order ammonium oxidation rate of just under 200 nM/h. This value is close to the actual measured concentrations of hydroxylamine in October and November 1983, corresponding to potential turnover times of a couple of hours or less for hydroxylamine. Similarly, using data from either of the winter profiles, when NH_4^+ and NH_2OH concentrations and NH_4^+ oxidation rates were all lower, we calculate ammonium oxidation rates of 10 to 50 nM/h. This agian would correspond to turnover times of minutes to hours were NH_2OH in steady-state and all NH_4^+ converted to NH_2OH.

We have no evidence, however, that all of the hydroxylamine produced was brought about by ammonium oxidation. We did find a similarly high ratio of ammonium oxidation to apparent hydroxylamine production for a stratified coastal lagoon (Chapter 5), where we used an improved, more reliable technique for the measurement of hydroxylamine (Chapter 3). Whether ammonium oxidation, heterotrophic nitrification, or fermentative nitrogen reduction was primarily responsible for the production of hydroxylamine in Yaquina Bay is not known. Heterotrophic nitrification, to be sure, has been considered small relative to chemautotrophic nitrification (Verstraete and Alexander 1972, 1973), but it cannot be ruled out at this time, as we have little information concerning the activity of these organisms in nature. Fermentative NO_3^- reduction also is considered small relative to other NO_3^- reducing

processes (Chen et al. 1972, Yordy and Ruoff 1981), but its contribution to NH_2OH production still is unknown. As for the fate of hydroxylamine, it either was consumed by these same microbes, or was converted abiotically to another form of nitrogen. The actual products of the abiotic oxidation would depend on pH, and on the concentrations of metals and organic material (Chapters 3, 4). In all probability, some N_2O was produced through the abiotic destruction of hydroxylamine, but the relative proportion of N_2O to other nitrogenous products is not known.

Hydrogen

Hydrogen gas generally was supersaturated throughout the estuary, and its distributions, like those of CO and NH_2OH, showed no consistent relationship to either salinity or depth. These concentrations and erratic patterns also were noted for the lower part of Yaquina Bay in 1980 (Lilley et al. 1980). Such high supersaturation (100% = 0.34 to 0.44 nM), along with distributions that imply high turnover rates, suggest the in situ formation and destruction of H_2 in Yaquina Bay waters. Little is known of the cycling of H_2 in oxidative systems, but associations with cyanobacteria have been suggested for production of H_2 in oxidative waters (Herr et al. 1981). Lilley et al. (1982), however, found high supersaturations of H_2 in the surface waters of Saanich Inlet, but found no evidence of the suspected nitrogen fixing bacteria. They did find an association of H_2 production with N2 production, implying a role of denitrifiers, perhaps within poorly oxygenated microenvironments as suggested by Scranton and Brewer (1977), Brooks et al. (1981), and Burke et al. (1983). Lilley et al. (1982) also noted

aggregates of protozoans on suspended particulate matter in these samples. It is possible, however, that hydrogen is produced in Yaquina Bay primarily through base metal reduction, as metal surfaces abound in the estuary.

Rapid consumption of H_2 in oxidative waters is plausible, as hydrogen is an energy rich substrate for certain photoheterotrophs that are tolerant to oxygen, as well as for sulfate-reducing bacteria and other facultative chemautotrophs (Fenchel and Blackburn 1979). However, owing to the extreme supersaturations of H_2 (100% = 0.05 to 0.06 nM), atmospheric evasion is still a significant sink in Yaquina Bay (Table 2.4).

SUMMARY AND CONCLUSIONS

Throughout the year, reduced trace gases were introduced into Yaquina Bay from anthropogenic sources, *via* runoff, from sediments, and by *in situ* production. Methane, carbon monoxide, nitrous oxide and hydrogen were supersaturated at all times, owing to high input rates relative to consumption. Methane, introduced predominantly from wastewater, was removed primarily through atmospheric evasion, which predominated over microbial processes. Carbon monoxide, however, was produced and consumed in the estuary, presumably by microbial processes in the water column. Microbial oxidation of CO was rapid, significantly overshadowing losses by atmospheric evasion. Nitrous oxide apparently was brought into the bay from a variety of sources, depending in part on season, and including runoff, wastewater discharge, upwelled seawater, and diffusion from sediments. Production *via in situ* oxidation of ammonium could not account for the losses of N_2O owing to atmospheric evasion, which, as for all of the gases, was considerable. Hydrogen also was supersaturated, but its sources and sinks in these oxidative waters are not as well understood.

We had difficulty obtaining consistent recoveries in the measurement of hydroxylamine by the method of von Breymann *et al.* 1982, owing to pH and salt effects in the estuary, but we were able to obtain satisfactory data by use of standard additions. Hydroxylamine concentrations correlated with ammonium oxidation, implying nitrification as a source. Although ammonium oxidation rates were on

the same order of magnitude as predicted hydroxylamine degradation rates, we cannot be certain at this time of the sources or the sinks of hydroxylamine. The high concentrations of hydroxylamine and its apparently rapid turnover suggest that abiotic destruction plays an important part in the removal of NH_2OH, but how this compares with microbial consumption is still uncertain.

ACKNOWLEDGEMENTS

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CHAPTER 3

AN IMPROVED GAS CHROMATOGRAPHIC METHOD FOR THE MEASUREMENT OF HYDROXYLAMINE IN MARINE AND FRESH WATERS

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ABSTRACT

We present here an improved method for the analysis of hydroxylamine at nanomolar levels, which involves oxidation by Fe(III) and the subsequent measurement of nitrous oxide by electron-capture gas chromatography. The relationship between the pH and salinity of natural waters and the conversion of hydroxylamine to nitrous oxide by Fe(III) is defined, the rates of the reaction are evaluated, and the effects of dissolved O_2, Cu(II), and Hg(II) on the reaction are investigated. The method is linear to more than 300 nM and the standard deviation for a single measurement is 1 nM in the 0 to 40 nM range, thus exceeding the sensitivity of the spectrophotometric methods by almost an order of magnitude. This method eliminates the effects of pH and salinity that have burdened an earlier gas chromatographic approach, making possible the investigation of this labile substance not only in seawater, but in fresh and brackish waters as well.

INTRODUCTION

Hydroxylamine remains a little understood intermediate of the nitrogen cycle in natural waters, owing in part to the lack of a suitable analytical method for its measurement at submicromolar levels. This is further compounded by the lability of hydroxylamine, which has rendered sample storage virtually impossible. Although over 30 methods for the analysis of hydroxylamine have been published in the literature, most have been designed for analysis of millimolar, or at best micromolar, solutions (Kolasa and Wardenki 1974, Dias and Jaselkis 1983, Verma and Gupta 1984). These methods are suitable only for assay of laboratory stock solutions, or for experiments involving artificially high concentrations of hydroxylamine. The aquatic chemist or biologist, however, is looking for very low, often nanomolar, concentrations of this substance in nature. Furthermore, some of these methods, such as ceric oxidation and a few of the earlier spectophotometric techniques, are of questionable value for natural waters, in that good precision is lacking or that interferences are a particular problem (Cooper and Morris 1952, Kolasa and Wardenki 1974).

Until recently, the primary method for the analysis of hydroxylamine in natural waters has relied upon iodine oxidation (Fiadeiro *et al.* 1967). Unfortunately, this method has a precision of $\pm$ 10 nM and a detection limit of 15 nM at best (Strickland and Parsons 1972). Although this is better than most published methods, it still

is not sufficiently sensitive to measure hydroxylamine adequately in most marine and fresh waters (Pitwell 1975, von Breymann et al. 1982). The method is subject to a variety of interferences, including both salinity and alkalinity, and, most importantly, it provides no means for sample storage beyond a few minutes (Strickland and Parsons 1972). Further, the method loses precision in high nitrite environments, precisely the locations where one might expect to find hydroxylamine (Kaplan 1983), and it may be subject to positive interference from hydroxamic acids (Gillam et al. 1981, Pietta et al. 1982).

An alternative approach involves the oxidation of hydroxylamine by Fe(III). Ferric oxidation is one of the more frequently used approaches for the quantitative analysis of hydroxylamine; a large proportion of the 66 papers reviewed by Kolasa and Wardenki (1974) involved ferrimetry. Ferric methods can rely on end-product analysis, but generally have involved a volumetric, photometric, potentiometric, or coulometric measurement of the amount of Fe(II) produced. The assumed reaction for most of these analyses requires that N_2O be the sole nitrogenous product, i.e.:

$$4Fe^{3+} + 2NH_2OH = 4Fe^{2+} + N_2O + H2O + 4H^+$$

However, complete conversion to N_2O has not always been attained. A method for the quantitative measurement of nM concentrations of hydroxylamine, developed by von Breymann et al. (1982), demonstrated that, in certain seawater samples at least, only 50% of the NH_2OH was converted to N_2O after stoichiometry was considered, and that this conversion ratio was consistent among the samples tested. The

implication was that even though the oxidation by Fe(III) did not produce 100% N_2O as a residual product, the conversion ratio of 50% could be trusted for quantitative purposes.

In some of our recent work on trace gases and nitrogen cycle intermediates in Yaquina Bay, Oregon (Chapter 2), we found that this ratio of 50% does not apply under all circumstances. Recoveries of N_2O from field samples with standard additions ranged from 20 to 80%, most falling within a 40 to 60% range. The recoveries appeared to bear some relation to the mixing ratio of freshwater and seawater and to certain anthropogenic inputs. Characteristics that could affect hydroxylamine oxidation and that vary with this mixing ratio are pH, salinity, and both organic and inorganic trace substances. This variable recovery of N_2O indicates that reactions which give rise to other nitrogenous products compete with the production of N_2O from NH_2OH. There could be more than one reaction and any number of products, but data from the literature (Anderson 1964a, 1966; Erlenmeyer et al. 1969; Hughes & Nicklin 1967, 1970a, 1970b, 1971) indicate that nitrous oxide and nitrite would predominate and that the relative amounts of these substances produced depends upon pH and, at extremely low levels, dissolved oxygen concentration.

We decided to evaluate the dependence of N_2O production by Fe(III) on a suite of environmental and experimental parameters. These included pH, salinity, dissolved oxygen, Cu(II), and Hg(II). We also examined the effects of different sample waters on the reaction. Upon consideration of our results, we offer a modification of the method of

von Breymann *et al.* (1982) to account for the observed dependencies, thereby achieving the accuracy and precision necessary for oceanographic, coastal, and limnological studies.

METHODS

Reagents and Equipment

All reagents used during these experiments were analytical-reagent grade. To account for possible trace contamination, three batches of hydroxylamine hydrochloride from three different manufacturers were tested, and both ferric ammonium sulfate ($FeNH_4SO_4 \cdot 12H_2O$) and ferric chloride ($FeCl_3 \cdot 6H_2O$) were used as sources of Fe(III) in the reaction. The shelf stocks of hydroxylamine hydrochloride were assayed periodically by copper-catalyzed ferrimetry and backtitration with permanganate (Rao and Rao 1957). Initially, hydroxylammonium solutions (5 mM) were prepared by crushing the salt, placing it in a desiccator for 1 to 2 days, weighing out 0.3477 g, and making up 1 l of solution in distilled de-ionized water (DDW), acidified to pH 3 with 1.0 ml of 1.0 N HCl (Strickland and Parsons 1972). Later, however, we eliminated the desiccation step out of concern for the salt degrading slightly while in the desiccator and found no difference in the results.

The pH of the 5 mM stock solutions of hydroxylamine used for this study was well below the pK_a of 5.97 for the NH_2OH/NH_3OH^+ couple (Erlenmeyer et al. 1969), thus virtually all of the hydroxylamine was present as the hydroxylammonium ion. Stock solutions stored at 4 C in 125 ml flint glass bottles for up to eight months degraded slowly, but somewhat erratically, whereas standards prepared from a stock solution

kept in a 500 ml Pyrex^R bottle indicate that essentially no degradation had occurred over two months. We have conducted no long term tests with micromolar solutions, but have noted the stability of uM hydroxylamine solutions made to pH 3 with HCl and kept at room temperature for over 3 days. Unacidified, micromolar solutions degraded by about 30% within three hours at room temperature. Hence, working (uM) standards were prepared daily and acidified to pH 3 with HCl.

Nitrous oxide was measured by electron-capture gas chromatography as described by Cohen (1977), with the following modifications: The calibration gas used was Scott^R 25.0 $\pm$ 0.25 ppm N_2O in N_2. N_2O was stripped with purified He onto a liquid-nitrogen cooled trap, which was then heated to 250 C with the stainless steel trap serving as its own resistance heater, thus passing the gas through a three foot column packed with 80/100 mesh molecular sieve 5A. The column, isothermal at 250 C, was then swept with a stream of purified nitrogen to a Valco^R tritiated-scandium electron-capture detector, operated at 320 C, with an Analog Technology^R Model 140-A electrometer. Data were integrated with a Hewlett-Packard^R Model 3388A computing integrator. The overall gas chromatograph configuration was nearly identical to that described by Redden (1983). The standard deviation for a single analysis of N_2O stripped from water was about 0.2 nM. For hydroxylamine standards of 0 to 40 nM, the error was about 0.4 nM as N_2O, owing in part to increased sample handling.

pH was measured at 25 C with an Orion^R 801 pH meter and either an Orion^R 91-02 (AgCl reference) or a Corning^R 476182 (calomel reference) combination pH electrode. The electrode was calibrated with phthalate (4.008) and phosphate (7.413) buffers prepared in our laboratory

(Culberson et al. 1970). The pH of all solutions would have been affected by the slow formation of hydrated ferric complexes (Stumm and Morgan 1981), and the pH of the poorly buffered solutions above pH 5 was likely affected by atmospheric exchange of CO_2 (Bates 1964), although care was taken to minimize this effect. As the pH of the solutions was measured after N_2O had been subsampled and analyzed, hence hours after the reaction was initiated, both of these processes would be expected to have some effect on the measured pH of the samples. Consequently, we estimate that the pH data are reliable only to the nearest 0.1 pH.

Dependence on pH, Salinity, and Dissolved Oxygen

Hydroxylamine standards were made up in batches of deionized, distilled water (DDW), natural seawater (NSW), and salt solutions (NaCl, $MgSO_4$, "artificial seawater" or ASW) that either were aerated or had been allowed to equilibrate with the atmosphere. The seawater used for most experiments was North Pacific Gyre surface water, thus low in dissolved trace metals and organic compounds. The alkalinities of about eight subsamples from each batch were adjusted to give a range of final pH's. The alkalinity of distilled water was adjusted by adding sodium bicarbonate; the alkalinity of seawater was adjusted by the addition of HCl. Buffers, including borate and acetate, were used to check for possible chemical interferences of the bicarbonate buffers (Table 3.1). (Phosphate buffers and buffers of some dicarboxylic acids severely reduced the recoveries of N_2O, presumably by reacting with Fe(III); hence these buffers were rejected for further work.) After the alkalinities had been adjusted, subsamples were distributed into acid-

TABLE 3.1. SAMPLE SOLUTIONS. pH AFTER ADDITION OF Fe(III) TO 200 uM

Additive	None	Acetic Acid	Bicarbonate	Borate	*HCl
Conc (M)		(10^{-1})	(10^{-5} - 10^{-2})	(10^{-2})	(10^{-5} - 10^{-2})
DDW	3.4	2.9 - 5.2	3.4 - 8.6	9.5	--
NSW	6.9	2.9 - 3.8	7.2 - 8.6	8.6 - 9.4	2.9 - 6.6

*HCl additions to seawater reduced the buffering capacity of the natural bicarbonate system, thus lowering the pH following Fe(III) addition.

washed and DW rinsed, volume-calibrated, opaque, 125 ml bottles with greased, ground-glass stoppers. A few glass beads (approximate volume, 1.0 ml) were added to each bottle to enhance mixing of the reagents. Two ml of a 5.0 uM solution of NH_2OH was added to each bottle, which was immediately restoppered and shaken vigorously. The stopper was then removed and 1.0 ml of 25 mM ferric ammonium sulfate (FAS) was added. The bottle was quickly restoppered and reshaken to distribute the Fe(III). Unless the reaction rate was being investigated, the bottles were allowed to stand at least three, but no more than 30, hours to allow completion of the reaction.

After completion of the reaction, each sample was transferred, under weak pressure from a regulated aquarium pump, from the glass stoppered bottle to two 25 ml, volume-calibrated gas flasks with Teflon^R stopcocks for subsequent analysis of N_2O by gas chromatography. Redden (1983) determined that gas exchange during this transfer is negligible; however, it may have contributed in part to the slightly greater error for the analysis of NH_2OH relative to that for N_2O. The pH of the solution remaining in the bottle was measured. Because nitrous oxide is present in natural waters, hydroxylamine concentrations were calculated by difference. Additional corrections were necessary to account for stoichiometry of the NH_2OH to N_2O conversion and for reagent volumes. Recoveries were monitored by the method of standard additions.

When standards were prepared as above, but with the dilution water first stripped with nitrogen gas to remove dissolved O_2, the residual oxygen concentration was about 5 to 10% of saturation, as indicated by a helium ionization detector monitoring the purified helium stream in the

gas chromatograph. Presumably, this was due to rapid exchange of O_2 across the surface during sample transfer and during standard and reagent addition. Some of the oxygen also was introduced with the reagent solutions. Even at 5% saturation, the concentration of O_2, about 25 uM, far exceeded that of the hydroxylamine, about 40 nM. Consequently, the recovery of N_2O was identical to that for an air saturated solution. Chemical removal of O_2 with metabisulfite was not feasable, as the bisulfite interfered negatively, even when ferric ion was added far in excess of the bisulfite.

Therefore, to measure the effects of very low concentrations of oxygen, 25 ml of the dilution water was acidified to pH 3 with acetic acid, treated with Fe(III) to a concentration of 200 uM, placed in the stripping flask attached to the gas chromatograph, and stripped with He for 20 min at 100 ml/min. Likewise, the hydroxylamine standard addition solution (about 50 ml, 2.5 uM) was stripped of air with UHP nitrogen for about 30 minutes at the same rate. The flow of stripping helium in the GC was then diverted to bypass the stripping flask, and two ml of the hydroxylamine standard was injected directly into the flask. The reaction was given three hours for completion, then the N_2O was stripped and injected into the gas chromatograph.

Interferences

Cu(II) and Hg(II) each can react with hydroxylamine and both have been used in association with its oxidation by Fe(III), Cu(II) as a catalyst (Rao and Rao 1957) and Hg(II) as a preservative (von Breymann et al. 1982). $HgCl_2$ also is used widely to preserve gas samples,

including those for N_2O (Elkins 1980, Lilley et al. 1983, de Angelis and Gordon 1985). Hg(II), however, has been employed in the oxidation of hydroxylamine (James 1941, 1942), thus making it an unlikely preservative for hydroxylamine samples and a questionable preservative for N_2O samples collected from environments containing appreciable concentrations of hydroxylamine. Consequently, we tested the effects of these two ions on the recovery of N_2O by adding $CuSO_4$ and $HgCl_2$ to the reaction bottles before injecting hydroxylamine. Also, for a preliminary observation of the effects of naturally occurring trace substances on the reaction, we collected samples of fresh and saline water from a number of coastal and offshore environments and analyzed them with standard additions of hydroxylamine. The waters then were allowed to age in the presence of sunlight in the laboratory for a few months and the analyses were repeated.

RESULTS AND DISCUSSION

Dependence of N_2O Production on pH, Salinity, and Dissolved Oxygen

In both deionized distilled water and natural seawater the recovery of N_2O increased from near zero at elevated pH's to about 80% in acid solution (Figure 3.1). The curve for the NSW, however, is shifted toward higher pH by 2 - 3 units. The two curves converge to about 80% recovery below pH 3.5 and remain approximately constant below that pH. This behavior invokes a mechanism similar to that proposed by Anderson (1964a) for the oxidation of hydroxylamine by Cu(II), and by Hughes and Nicklin (1970a, 1970b) for its oxidation by molecular oxygen, in which Fe(III) would oxidize the hydroxylamine to an unstable (+1) intermediate (Figure 3.2). This intermediate, presumably nitroxyl (HNO), would then decompose via different pathways to nitrous oxide and nitrite, with nitrite production favored in alkaline solution.

The pH shift in the DDW and NSW curves is not likely to result from ionic strength effects alone. Such a large difference probably results from specific ions kinetically favoring the production of some compound other than N_2O, perhaps nitrite, as more OH^- is made available (Anderson 1964, 1966). For example, the reaction in artificial seawater, buffered with bicarbonate, resulted in a point that fell near the DDW curve, not the NSW curve, in Figure 3.1 (Table 3.2). Chloride, however, seemed to reduce the recovery of N_2O in unbuffered artificial seawater solutions,

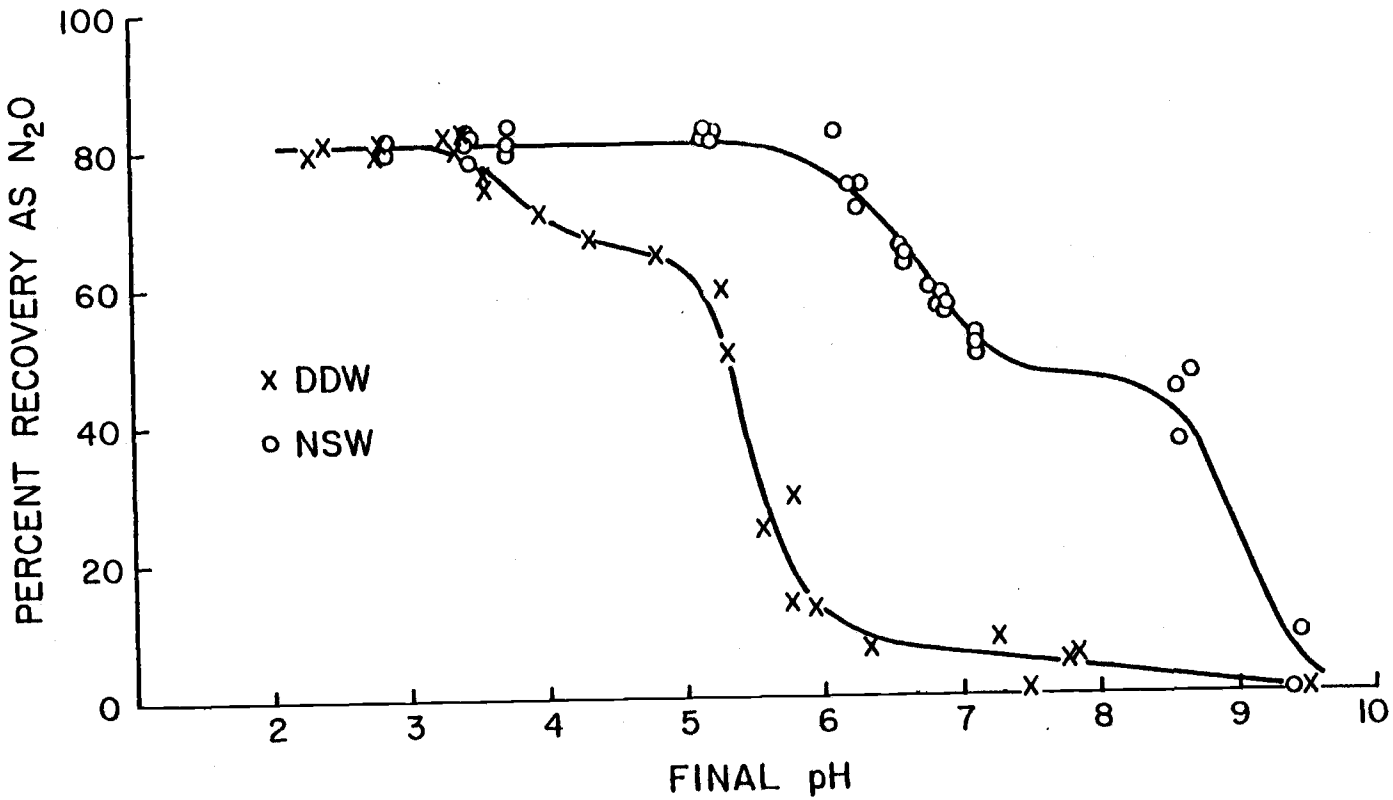

Figure 3.1. Recovery of N_2O in the ferric oxidation of hydroxylamine, as a function of pH.

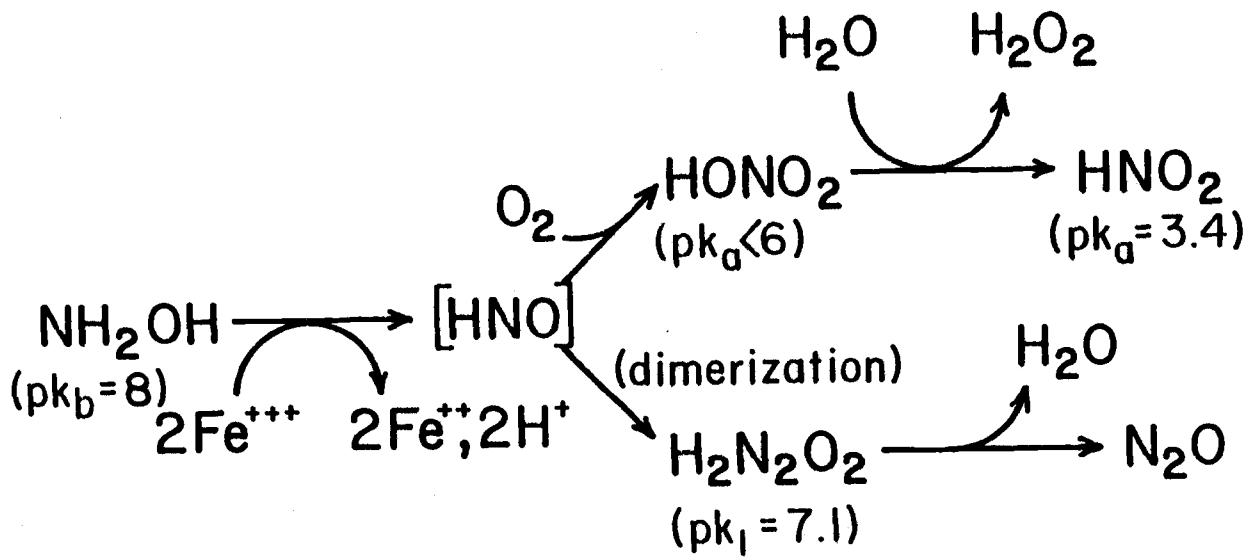

Figure 3.2. Possible mechanism for the ferric oxidation of hydroxylamine to nitrite and nitrous oxide.

TABLE 3.2. HYDROXYLAMINE RECOVERY AS N_2O FROM NATURAL SEAWATER (NSW) AND VARIOUS SYNTHETIC SOLUTIONS

Solution	Conc. (molal)	Ionic Strength (molal)	Final pH	Recovery (%)	Time Required for Completion (minutes)
DDW	--		3.4	79.8	90 - 115
NSW (+HCl)	--		3.0	80	30
NSW	--		6.9	53.3	< 15
NaCl	0.75	0.75	3.4	69.2	130
NaCl	0.08	0.08	3.4	77.4	
$MgSO_4$	0.18	0.72	3.5	80.0	
$MgSO_4$	0.02	0.07	3.4	79.0	
ASW	*	0.67	3.5	73.2	< 20
ASW (10%)	*	0.07	3.4	78.0	
ASW + $CaCl_2$	0.01(Ca)*	0.69	3.5	75.2	
ASW + $NaHCO_3$	0.002* (HCO_3)	0.67	6.7	22.1	< 20

*"ASW" was a mix of NaCl and $MgSO_4$ with final concentrations of 0.55 m NaCl and 0.03 m $MgSO_4$.

whereas neither magnesium nor sulfate had any apparent effect on the overall recovery. On the other hand, magnesium or sulfate may have been responsible, in part, for the faster reaction in seawater solutions, whereas chloride clearly was not.

Our studies of the effect of dissolved oxygen on the reaction are less conclusive. Although our stripper may have been able to remove virtually all of the oxygen in the water, small, but significant, amounts of oxygen were probably introduced in handling of the standard before injection, thus leaving a residual concentration of about 200 nanomolar (<.1% sat), as measured by the HID. This is an excess of oxygen over the concentrations of NH_2OH we wished to investigate, 80 nM, but it is on the same order of magnitude. The reaction in the presence of these low oxygen concentrations did result in a greater recovery of NH_2OH as N_2O, but by a barely significant improvement, 4 to 6%. When we did not remove the oxygen from the standard solution, resulting in a residual O_2 concentration of about 10 uM in the stripper, the recovery of N_2O was again 80%. This is further evidence of oxygen being involved in some reaction or reactions competing with the production of N_2O. On the other hand, the recovery of hydroxylamine as N_2O can be expected to remain near 80% even in waters collected from low oxygen environments, as the oxygen injected with the reagents should be more than sufficient to prevent an elevated recovery.

Finally, it is possible that the reaction shown in Figure 3.2 is incomplete and that some product not requiring oxygen for its formation is produced. The final products in the oxidation of hydroxylamine are known to depend to some extent upon the oxidant, and there is evidence for the formation of other nitrogenous compounds by different reactions

with hydroxylamine. Nitrogen gas, for example, is a likely product in the oxidation of NH_2OH by ferricyanide (Anderson 1964, Kolasa and Wardenki 1974). A disproportionation yielding both ammonium and nitrogen gas has been suggested for the oxidation of hydroxylamine by vanadate (Gowda et al. 1957).

The rate of N_2O production also depends upon pH and salinity (Table 3.2). Early investigators found that the ferric oxidation of hydroxylamine took considerable time in acidic solution, thus requiring heat (Bray et al. 1919) or Cu(II) (Rao and Rao 1957) to speed the reaction. Rao and Rao found that the reaction was complete in five minutes in the presence of Cu(II), but took over two hours for the quantitative production of Fe(II) in the absence of Cu(II). In 0.1 N acid, the reaction was not complete in 15 hours. In our case of far more dilute solutions of hydroxylamine and a far greater excess of Fe(III) than in Rao and Rao's investigations, we too found that the reaction in DDW required a few hours to reach completion at pH 3.4 and even longer at lower pH. In natural seawater, however, the reaction was complete in less than 15 min at pH 3.5 and greater, although at pH near 3 the reaction took more time (Table 3.2). Whether the reaction is slowed at the same step as that noted by Rao and Rao (1957), i.e. - the oxidation of NH_2OH by Fe(III) to some +1 intermediate, we cannot say at this time. It is possible that pH affects more strongly the decomposition rate of one of the nitrogenous intermediates such as hyponitrite or peroxonitrite (Yagil and Anbar 1964, Anderson 1966, Hughes and Nicklin 1970a, 1970b).

Interferences

Hg(II) interfered with the reaction in the unacidified samples (Table 3.3), but the interference was suppressed below pH 3. This indicates that Hg(II) can be used in association with the analysis of NH_2OH. However, because of potential effects of pH and ionic strength on the involvement of Hg(II) in this reaction, we feel this preservative should be used cautiously at this time. The best approach would be to add $HgCl_2$ after the reaction has completed.

Cupric ion reduced the recovery of N_2O at pH 3 in both DDW and NSW, but increased the recovery of N_2O in the unacidified NSW (Table 3.3). The increase, however, is not so much a function of the cupric ion as it is a function of the change in pH owing to the additional Cu(II) added (Figure 3.1). The use of Cu(II) as a catalyst for the ferric oxidation of NH_2OH was first recommended by Rao and Rao (1957), who noted that the use of Cu(II) did not lower the production of Fe(II), only that it speeded up the reaction. The authors, however, were concerned with the back-titration of Fe(II), not the production of N_2O, so any interference by Cu(II) after the conversion of hydroxylamine to a (+1) intermediate would not have affected the recovery of Fe(II). Later, Cu(II) was investigated in more detail in the oxidation of hydroxylamine by O_2 (Anderson 1964 a,b, 1965). Anderson was concerned with an entirely different reaction than the one we are investigating, but the effects of this reaction do constitute a potential interference. In fact, our results indicate that, if one is attempting to measure N_2O produced from the ferric oxidation of hydroxylamine, then it is not advisable to use Cu(II) as a catalyst.

TABLE 3.3. EFFECTS OF CU(II) AND HG(II) ON N_2O RECOVERY.

Cations Added	Percent NH_2OH Recovered as N_2O			
	DDW		NSW	
	Unbuffered pH 3.4	Acetic Acid pH 2.9	Unbuffered (pH)	Acetic Acid pH 2.9
Control (Fe(III) only)	78	80	54 (6.9)	80
Hg(II) (600 uM)	35	81	20 (6.8)	78
Cu(II) (1.7 mM)	27	29	65 (6.6)	18

The final Fe(III) concentration was 200 uM, and all reagents were added before hydroxylamine. pH given is the pH of the solutions after adding the reagents. Only the pH of the unbuffered seawater varied significantly, and is noted separately for each solution.

Although acidifying a sample to pH 3 with a weak acid removes the effects of pH, salinity, Hg(II), and Cl^- on the recovery of N_2O, other unidentified trace substances in natural waters (or laboratory reagents!) are capable of oxidizing NH_2OH and might affect the analysis. These include microbes, trace metals, and perhaps trace organic compounds. Ammonium oxidizing bacteria can both produce and consume hydroxylamine, and they are virtually ubiquitous in marine and fresh waters (Yoshida and Alexander 1964,1971; Fenchel and Blackburn 1979). They are likely present in all of the waters tested in these analyses, with the possible exception of the DDW. However, the potential effect of nitrifying bacteria on this reaction is minimal; in the analytical procedure most of the hydroxylamine is converted to N_2O within seconds or minutes, far less time than it would take for the organisms to adjust to the change in acidity and to induce the enzymes necessary for the oxidation of NH_2OH (Focht and Verstraete 1977; Fenchel and Blackburn 1979).

The effects of trace metals on the oxidation of hydroxylamine, and on the oxidation of some of the likely intermediates formed during the course of the reaction, are discussed throughout the literature (e.g. - Anderson 1964a; Hughes and Nicklin 1970a, 1970b, 1971). The effects of trace organic substances in aqueous solution are hardly understood at all, but hydroxamic acids and oximes both are generated by microbes (Amarger and Alexander 1968; Pietta et al. 1982), and hydroxylamine is able to form oximes by condensation with certain carbonyl compounds in acid media. How much of this occurs in natural waters we do not yet know. However, we at times have found low recoveries in waters that had an elevated biological activity or that we

suspect were high in dissolved organic material (Table 3.4). In water from one location, Big Lagoon, whatever caused the low recoveries was partially removed by aging the water. The recoveries both before and after aging were consistent among all of the Big Lagoon samples analyzed, and may have been the result of biological alteration of trace metals or labile organics. This demonstrates the need for careful monitoring of recoveries by use of standard additions.

Recommended Method

For the quantitative measurement of hydroxylamine by Fe(III) oxidation in natural waters, samples must be acidified to pH < 3.5, but not less than pH 2.8. A weak, monocarboxylic acid, such as acetic acid, insures a reasonably constant final pH in coastal or estuarine waters of variable alkalinity. Because interferences can differ among samples, standard additions should be made to duplicate samples until a clear picture of N_2O recovery is developed for the waters being analyzed. We recommend the following procedure:

1. Collect samples in well greased, ground glass-stoppered, volume-calibrated, opaque, 125 ml bottles that contain a few glass beads (included in the calibration) to enhance mixing of the reagents.
2. Add 1.0 ml of glacial acetic acid (17.5 M) into each bottle immediately after collection, restopper, and shake well. The acetic acid, as well as all reagents, should be added by carefully injecting just below the surface of the

TABLE 3.4. HYDROXYLAMINE RECOVERY AS N_2O IN VARIOUS NATURAL WATERS

Source	Description	Percent Recovery
North Pacific Gyre Surface	34.5 o/oo, oligotrophic, aged 1 year in lab	80 ± 2 (16)
Oregon Coast Surface (250 mi offshore)	33.5 o/oo, high nutrients, aged 1 year in lab	83 ± 2 (4)
Yaquina Bay (near mouth)	32 o/oo, eutrophic, high nutrients, aged 3 mos.	81 ± 2 (4)
Yaquina Bay (upstream)	<1 o/oo, near marina, scum on surface, aged 3 mos.	77 ± 2 (4)
Yaquina River (no tidal influence)	Fresh water running through pastures, aged 3 mos.	64 ± 2 (4)
Big Lagoon (N. Calif. Coast)	Seasonally isolated lagoon, 6 to 26 o/oo, not aged	40 ± 3 (11)
Big Lagoon	Same, but aged 2-3 mos.	69 ± 2 (4)

The error is given as one standard deviation. The number of samples analyzed is noted in parentheses.

sample. The final molarity of the acetic acid is around 140 mM, far greater than any other weak acid in unpolluted natural waters. The resultant pH should fall between 2.9 and 3.0 for most marine and fresh waters.

3. Add 1.0 ml of 25 mM ferric ammonium sulfate. Restopper the bottle and shake well. (Ferric chloride may be substituted for FAS.) The final concentration of ferric ion is 200 uM.
4. After 3 hours analyze for N_2O by electron capture gas chromatography (e.g. - Cohen 1977, Elkins 1980).
5. Repeat steps 1 - 4 with replicates to which standard additions of NH_2OH have been made. Standard additions should be made after the addition of acetic acid and FAS, so that microbial activity is temporarily arrested and Fe^{+++} is the dominant reactive cation in solution.
6. A separate analysis for N_2O originally in the sample and corrections for the addition of reagents are required.

A plot of the results from analyzing standard solutions of hydroxylamine, ranging from 4 to 300 nM in both seawater and DDW, is essentially linear (Figure 3.3). The least-squares fitted straight line shown gave a regression coefficient of 0.9983 and a slope of 0.795; the curve virtually intersects the origin. The slope corresponds approximately to an 80% recovery of NH_2OH as N_2O over a range of concentrations that encompasses and exceeds those previously reported

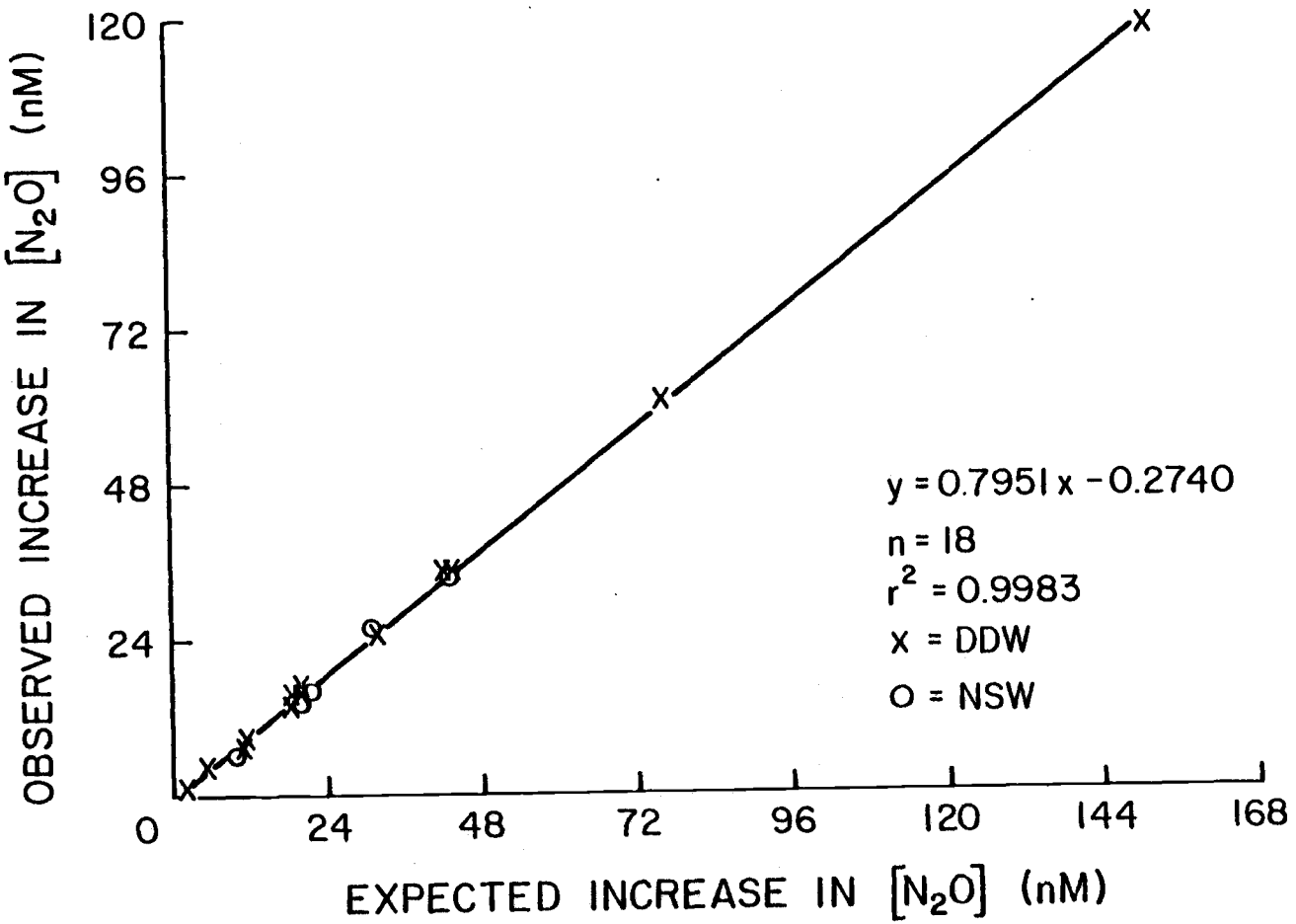

Figure 3.3. Calibration curve for the recommended method.

for natural waters (Tanaka 1953, Baxter et al. 1973, Pitwell 1975, von Breymann et al. 1982). Since the reaction at pH 2.9 - 3.0 gives identical recoveries for seawater and DDW, it is applicable to both fresh and marine waters.

A mixed reagent of acetic acid and FAS or $FeCl_3$ results in a slightly lower recovery of N_2O, so we recommend adding the reagents separately. If the samples are to be held for a prolonged time before analysis, we recommend adding 1.0 ml of 1% $HgCl_2$ 3 hours after the FAS.

CONCLUSIONS

Of the techniques available for the quantitative analysis of hydroxylamine, the analysis of N_2O evolved is the only method of which we know for measuring NH_2OH at the levels that it occurs in natural waters. Nevertheless, in contrast with the work of von Breymann et al. (1982), we have determined that the fraction of NH_2OH nitrogen evolved as N_2O depends upon both pH and salinity. As a result, we have developed a technique that effectively eliminates these influences and is suitable for use in seawater, fresh water, and brackish water of estuaries. Our recommended method provides 1 nM precision (1 s.d.) over a concentration range of 1 to 40 nM, and about 2% precision for concentrations above 40 nM.

Also in contrast with the results of von Breymann et al. (1982), we have found that use of Cu(II) and Hg(II), under certain conditions, can lower the recovery of N_2O. Chloride, in concentrations found in marine waters, can negatively affect the recovery of N_2O, but its effect, as well as that of Hg(II), is eliminated by acidifying the sample to pH 3 with acetic acid. Other substances found in natural waters can interfere with the conversion of NH_2OH to N_2O, hence the need for internal standards.

The maximum recovery of NH_2OH as N_2O by this method is 80%. This is reproducible below a final pH of 3, but drops considerably at elevated pH, with different pH dependencies in seawater and freshwater. The recovery falls to zero above a final pH of 9.5. This behavior

indicates that more than one end-product is formed by the ferric oxidation of hydroxylamine, and that the products are formed by competing reactions which, in turn, are influenced by pH and probably trace metal composition of the sample.

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CHAPTER 4

KINETICS OF THE OXIDATION OF MICROMOLAR AND SUBMICROMOLAR HYDROXYLAMINE BY IRON(III)

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ABSTRACT

The dependence of the rate of N_2O formation on the reactants and on pH in the oxidation of NH_2OH by Fe(III) has been investigated over a range of reactant concentrations, with emphasis on low concentrations of hydroxylamine. The production rate of N_2O was pseudo-first order with respect to total iron, pseudo-first order or less with respect to total hydroxylamine, and inversely proportional to $[H^+]^{2.5}$. The reaction is highly sensitive to temperature. Of the competing reactions producing nitrogenous products other than N_2O, at least one is catalyzed by light. An empirical rate law, based on the total concentrations of the reactants, is presented and a more general rate law, based on the concentrations of presumed reactive species, is derived.

INTRODUCTION

Hydroxylamine is reactive and unstable in oxygenated water (Moews and Audrieth 1959). In aqueous solution, it is oxidized readily by oxygen, peroxide, and an array of transition metal cations (Szilard 1963, Erlenmeyer et al. 1969, Hughes and Nicklin 1971); it also will condense with aldehydes and ketones to form oximes (Sharon and Katchalsky 1952). These properties of hydroxylamine make it particularly valuable for industrial and synthetic applications, but also render it labile and, historically, difficult to analyze with good precision (Bray et al. 1919, Kolasa and Wardencki 1974). In natural waters, where hydroxylamine is produced and consumed by nitrifying bacteria, both its biochemical activity and its abiotic lability result in nanomolar to submicromolar concentrations that, until recently, have eluded detection and measurement by aquatic chemists and biologists (Baxter et al. 1973, Fiadero et al. 1967, von Breymann et al. 1982).

Recently, we and our colleagues have developed and improved a gas chromatographic technique for the analysis of nanomolar levels of hydroxylamine in natural waters (von Breymann et al. 1982; Chapter 3). As for many earlier techniques (Kolasa and Wardencki 1974), this method relies on the quantitative oxidation of hydroxylamine by Fe(III), where

$$4Fe(III) + 2NH_2OH = 4Fe(II) + N_2O + H_2O + 4H^+ . \qquad (1)$$

Our technique differs from earlier ones in that, rather than measuring the residual Fe(II), we analyzed for N_2O by electron-capture, gas chromatography. This has led to a far greater sensitivity than reported before, and, for the first time, permits the measurement of hydroxylamine at ambient concentrations in aquatic systems.

However, in developing the technique, we found that the amount of N_2O produced was not stoichiometric with hydroxylamine as indicated by equation (1), that the change in N_2O concentration depended systematically on the pH and salinity of the solution, and that cations, notably Cu(II) and Hg(II), negatively interfered (Chapter 3). Because the effect of salinity on the production of N_2O could not be attributed alone to ionic strength, we concluded that the difference must be a result of the kinetics of competing reactions. These competing reactions, however, must provide for the oxidation of hydroxylamine to a +1 state by Fe(III) if Fe(II) is to be produced quantitatively. These considerations led us to investigate further the kinetics of this reaction under conditions that are near those of the analytical method applied to natural waters. We present here our findings on the effects of iron, hydroxylamine, and hydrogen ion concentrations on the kinetics of the oxidation of hydroxylamine by Fe(III) in acid solution.

EXPERIMENTAL

Apparatus and Reagents

The apparatus and reagents are described in detail in an earlier paper (Chapter 3). All chemicals used were analytical-reagent grade. Hydroxylammonium (pKa = 5.97) stock solutions were acidified to pH 3 and stored at 2 C between experiments to retard degradation, and working standards were prepared fresh daily. Nitrous oxide was measured by electron-capture gas chromatography with a technique that involves stripping the N_2O from solution onto a liquid-nitrogen cooled trap for subsequent injection into the gas chromatograph (Cohen 1977). The coefficient of variation (s/x x 100) for a single analysis of N_2O was about 2%.

Procedure

Our approach involved primarily the measurement of initial rates of N_2O production following the injection of hydroxylammonium standard into a suitable reaction medium in a gas-tight container. Fe(III) concentrations were varied from 80 nM to 1.2 mM, hydroxylammonium from 80 nM to 4 uM, and pH from 1.0 to 2.6. Because of the pronounced effect of pH on reaction rate, the most reliable measurements of the reaction rate were attained below pH 1.7. Tests of incremental amounts of iron

and hydroxylammonium were conducted in solutions of pH 1.40. N_2O was measured when the reaction was between 5 and 10 percent complete, usually about 1.5 hours, but much shorter at higher pH.

For each series of experiments, deionized, distilled water (DDW) was acidified to the appropriate pH with HCl and distributed into acid-washed, DDW rinsed, volume-calibrated, 150 ml bottles with greased, ground-glass stoppers. A few glass beads (approximate volume, 1.0 ml) were added to each bottle to enhance mixing of the reagents. Ferric ammonium sulfate (FAS) was injected into each bottle to obtain the desired concentration, and the bottle restoppered and shaken to distribute the Fe(III). A hydroxylammonium standard was then injected into each bottle, which was shaken again and allowed to stand for 1.5 hours before analysis for N_2O. Analysis of N_2O involved drawing a portion of the sample into a syringe and injecting it via a septum into the stripping flask of the gas chromatograph; the pH of the solution in the stripping flask was kept below 0.5 to stop the reaction during stripping, which took about 7 minutes. Corrections for N_2O originally in the reaction medium and for the effects of reagent and standard additions on pH were included in the calculations.

In addition to the measurements of initial reaction rate, the reaction in the presence of excess Fe(III) was followed to completion at pH 1.0 and 1.4. Potential surface effects were evaluated by measuring the reaction rates in bottles of different volume, and the role of a potentially interfering free-radical mechanism, the decomposition of hyponitrous acid to N2 and $NO3^-$, was investigated by conducting the

reaction at pH 3 in the presence of 0.1 mole% ethanol (Buchholz and Powell 1962). The effect of temperature was observed by conducting the reaction at 1.8 C and 20.4 C.

RESULTS

Effect of Total Fe(III) on the Reaction Rate

With Fe(III) added in considerable excess of hydroxylamine, the production of N_2O appeared pseudo-first order with respect to Fe(III) over nearly three orders of magnitude (Figure 4.1). This was unexpected because the stoichiometry of the reaction according to equation (1) requires the consumption of four Fe(III) ions for every N_2O produced. However, there is no reason to expect that the reaction would be as simple as written in equation (1); earlier investigations indicate the production of nitrogenous compounds other than N_2O, requiring a sequence of reactions (von Breymann et al. 1982; Chapter 3).

The pseudo-first order dependence on total Fe(III) is not explained by iron speciation alone. The proportions of all species change with increasing [FAS] (Table 4.1), the hydroxylated monomers and chlorides dropping in response to significant increases in $[FeSO_4^+]$. The fraction of $Fe_2(OH)_2^{+4}$, a particularly appealing form in that the reaction requires the transfer of two electrons to each hydroxylamine, increases linearly with total Fe(III). Hence, were the reaction rate dependent on the dimer, it would have to be a square-root dependence, an unlikely circumstance on inspection. $FeSO_4^+$ also could be ruled out on similar grounds. If the rate limiting step does involve a particular Fe(III) species, then one of the other monomeric forms, for which the

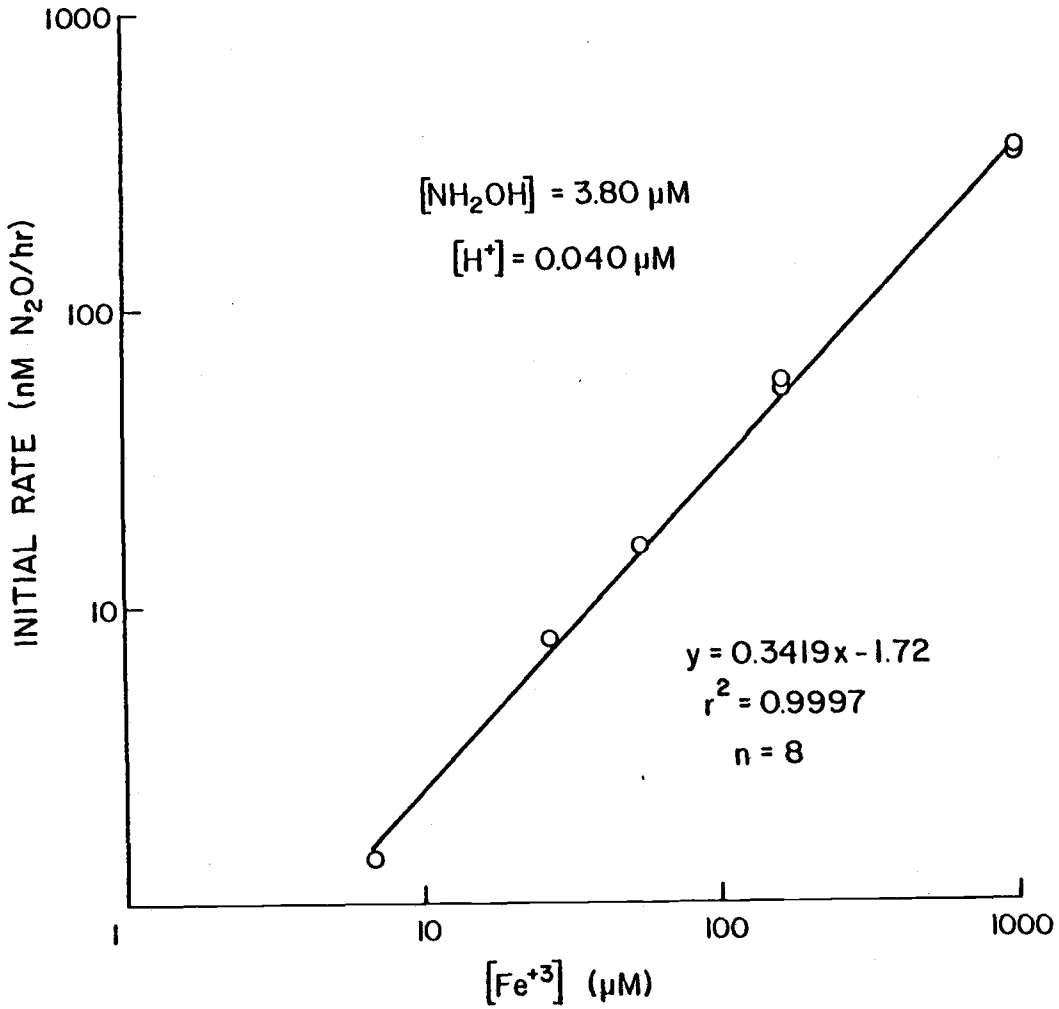

Figure 4.1. Initial N_2O production rate vs total Fe(III).

Table 4.1. DISTRIBUTION OF FE(III) SPECIES IN AQUEOUS SOLUTION AS A FRACTION OF TOTAL FE(III) CONCENTRATION AT pH 1.40.[a]

Species	Fe^{+3}	$FeOH^{+2}$	$Fe(OH)_2^{+2}$	$Fe_2(OH)_2^{+4}$	$FeCl^{+2}$	$FeCl_2^{+}$	$FeSO_4^{+}$
pK	- -	2.37[b]	7.13[b]	2.33[c]	-1.1[b]	-.28[b]	-3.16[d]
[FAS][e]							
6.8	.616158	.065956	.000029	.000008	.309966	.001877	.006008
27.0	.605584	.064823	.000028	.000029	.304642	.001844	.023050
54.2	.592413	.063412	.000028	.000056	.298010	.001804	.044277
169.0	.546894	.058535	.000026	.000149	.275092	.001665	.117640
1018.0	.393057	.042029	.000018	.000462	.197518	.001196	.365720

(a) Calculated for $[Cl^-]$ = 0.04 M; ionic strength, I = .04 M; and with ferric ammonium sulfate (FAS) as the source of Fe(III)
(b) Kester et al. (1975)
(c) Stumm and Morgan (1981)
(d) Willix (1963)
(e) FAS concentrations given in uM units

concentration changes much less with Fe(III), would be more likely.

Effect of Total Hydroxylamine on the Reaction Rate

The relationship of the N_2O production rate to total hydroxylamine was somewhat more complicated. Above a hydroxylamine concentration of 380 nM the reaction appeared pseudo-first order; however, the line generated by those points missed the origin significantly and, below 380 nM hydroxylamine, the data, although scattered, defined a steeper curve (Figure 4.2). Below 80 nM, the production of N_2O was insignificant. This pattern implied the involvement of other reactions that may have predominated at lower concentrations. We found no apparent bottle effect at uM or nM concentrations of hydroxylamine, indicating that neither the production of N_2O nor any major competing reactions were catalyzed by glass surfaces. However, we did find that ambient light in the laboratory negatively affected the production rate of N_2O (Figure 4.3). This phenomenon was virtually zero order with respect to hydroxylamine concentration, hence its relative effect was more pronounced at lower hydroxylamine concentrations. Hydroxylamine is photooxidized, both as vapor (Smith and Leighton 1944, Betts and Back 1965) and in aqueous solution (Behar et al. 1972), yielding products other than N_2O. There is no evidence, however, that the same mechanism governs this reaction.

By allowing the reaction to go to completion in both light and dark bottles at pH 1.4, we found that the total production of N_2O also was reduced by light (Figure 4.4). The curves in Figure 4.4 are pseudo-first order according to the equation,

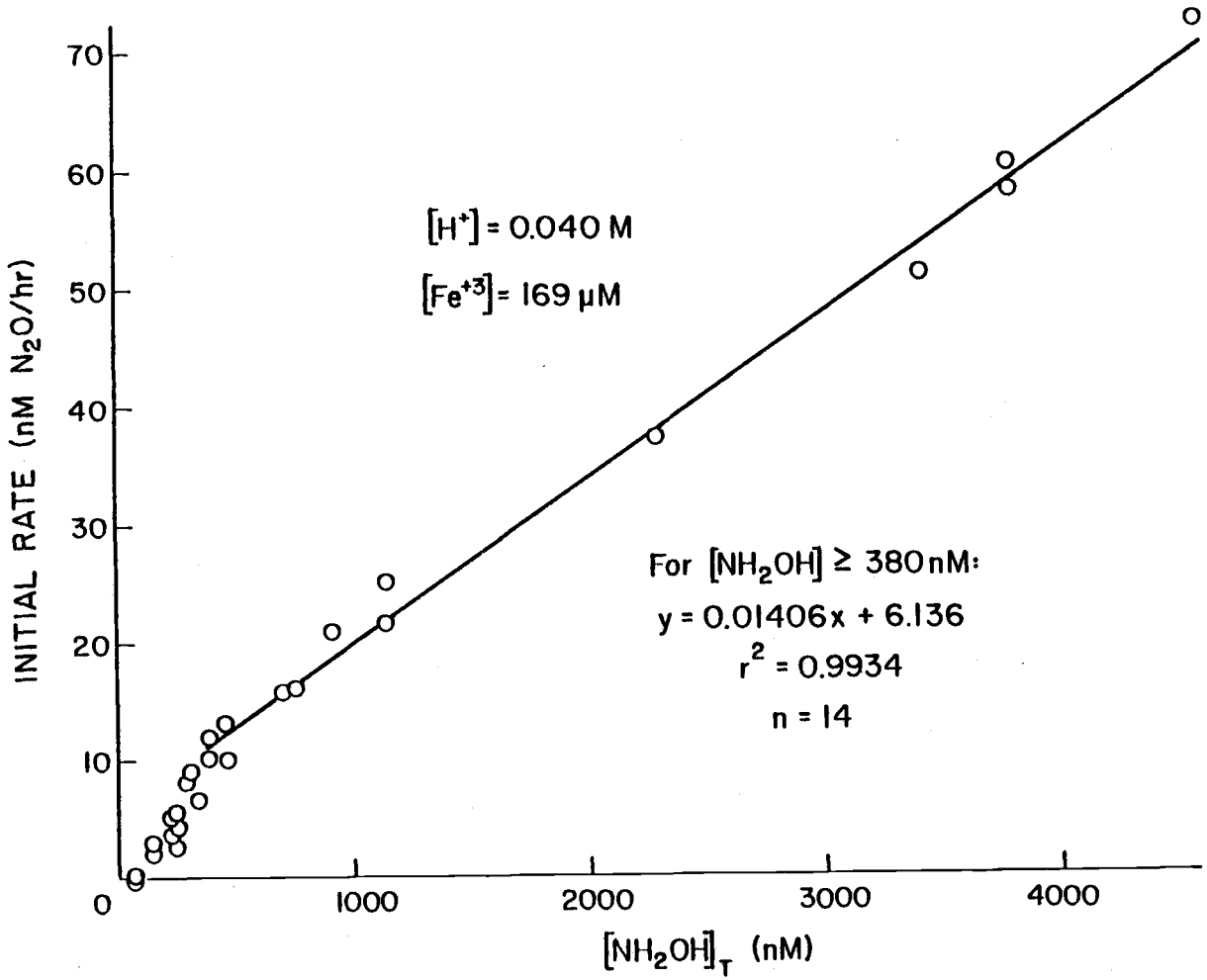

Figure 4.2. Initial N_2O production rate vs total NH_2OH.

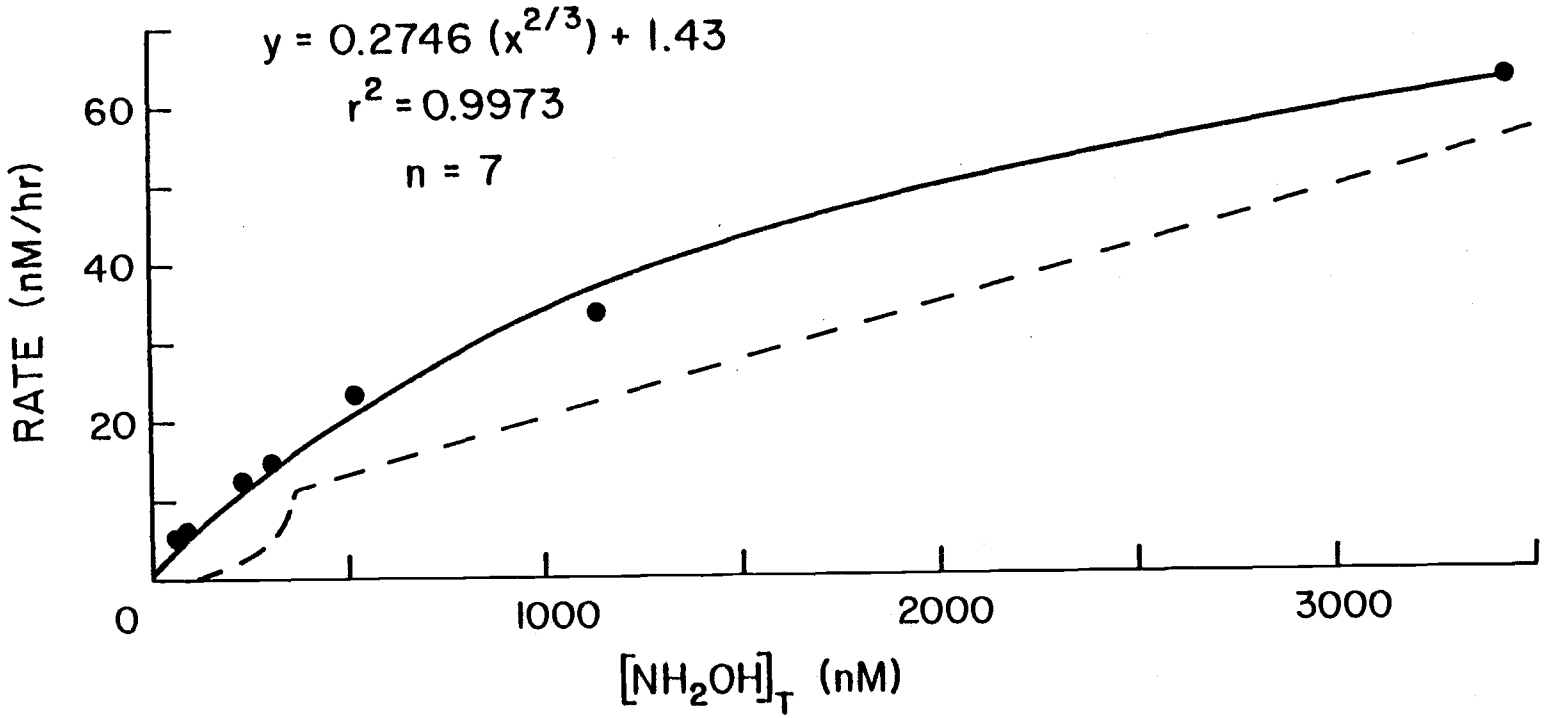

Figure 4.3. Initial N_2O production rate vs total [NH_2OH] in absence of light. Dashed line represents reaction in presence of light (from Fig. 4.2).

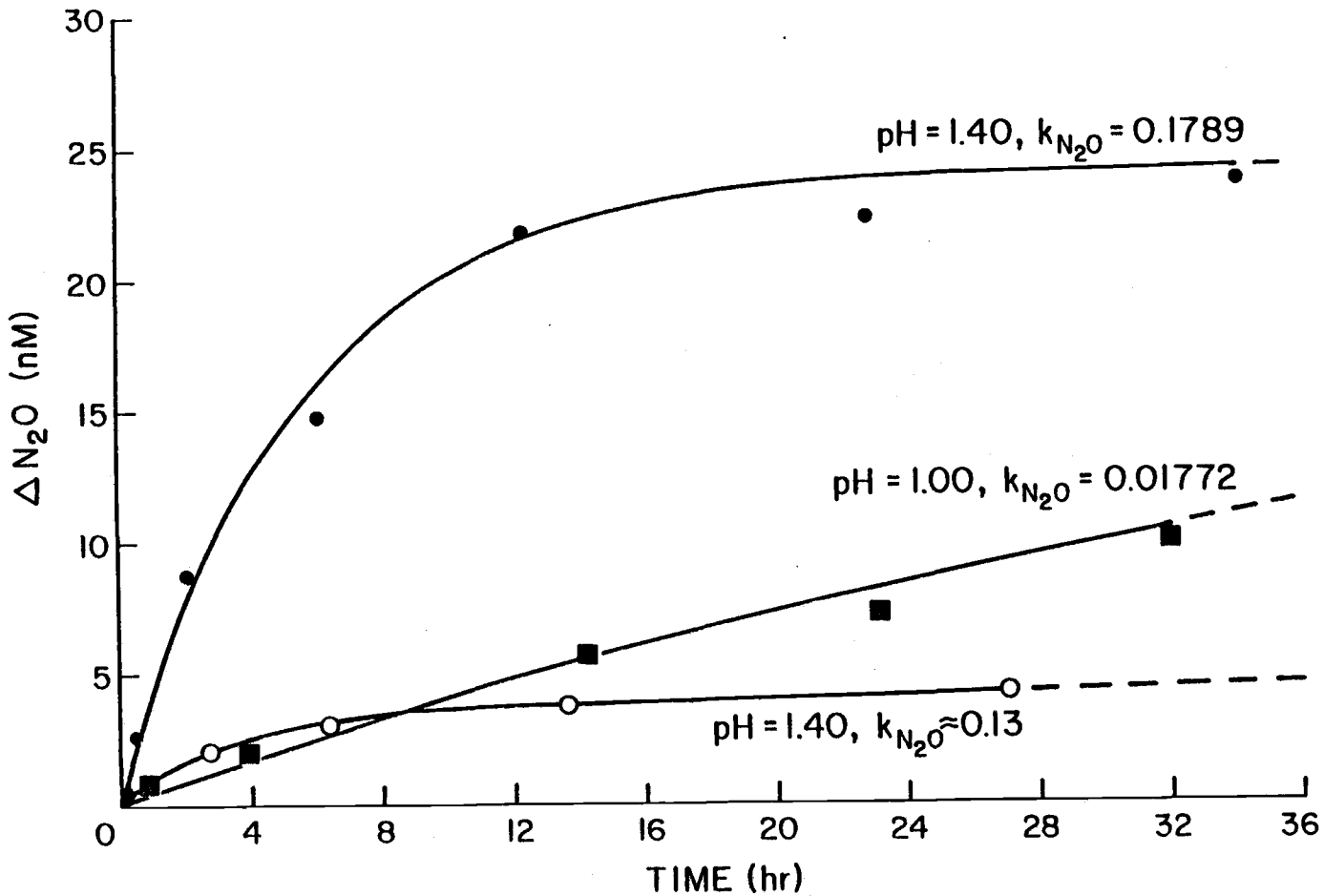

Figure 4.4. Initial N_2O production vs time. Open symbols represent reaction done in the light.

$$[N_2O]_t = [N_2O]_{max} \times [1 - e^{-(k_{n2o} \times t)}] , \qquad (2)$$

where $[N_2O]_t$ represents the amount of N_2O produced at time t, $[N_2O]_{max}$ represents the amount of N_2O produced by the reaction at completion, and k_{n2o} is the first order rate constant. Because the maximum amount of N_2O produced dropped considerably in the presence of light, yet the apparent rate constant changed very little, it is likely that the light catalyzed a competing reaction, rather than retarding the reaction that gave rise to N_2O.

The effect of hydroxylamine on the reaction rate in these experiments would seem defined by three concentration ranges. However, a more plausible explanation, and one that is consistent with the results from dark bottle experiments (Figure 4.3), is that the reaction is less than first order with respect to hydroxylamine over the entire range tested and that the apparent, higher order relationship betweeen 80 and 380 nM is an artifact produced by the competing, light-catalyzed reaction. The relationship to hydroxylamine concentrations then would appear first order over a limited range, as was observed. The less than first order fit could be the result of either inhibition of an activated complex, or competition with yet another reaction.

Effect of Hydrogen Ion on the Reaction Rate

The rate of N_2O production was inversely proportional to $[H^+]^{2.5}$ within the pH range of 1.0 to 1.7 (Figures 4.4, 4.5). This non-integral, higher order effect implies a complex involvement of hydrogen ion with

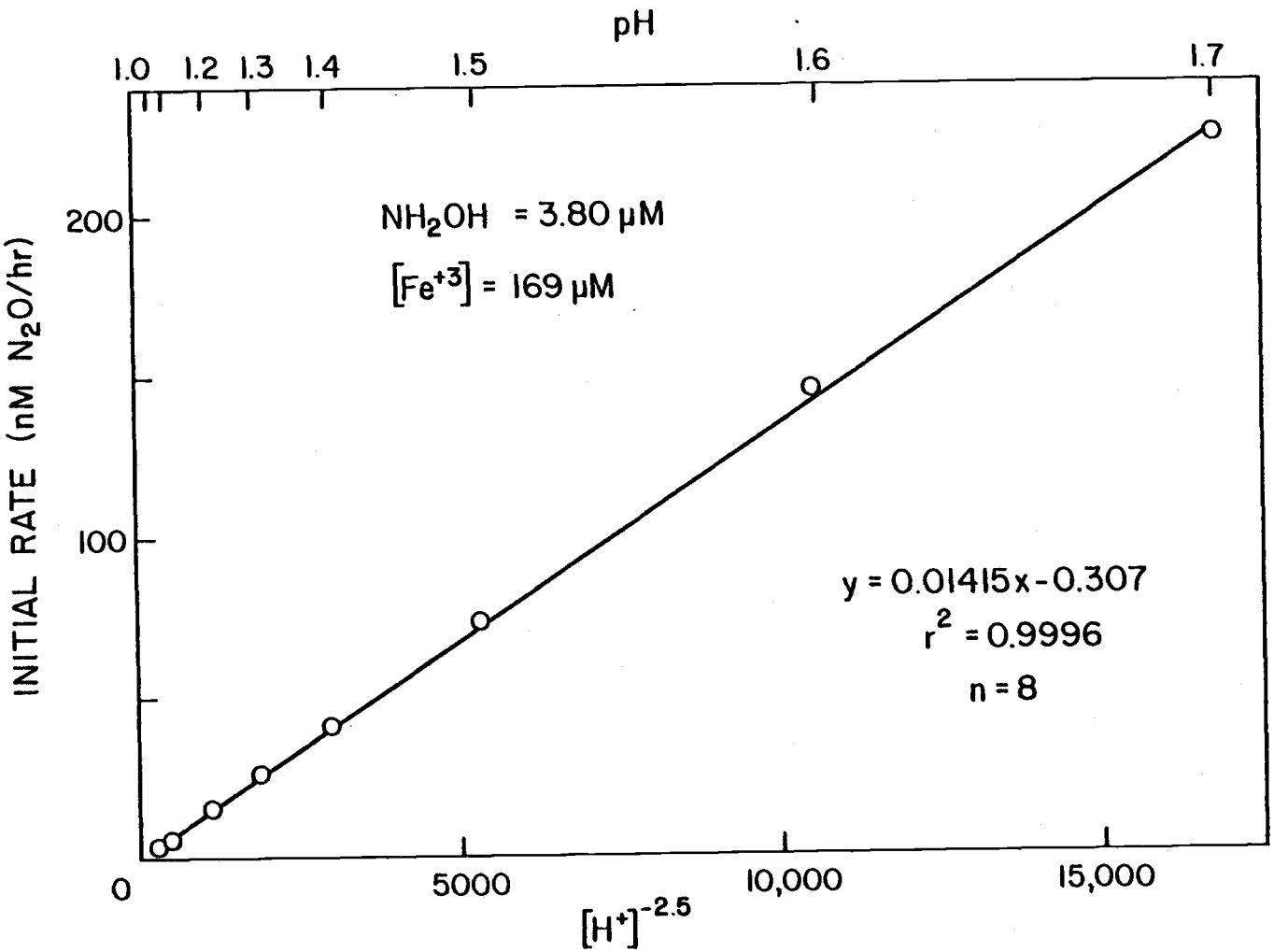

Figure 4.5. Initial N_2O production rate vs $[H^+]^{-2.5}$.

the reactants, indicating that the speciation of the reactants is important in the production of N_2O.

At low pH, hydroxylamine is present predomimantly as the hydroxylammonium ion (pK_a = 5.97). However, the reactive species is most likely the un-ionized form. Investigators working with other cations have suspected this (Hughes and Nicklin 1974, Anderson 1966, Jindal et al. 1970) and the rapid disappearance of hydroxylamine from alkaline solutions supports this contention (Moews and Audrieth 1959). Further, a molecule with a free electron pair would have a greater affinity for a cation than would another positively charged ion. The effect of H^+ on the concentration of the hydroxylammonium ion at low pH is insignificant; however an increase in pH from 1.0 to 1.7 results in a five-fold increase in the concentration of un-ionized hydroxylamine (Table 4.2).

Similarly, the effect of pH on the concentrations of the chlorides, sulfate, and unassociated Fe(III) is nil, but the hydroxylated forms vary significantly with changing pH (Table 4.2). If we assume that the only effect of the hydrogen ion in the reaction is that of altering the relative composition of the reactive species, we can use these data to deduce which of these species are reacting. For the reaction,

$$4Fe(OH)_2^+ + 2NH_2OH = 4Fe(OH)^+ + N_2O + 5H_2O \ , \qquad (3a)$$

where NH_2OH is the un-ionized hydroxylamine in solution, the second order rate law would be

$$\frac{d[N_2O]}{dt} = k(o)' \times [Fe(OH)_2^+] \times [NH_2OH] \ . \qquad (3b)$$

k(o)' is nearly constant over the pH range tested, although a systematic trend with pH is present (Table 4.2). Since the concentrations of

Table 4.2. FE(III) AND HYDROXYLAMINE SPECIATION AND MEASURED N_2O PRODUCTION RATES FROM pH 1.0 TO 1.7.

pH	N_2O Prod Rate	$Fe(OH)^{+2}$	$Fe_2(OH)_2^{+4}$	$Fe(OH)_2^{+}$	NH_2OH	k(o)'	k(o)''
.99	-8.52	-5.40	-8.39	-9.17	-10.40	9.99	6.56
1.09	-8.26	-5.30	-8.19	-8.97	-10.30	9.95	6.55
1.22	-7.81	-5.18	-7.94	-8.72	-10.17	10.01	6.65
1.31	-7.57	-5.09	-7.77	-8.54	-10.18	9.99	6.66
1.39	-7.37	-5.01	-7.62	-8.38	-10.00	9.94	6.64
1.49	-7.12	-4.92	-7.43	-8.19	- 9.90	9.90	6.63
1.61	-6.82	-4.81	-7.21	-7.96	- 9.78	9.84	6.62
1.69	-6.63	-4.74	-7.07	-7.81	- 9.70	9.80	6.59

Fe^{+3}, $FeCl^{+2}$, $FeCl_2^{+}$, and $FeSO_4^{+}$ have been omitted as they are essentially constant. Values for N_2O production rate are molar h^{-1}, expressed as $\log_{10}$; hydroxylated Fe(III) species, and un-ionized hydroxylamine are molar concentrations expressed as $\log_{10}$. Total Fe(III) is 169 uM, total hydroxylamine is 3.8 uM. k(o)' and k(o)'' are as described in the text. Formation constants are as noted in Table 1.

$Fe(OH)_2^+$ and NH_2OH are nearly proportional to the concentrations of their total counterparts, a reaction such as this would be consistent with the apparent first-order dependencies on Fe(III) and total hydroxylamine.

Other Observed Effects

In our previous work (Chapter 3) we noted that the maximum amount of N_2O produced in the oxidation of hydroxylamine by Fe(III) was around 80% of that expected for a complete reaction consistent with equation (1). This maximum was attained at pH 3. We postulated a reaction sequence, based on our work and the findings of other investigators, that involved cis- or trans- hyponitrite as an intermediate. Buchholz and Powell (1962) working with trans-hyponitrite, found that a free radical reaction of hyponitrite interfered with the production of N_2O below pH 1.4, and that the interfering reaction could be inhibited completely by addition of excess ethanol as an OH radical trap. In this study, we added ethanol to a concentration of 0.1 mole % in our reaction bottles, and found that the maximum production of N_2O from hydroxylamine at pH 3 was still 80% of theoretical. This result indicates that trans-hyponitrite is not an intermediate in the reaction sequence and that the production of N_2O is not a chain reaction involving OH radicals. Cis-hyponitrite could be involved, as suggested by Hughes and Nicklin (1971), but it also is possible that the reaction does not involve any free nitrogenous intermediates, that N_2O is formed directly from an iron-nitrogen complex.

The rate of N_2O production was strongly temperature dependent (Table 4.3). An increase of 18.6 C accelerated the reaction rate by 20 times, corresponding to an activation energy of 25.9 kcal/mole and a van't Hoff Q_{10} of 5.0, both somewhat high. The entropy of activation at the reaction pH of 1.4 was 5.3 eu. Possible involvement of another reaction that may be more or less temperature sensitive than the production of N_2O restricts our interpretation of these data at this time. The actual activation energy may be somewhat less than what we have calculated.

Table 4.3. EFFECT OF TEMPERATURE ON THE PRODUCTION RATE OF N_2O.

Temperature (C)	Rate (nM/h)	n	s
1.8	6.7	4	0.5
20.4	134.1	4	4.2

[Fe(III)] = 1.69 uM; $[NH_2OH]_T$ = 3.8 uM; pH = 1.4

DISCUSSION

Rate Laws

These results lead to two possible rate law expressions. One is empirical and based on the total concentrations of the reactants in solution. The other is a more fundamental rate law and takes into account the speciation of the reactants and the role of competing reactions. The empirical rate law for N_2O production as a function of the total hydroxylamine, total iron, and pH is

$$\frac{d[N_2O]}{dt} = k_o \times \frac{[Fe(III)] \times [NH_2OH]_T}{[H^+]^{2.5}} , \qquad (4)$$

where $[Fe(III)]$ and $[NH_2OH]_T$ represent the total concentrations of ferric iron and hydroxylamine. This would apply for Fe(III) concentrations of up to 1.2 mM, for hydroxylamine concentrations of 0.4 to 4 uM, and for a pH range of 1.0 to 1.7. Extrapolation beyond these ranges is inadvisable since the relationship with hydroxylamine is not truly linear and we know so little of the nature of the competing reactions. Using data from the curves in Figures 1, 2, and 5, we arrive at a rate constant, k_o, of .025 $M^{1.5}\ h^{-1}$ ($6.92 \times 10^{-6}\ M^{1.5}\ sec^{-1}$) for the reaction.

At lower levels of hydroxylamine, the empirical rate law still applies if the concentration range is not too great. For reactions with concentrations of hydroxylamine of less than 80 nM (Figure 4.4), k_o can

be calculated from k_{n2o} using the equation,

$$k_o = \frac{[N_2O]_{max}}{2x[N_2O]_{th}} \times \frac{[H^+]^{2.5}}{[Fe(III)]} \times k_{n2o} , \qquad (5)$$

where k_o, k_{n2o}, $[N_2O]_{max}$, and Fe(III) are as described earlier, and $[N_2O]_{th}$ is the amount of N_2O that would be produced were all hydroxylamine converted to N_2O. For the dark bottle reaction at pH 1.4, k_o at these low concentrations was about 0.107 $M^{1.5}$ h^{-1} (3.0 x 10^{-5} $M^{1.5}$ sec^{-1}); for the reaction in clear bottles at the same pH, k_o was about 0.08 $M^{1.5}$ h^{-1} (2.2 x 10^{-5} $M^{1.5}$ sec^{-1}), although, as noted earlier, variability in the reaction with such low recoveries make the latter number less reliable.

A more theoretically based rate law must consider the lower order of the reaction with respect to hydroxylamine and must address the speciation of both reactants. The N_2O production rate in dark bottles was best described by a 2/3 power function for hydroxylamine (Figure 4.3), implying an inhibitory role of hydroxylamine in the reaction. Considering this relation along with the speciation data (Table 4.2), the rate law then becomes

$$\frac{d[N_2O]}{dt} = k(o)'' \times [Fe(OH)_2^+] \times [NH_2OH]^{0.67} , \qquad (6)$$

where the power of 0.67 for NH_2OH represents the empirically derived order for a greater range of hydroxylamine concentrations. Use of this equation results in a much better fit for the rate constant than does equation (3b) (Table 4.2).

Mechanism

A two-electron transfer from iron as an iron dimer ($Fe_2(OH)_2^{+4}$) to hydroxylamine is an attractive step in the mechanism. However, as already noted, direct involvement of $Fe_2(OH)_2^{+}$ is unlikely. This leaves us with a rather unsatisfactory set of circumstances. To meet the requirements of first order dependence on Fe(III) and less than first order dependence on hydroxylamine, the reaction must involve, as an initial step, the formation of an activated complex comprising a single Fe(III) ion and a single NH_2OH molecule. The remaining steps must be more rapid, must involve another Fe(III) ion for each hydroxylamine, and must favor dimerization of oxidized N. The probability of encounters among reactive intermediates is low, hence the sequence must involve a number of highly specific reactions leading to the production of N_2O. We can only speculate at this time as to the nature of these reactions.

Equation (1) does not adequately describe the reaction of Fe(III) with hydroxylamine. One or more reactions, at least one of which is catalyzed by light, yield nitrogenous products other than N_2O. However, it also is apparent from other studies (Kolasa and Wardencki 1974) that the amount of Fe(II) produced is consistent with equation (1). If this is true, then the competing reactions either must occur after the Fe(III) has oxidized the hydroxylamine to a +1 intermediate[11], or, if they involve the formation of different ferric hydroxylamine complexes, then they must adhere to the same stoichiometry; later steps could then lead to any of a number of products.

Further understanding of this reaction sequence requires additional study of the competing reactions and their products, particularly with

respect to the role of light. Whether the reaction catalyzed by light is the same as the reaction that remains operative in the dark, and whether these reactions proceed by formation of separate complexes with iron, or, alternatively, involve the reorganization of an oxidized nitrogenous intermediate, are questions that need to be resolved before this reaction mechanism can be further elucidated.

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CHAPTER 5

CYCLING OF METHANE, CARBON MONOXIDE, NITROUS OXIDE, AND HYDROXYLAMINE IN A STRATIFIED COASTAL LAGOON

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ABSTRACT

The vertical distributions of trace gases, nutrients, and hydroxylamine were measured in a seasonally stratified, coastal lagoon in Northern California. Vertical eddy diffusivity coefficients were estimated from salinity profiles, supported by temperature data. The production of gases and nutrients was estimated from mass balance calculations where possible, including considerations for diffusion and microbial oxidation. From late spring through most of the summer the lagoon remained oligotrophic, with biological activity limited primarily to the pycnocline and the sediments. Methane, attaining high levels of supersaturation, was produced in sediments throughout the lagoon and in the water column of the hypolimnion. Its subsequent fate was governed primarily by transport, but also by microbial activity. Carbon monoxide also reached high concentrations, but, having a turnover time of a few hours, was regulated almost entirely by microorganisms. Nitrous oxide production was evident near the halocline throughout most of the study, but was apparent near the sediments only in the spring; N_2O in the hypolimnion was consumed in the sediments, presumably by denitrification, throughout the summer. Hydroxylamine was present in the spring when nitrous oxide was produced, but absent during the summer when nitrous oxide was being consumed in the hypolimnion. Hydroxylamine could have been generated either by nitrification or by fermentative nitrogen reduction. Nitrous oxide distributions, like those of methane, were governed by diffusion and microbial processes, but the

distributions of hydroxylamine, which had estimated turnover times of only a few hours, probably were regulated by microbes and *in situ* chemical oxidation.

INTRODUCTION

Nitrous oxide, methane, and carbon monoxide are of interest both because of their roles in shaping the properties of the atmosphere, and because they are useful as indicators of specific biochemical processes occurring in oceans, sediments, and soils. All of these gases undergo significant chemical reactions in the atmosphere (Logan et al. 1978) and contribute either directly or indirectly to the global retention of solar energy (Blake et al. 1982, Khalil and Rasmussen 1984, Wang et al. 1976). Recent estimates indicate that the contribution of these trace gases to global warming is significant, and that continued anthropogenic loading may result in a measureable increase in the earth's temperature (Ramanathan et al. 1985, World Meteoological Organization 1983).

However, estimates of anthropogenic effects must be tempered with an understanding of the natural fluxes of these gases and of the processes regulating their distributions. The fluxes of N_2O, CH_4, and CO are controlled by both biological and physical processes (McElroy et al. 1977, Conrad et al. 1983, Blake et al. 1982). Although they all are produced microbially in low-oxygen or anoxic environments, these gases are distributed widely throughout the geosphere by heterogenous advection and diffusion. Abiotic, chemical reactions aid in regulating the trace gas concentrations. For example, N_2O undergoes photolysis in the stratosphere (McElroy and McConnell 1971), both CH_4 and CO are consumed in stratospheric reactions involving the hydroxyl radical

(Logan et al. 1978), and CO is produced by the photolysis of low molecular weight aldehydes (Conrad et al. 1982, Redden 1983) and in the reaction of CH_4 with the hydroxyl radical (McConnell et al. 1971). In addition to these abiotic reactions, microbial sinks also exist for all three gases; methane is consumed by methylotrophs and nitrifiers, carbon monoxide is consumed by nitrifiers and other CO oxidizing bacteria, and N_2O can serve as an electron acceptor for denitrifying organisms (Jones and Morita 1983a, 1983b; Conrad and Seiler 1980, Fenchel and Blackburn 1979).

One reactive nitrogenous intermediate, hydroxylamine, may be particularly useful in identifying and quantifying the sources of nitrous oxide. Nitrous oxide is generated as a by-product during nitrification, and either as an intermediate or as a final product during denitrification. It is consumed microbially only by denitrifiers. Because hydroxylamine is an intermediate in nitrification, but is not involved in denitrification, its production should be related to the production of nitrous oxide by the ammonium-oxidizing nitrifiers. In fact, hydroxylamine is highly reactive, both chemically (e.g. - Moews and Audrieth 1959; Chapter 3) and biochemically (Yoshida and Alexander 1971), thus its mere presence is indicative of high rates of production. Unfortunately, nitrification is not the only process giving rise to hydroxylamine, as it also can be produced and consumed through dissimilatory reduction of oxidized nitrogen to ammonium (Yordy and Ruoff 1981; Figure 1). The relative importance of these processes in nature has been difficult to assess, owing, in part, to the lack of a suitable analytical method for measuring hydroxylamine at ambient concentrations in natural waters. However, we recently have

developed and improved a gas chromatographic technique for the measurement of nanomolar concentrations of hydroxylamine (von Breymann et al. 1982, Chapter 3) and now include it along with our investigations of trace gas distributions.

The purpose of this study, then, is to evaluate the distributions and fluxes of trace gases, nutrients, and hydroxylamine in a system that provides an interface between oxic and anoxic environments, and where oxidation, reduction, and transport all could be monitored. Big Lagoon, a seasonally stratified, coastal lagoon in Northern California, was selected for this study, as it provided well oxygenated surface waters, poorly oxygenated bottom waters, and anoxic sediments, throughout which a variety of kinetically regulated redox reactions could govern the production and consumption of light-element compounds. Our objective has been to determine the relative importance of biological and physical processes in controlling the fluxes of these compounds in a system that is, in some ways, analagous to larger and more widespread zones of global gas exchange.

STUDY AREA DESCRIPTION

Big Lagoon is located along the Northern California coast at about 41^{o} N. Latitude (Figure 5.1). The lagoon is one of a series of bodies of water in that region which, to some degree, are isolated from the Pacific Ocean by sand spits. The largest of these, Humboldt Bay, has been kept open and reasonably well-ventilated, owing to the presence of of permanent jetties. Another, Dry Lagoon, has filled in from the natural deposition of sediments. Big Lagoon lies at a stage between these other two bodies of water. During winter runoff, the sand spit breaches at the northern end, emptying much of the lagoon and allowing free exchange with the ocean. Within a few days, however, the breached portion of the spit begins to rebuild, again isolating the lagoon from the ocean. Continued rainfall elevates the level of the lagoon until it breaks open again, re-initiating the cycle. The sandspit usually breaks at least once each winter, and sometimes up to four times. After the last break, the lagoon continues to fill with freshwater as streamflow diminishes. By late spring or early summer, the lagoon stabilizes with a weakly brackish layer atop a more saline component. The resultant halocline is pronounced, often displaying a gradient of 20 o/oo over a vertical distance of less than one meter.

Once the lagoon stabilizes, phytoplankton blooms in both layers follow, depleting the surface layer of nutrients and depositing organic detritus in the sediments (Brady 1977). A suspension of particulates

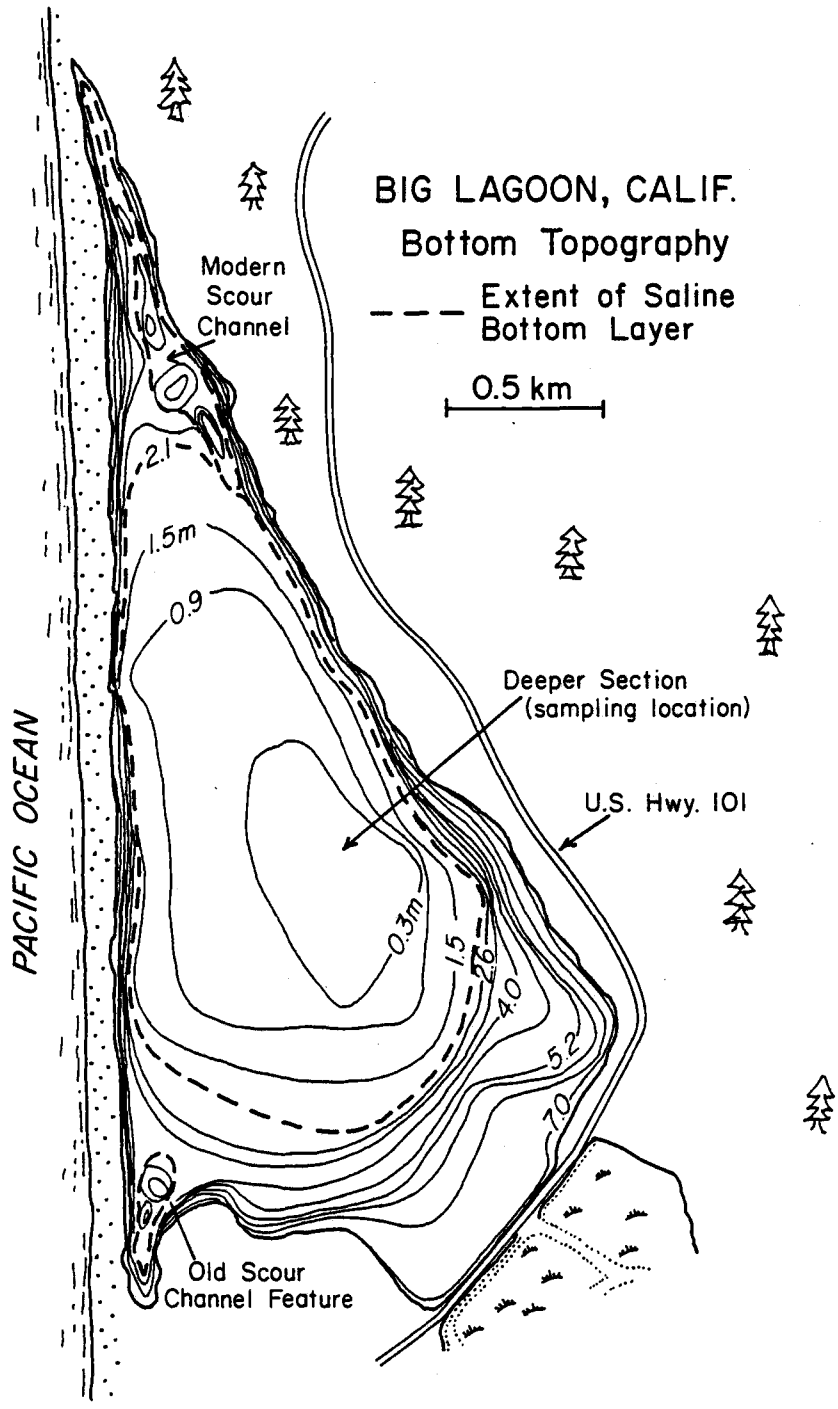

Figure 5.1. Map of Big Lagoon, California.

also is likely at the halocline, as evidenced by increased biological activity in this region (Crandell and Horacek 1973, Brady 1977). Although the surface layer is well-mixed throughout the summer, the bottom waters remain isolated by the sharp pycnocline. Subsequent oxidation in the sediments reduces the oxygen in the lower layer, at times making the waters virtually anoxic (Joseph 1958, Crandell and Horacek 1973).

The lagoon height drops steadily over the summer, owing to evaporation and seepage through the sand spit, with the wind-mixed layer penetrating closer to the bottom. In some years, the lagoon mixes completely by the end of the summer. Whether this happens depends on the initial height of the lagoon, the intensity of mesolimnetic heating, the sharpness of the halocline, and the speed and direction of the prevailing winds. Often, fall rains simply fill the lagoon to the point of breaking, at which point either turbulence or free exchange with the ocean re-aerates the bottom layer.

In 1985, the lagoon stabilized in the late spring with a depth of about 7.6 m, 5.0 m of which was the well-mixed surface layer. The salinity of the surface waters ranged from 6.33 o/oo to 7.50 o/oo; the mean salinity of the bottom layer held at about 26.4 o/oo throughout the study. The halocline in late spring was about 0.5 m thick, but narrowed to a thickness of 0.2 m or less as the summer progressed. The lagoon remained stratified throughout our study.

METHODS AND MATERIALS

Sample Collection

A single station in the deeper section of the lagoon was sampled on five occasions from late May to mid-August 1985 (Figure 5.1). To minimize vertical motion during sampling, the field work was conducted in the morning, between 0800 and 1000, while the lagoon surface was still smooth, and the skiff from which we sampled was anchored at three points. The station was located each time by triangulation. Vertical profiles with a resolution of 0.2 m were obtained by use of a discrete level sampling system designed specifically for this work (Figure 5.2). This system, when deployed across a density gradient, tends to draw water from isopycnal surfaces, thus minimizing vertical mixing. Since we collected the samples as the water intake was lowered, any disturbance of the water column occurred after each depth had been sampled. In situ temperature profiles were obtained with a thermistor kept near the water intake and connected to a Yellow Springs Instruments^{R} Model #43 Telethermometer^{R}

Evasion of gases during sampling was kept to a minimum by operating the pump at a very slow speed (300 ml/min). The sample stream was directed into a one liter bottle, which was allowed to overflow at least one volume. Samples for salinity, pH, oxygen, nutrients, and microbial activity were collected directly from the pump stream as it left the

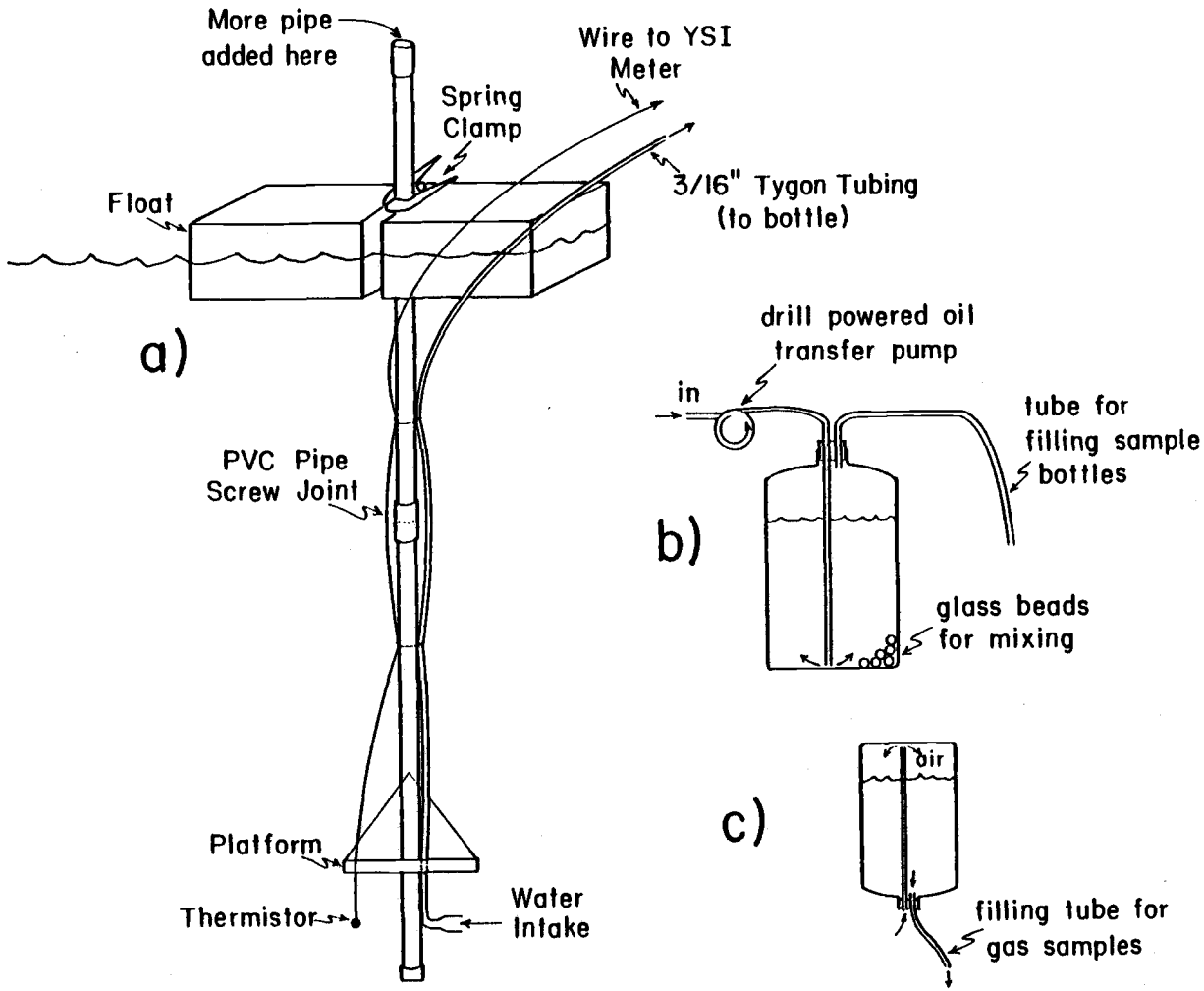

Figure 5.2. Discrete level sampling system.

bottle; samples for gases and hydroxylamine, however, were drawn from the bottle after its contents were well mixed (Figure 5.2). Complete mixing of the sample was necessary especially in this instance because hydroxylamine concentration was determined by difference (Chapter 3). The ability of this system to sample an isopycnal surface was demonstrated by occasionally collecting duplicate nutrient samples from a depth representing a suspected steep gradient. One sample was collected before the liter bottle was filled, and another was collected after all the gases had been subsampled. The largest observed difference between these samples was 4%. Usually, the difference was less than 2%.

Salinity samples were collected in wire-bail citrate bottles, and pH samples were drawn directly into 50 ml Luer Lok^R syringes to minimize exposure to the atmosphere. Dissolved oxygen samples, distributed into ground-glass stoppered bottles, were fixed immediately with $MnSO_4$ and alkaline iodide, and pH, nutrient, and microbial samples were placed immediately into an ice bath. Trace gas and hydroxylamine samples were collected in opaque, volume-calibrated, greased, ground-glass-stoppered bottles. Hydroxylamine samples were treated in the field with acetic acid and ferric ammonium sulfate (Chapter 3). After six hours, they were preserved with $HgCl_2$. Gas samples were preserved immediately with $HgCl_2$.

We deviated from this sampling plan on a few occasions. On the first trip (May 31), our sampling pump failed, so we collected the samples with a Van Dorn bottle. This left us with a vertical depth resolution of 0.3 to 0.4 m. Satisfactory ammonium data were not obtained on this date. We were unable to obtain reliable temperature

profiles on the third trip (July 15), and microbial rates were measured at selected depths and only on four of the five cruises. Finally, we had a little difficulty arriving at the exact position each time, hence the absolute depth of sampling varied by about a meter over the entire period. This was resolved by measuring the change in lagoon height on each sampling and matching salinities of the bottom 0.5 m.

Sample Analysis

Samples were analyzed for salinity and for the more labile consitituents - - dissolved oxygen, pH, ammonium, and nitrite -- at Humboldt State University's (HSU) marine laboratory within a few hours of collection. Salinity was measured with a Beckman^R inductive salinometer, dissolved oxygen was determined by Winkler titration (Strickland and Parsons 1972), and ammonium and nitrite were measured with manual methods modified from Strickland and Parsons (1972). Absorbances were measured through a 10 cm cell. pH was determined at 25 C in a constant temperature electrode chamber, which allowed minimal atmospheric contact.

Samples for automated nutrient analysis were quick-frozen at HSU and analyzed at Oregon State University (OSU) the following day for NO_3^-, PO_4^{-3}, and $Si(OH)_4$ on a Technicon^R Autoanalyzer^R (Atlas et al. 1972). Trace gases were measured from a single sample by use of a split-flow gas chromatograph, equipped with both a flame-ionization detector (FID) and an electron-capture detector (ECD) (Redden 1983). The gases were stripped from the sample with a purified helium stream onto a liquid

nitrogen-cooled, Molecular Sieve^R 5A (MS-5A) trap, which, in turn, was heated to 250 C for injection into the gas chromatograph. The gases were separated on a three foot long, 1/8" diameter column packed with MS-5A and heated to 250 C. CH_4 and CO were separated further on a second MS-5A column, heated to 90 C, and analyzed with a Fisher^R flame ionization detector (FID), CO being converted to CH_4 by a heated (310 C), nickel oxide-plated, firebrick catalyst in a hydrogen stream. N_2O was swept from the first column with purified nitrogen gas and directed to an Analog Technology^R Model 140 A electron capture detector (ECD), with a tritiated-scandium foil. The ECD was maintained at 320 C. Standard gases, a Scott^R mixed standard of 25.3 ppm CH_4, 11.9 ppm CO, and 11.5 ppm H_2 diluted in He, and a Scott^R 25.0 ppm N_2O standard diluted in N_2, were injected with 2.0 and 0.5 cc sample loops attached to a Carle^R gas sampling valve.

Hydroxylamine was determined by ferric oxidation to N_2O, and subsequent measurement by electron capture gas chromatography (Chapter 3). Corrections were made for reagent additions and for nitrous oxide originally in the sample. This method typically results in an 80% recovery of hydroxylamine as N_2O, but the exact recovery can vary, depending on the trace composition of the water being sampled. Consequently, standard additions were run with nearly every hydroxylamine sample collected. Recoveries in Big Lagoon waters were lower than 80%, but reasonably consistent, implying interference from a ubiquitous trace contaminant.

Estimates of microbial oxidation rates of CH_4, CO, and NH_4^+ were based on C-14 techniques (Jones et al. 1984, Jones and Morita 1983a,b), with ammonium oxidation estimated by difference from the continued

oxidation of CO after addition of N-Serve^{R}. An empirical factor of 1.5 x 10^{-3} nM CO/nM NH_4^+ was used for converting nitrifier oxidation of CO to potential oxidation of NH_4^+. *In situ* concentrations were used to convert potential oxidation rates to estimates of *in situ* oxidation.

RESULTS AND DISCUSSION

Salt and Heat Balance

Because we needed to rely on the distribution of salt, and, to a lesser extent on the distribution of heat, for calculating the diffusivities, we felt it necessary to test some of our assumptions concerning the transport of salt and heat by balancing these properties for the entire lagoon. The two budgets should be compatible with respect to evaporation, seepage through the sand spit, and streamflow into the lagoon, and they should result in a calculated change in lagoon height that is close to the measured value.

Areas of isobaric surfaces were determined by planimetering contours on a bathymetric map of Big Lagoon (Figure 5.1). The map was prepared from soundings made in the early 1960's (R.W. Thompson - unpublished data), so minor corrections were made for some obvious, partial filling of shallower areas that has occurred since then. Because the original contours were drawn at two-foot intervals, we interpolated between them to obtain incremental volumes and isobaric surface areas by 0.2 meter intervals. Although we were unable to account for filling that may have occurred in the deeper portions of the lagoon since the map was drawn, selected soundings indicated that major features had not changed.

Salt and heat budgets were calculated with a vertical, finite-increment model, using data from the June 18 and August 13 samplings, and including considerations for streamflow, evaporation, and seepage. These two data sets extended almost to the maximum depth of the lagoon and represented virtually the entire period of study (Figure 5.3). Because we sampled only one station on each trip, we had to assume that the horizontal distributions of heat and salt were uniform throughout the lagoon. This assumption, though tentative, was supported by our initial observations. The surface layer was well mixed, resulting in both horizontal and vertical uniformity, the bottom layer was highly stratified and resistant to vertical flow, and the extremely sharp pycnocline provided a substantial barrier between the two (Figure 5.3). Boundary interferences such as streamflow and seepage through the spit were small relative to the size of the lagoon, hence should not have led to any significant heterogeneity.

Over 56 days the total amount of salt in the lagoon decreased by 2.62×10^7 kg (Table 5.1). Assuming that ocean salt spray was insignificant and that all of the salt was removed by seepage of the surface layer through the sandspit (mean salinity = 6.91 o/oo), we calculated an export of 0.79 m^3/sec of water from the surface layer through the sandspit. Evaporative loss, whether calculated from air temperatures (Chow 1964) or taken from Wust's 1954 tables (McLellan 1968), should have been 0.15 m during this time. Average streamflow was determined as the difference between the calculated export and the calculated change in lagoon volume, including compensation for evaporative loss. The streamflow value of 0.28 m^3/sec agreed exactly with our estimate obtained by comparing the 1985 seasonal rainfall with

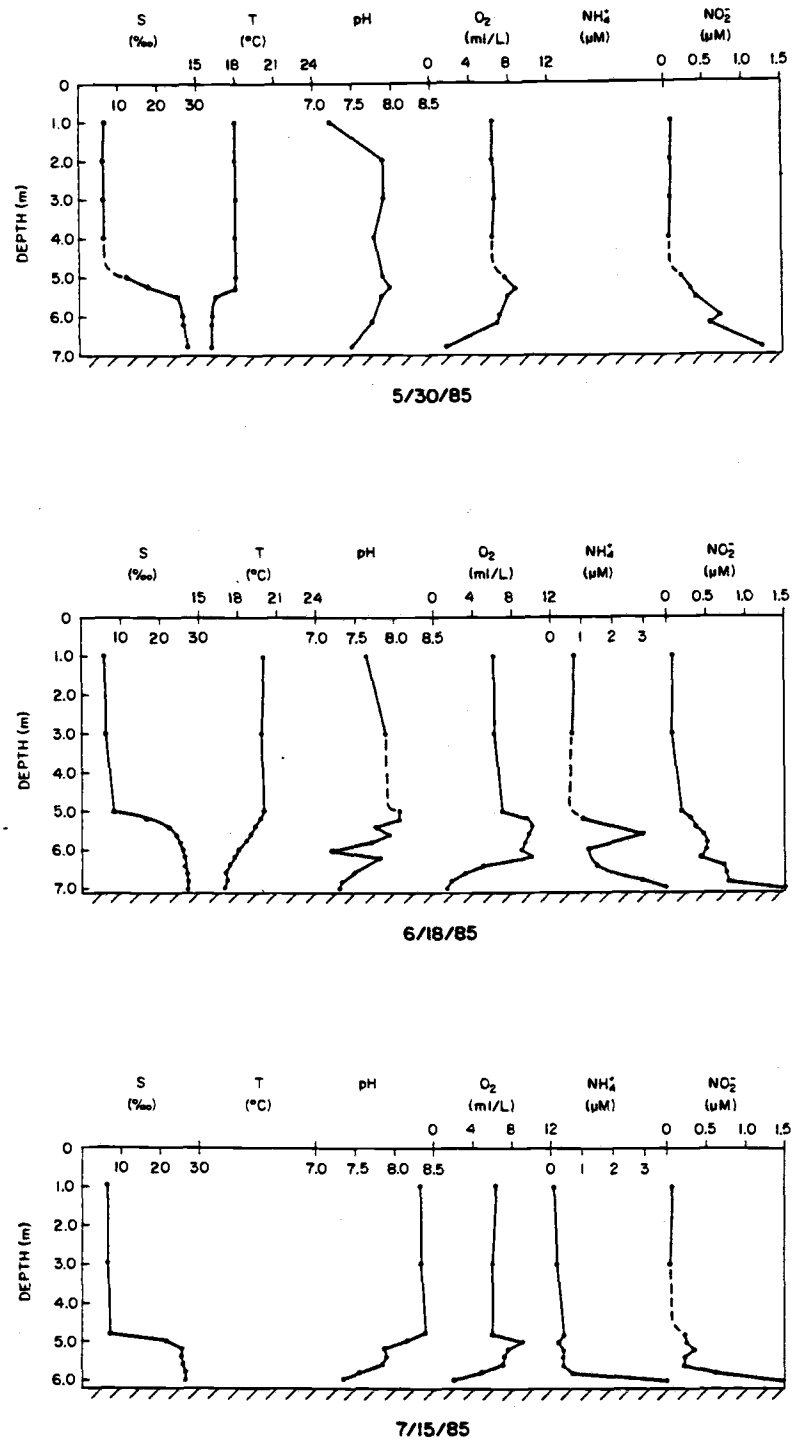

Figure 5.3a. Hydrographic and nitrogenous nutrient profiles on 5/30/85, 6/18/85 and 7/15/85. Nitrate was essentially absent except near the sediments on 30 May. Dashed lines indicate probable distributions through the epilimnion.

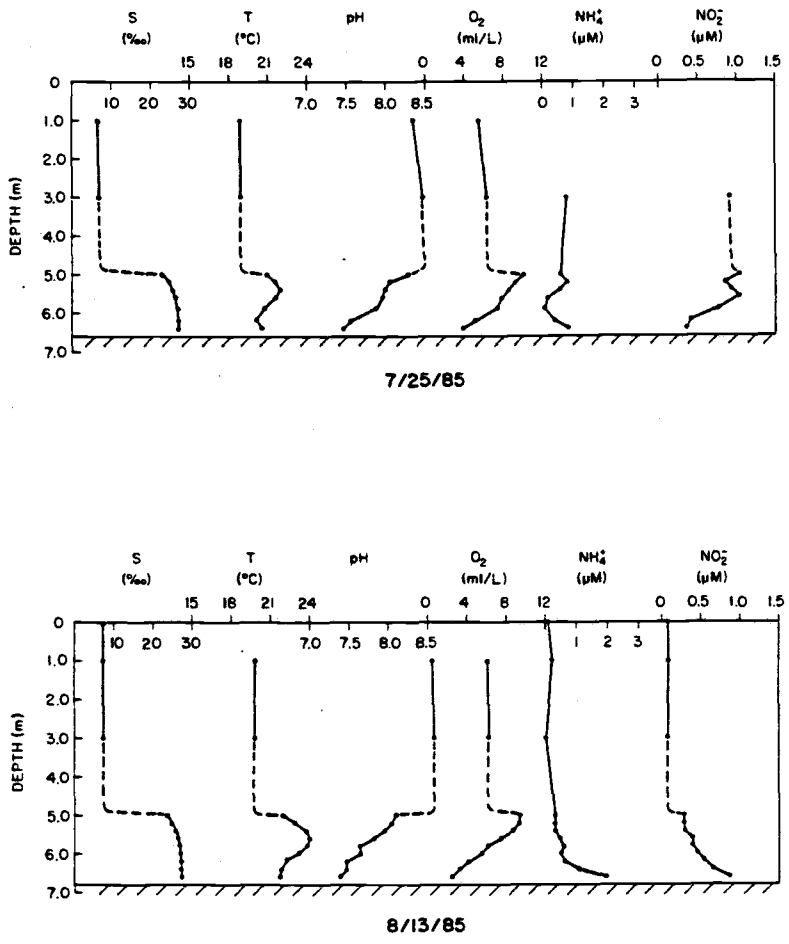

Figure 5.3b. Hydrographic and nitrogenous nutrient profiles on 7/25/85 and 8/13/85. Nitrate was essentially absent except near the sediments on 30 May. Dashed lines indicate probable distributions through the epilimnion.

that of 1957 when actual flow was measured (Joseph 1958). The result also concurred with an estimate obtained by comparing watershed size of Maple Creek to watershed size and flow rates of other rivers in the area.

The calculated change in lagoon height, although close, was slightly greater than the measured change (Table 5.1). This could have been the result of errors in the volume estimates, owing to partial filling of the lagoon, or it could have resulted from one of the assumptions concerning water or salt transport. Salt contributions from ocean spray were assumed negligible, but spray may have brought significant amounts of salt to the surface layer, as strong winds off the ocean are a regular afternoon occurrence. Were this the sole source of salt, the export rate would only have to drop to 0.5 m^3/sec to account for the difference in lagoon height. Given the allowable error in our assumptions, we feel that the agreement is good.

Actual changes in heat within the lagoon were determined with the same finite increment model used for computing the salt balance. However, the heat budget is at best an approximation; the calculations were done only as a check on our assumptions in balancing the salt transport. We did not measure incident radiation throughout this study, but rather estimated total sun and sky radiation from pyrheliometer readings taken at Big Lagoon and Humboldt Bay during the same months of previous years. This estimate of 450 cal/cm^2/day agreed well with the monthly values given by Kimball (c.f. - McLellan 1968), for the Northern California coast. Effective back-radiation was determined for a lagoon surface temperature of 20 C and a relative humidity of 70-80 % (Sverdrup et al. 1942). Heat loss through evaporation was taken as 585 cal/g at

TABLE 5.1. BIG LAGOON SALT BALANCE 18 JUNE THROUGH 13 AUGUST 1985

	18 June		13 August	
	Surf	Bottom	Surf	Bottom
Area (m^2)	3.15×10^6	1.88×10^6	2.92×10^6	1.61×10^6
Depth (m)	5	2.6	4.9	1.9
Volume (m^3)	1.25×10^7	3.07×10^7	1.09×10^7	1.81×10^7
Mean Salinity (ppt)	6.33	26.2	7.49	26.4
Density (kg/m^3)	1003	1019	1004	1018
Total Salt (kg)	7.97×10^7	7.59×10^7	8.19×10^7	4.74×10^7
Salt Loss (kg)	2.63×10^7			
Volume Loss (m^3)	2.89×10^6			
Export (m^3)	3.81×10^6			
(m^3/sec)	.79			
(m)	1.13			
Streamflow (m^3)	1.37×10^6			
(m^3/s)	.28			
(m)	.23			
Potential Evap (m)	.15			
Calc. Ht. Change (m)	1.0			
Meas. Ht. Change (m)	.8			

Export calculated from change in salt, assuming all loss was from the surface layer.

20 C and sensible heat loss was considered to be 20% of the evaporative loss (McLellan 1968). In spite of the errors associated with making these assumptions, the calculated radiative input agreed surprisingly well with the measured heat gain, giving further support to our assumptions of lagoon dynamics (Table 5.2).

Diffusion in the Hypolimnion

The epilimnion was well mixed throughout the study, owing presumably to wind stress. Salinities and temperatures were constant within the upper five meters, changing uniformly with rainfall, salt intrusion from the lower layer, and evaporation (Figure 5.3). The hypolimnion, however, was isolated from this turbulence by a sharp halocline. The salinity of the bottom waters changed little throughout the study, although it was clear that water was being entrained slowly into the surface layer. Vertical diffusion within the hypolimnion was likely to be slow, governed either by weak eddies or molecular processes.

Salt

The upward movement of salt was modelled initially by use of an analog of Fick's first law,

$$J = K_z \times \frac{dS}{dz} \quad ,$$

where J is the flux of salt across an isohaline layer, K_z is the vertical eddy diffusivity coefficient, and dS/dz is the vertical

TABLE 5.2. HEAT BUDGET FOR BIG LAGOON 18 JUNE THROUGH 13 AUGUST 1985

Heat Balance

Initial Heat Content (cal)	
Lagoon	3.03×10^{14}
Stream (13.2 C)	1.81×10^{13}
Final Heat Content	
Lagoon	2.59×10^{14}
Exported Water	7.55×10^{13}
Heat Gain	1.34×10^{13}

Radiation Balance

Source	($cal/cm^2/d$)
Sun and Sky	450
Backradiation	-254
Evaporation	-157
Sensible	- 31
Mean Daily Input	8
Rad Ht (cal/day)	2.42×10^{11}
Total Input (cal)	1.36×10^{13}

salinity gradient. We again chose to use the June 18 and August 13 samplings because any anomalies owing to depth resolution were minimized by the greater changes in salinity that occurred over the longer period. Nevertheless, changes in salinity still were small in much of the hypoliminion, particularly near the bottom (Figure 5.3).

The apparent diffusivity coefficients were variable with depth (Table 5.3). Although the salinity differences near the bottom were not great enough to compute a diffusivity coefficient, K_z did remain small within the 0.6 to 1.4 m depth range, being about an order of magnitude above molecular diffusion.

Slow diffusion within the hypolimnion was further comfirmed by use of non-steady state calculations for the late spring and early summer samplings. Because Fick's first law required making some assumptions that were not necessarily true, i.e. - that the system was in steady state and the source of salt was essentially an infinite reservoir, we chose to check our findings by applying the analog of Fick's second law for those portions of the salinity profile where the change in slope with depth was measureable, but still below the sharp halocline. This application, nevertheless, was limited even more by the small differences in salinity. Fick's second law, which describes the non-steady state for diffusion and is used where a gradient changes with distance, can be stated as

$$\frac{dS}{dt} = K_z \times \frac{d^2S}{dz^2} \quad ,$$

where dS/dt is the time rate of change in salinity at a fixed depth, K_z is the vertical eddy diffusivity coefficient, and d^2S/dz^2 is the depth

TABLE 5.3. COMPUTATION OF K_z FOR SALT BY FICK'S FIRST LAW (18 JUNE THROUGH 13 AUGUST 1985)

Height (cm)	Area (cm^2) ($\times 10^{-9}$)	Vol (cm^3) ($\times 10^{-10}$)	6/18 (o/oo)	8/13 (o/oo)	Salt Change (g) ($\times 10^{-7}$)	dS/dz (g/cm^4) ($\times 10^5$)	k(z) (cm^2/s) ($\times 10^4$)
200	16.3		24.65				
180	16.1	16.2	25.56	23.97	51.5	4.540	3.4
160	14.8	30.9	26.12	24.83	39.8	3.580	2.6
140	13.5	28.3	26.49	25.79	19.9	3.302	1.3
120	12.0	25.5	26.91	26.86	1.30	3.717	0.4
100	10.4	22.4	27.13	26.98	3.34	0.875	1.5
80	8.86	19.2	27.26	27.13	2.62	0.703	1.1
60	6.89	15.7	27.26	27.22	6.77	0.228	0.9
40	4.91	11.8	- -	27.27	0		
20	2.94	7.85	- -	27.29	0		
0		2.94					

Salinity gradients were computed as averages of those from both dates over 0.2 m intervals, except for the uppermost value, where the gradient was taken from a single 0.2 m interval.

dependent change in dS/dz. For the height range of 1.4 to 2.0 m, this resulted in a K_z of 6.6 x 10^{-4} cm^2/sec, a little higher than, but close to the estimates for the upper halocline by use of Fick's first law.

An increasing diffusivity near the steep portion of the halocline seems, on inspection, anomalous, as vertical eddy diffusivities generally decrease with increasing water column stability (Broecker and Peng 1982, Lerman 1979). However, for most of the study, the temperature also increased with depth in this region, in part destabilizing the water column and allowing for double diffusion (Turner 1965, 1967, 1968). The relative contribution of heat and salt to the density of the water at any depth is represented by the equation:

$$\frac{a \times dS}{b \times dT} .$$

where a is the mass-weighted coefficient of thermal conductivity, b is the mass-weighted coefficient of saline contraction, and dS and dT are incremental changes in salinity and temperature over a specified depth interval. When this ratio lies between 2 and 15, salt-fingering is possible (Turner 1965, Neshyba et al. 1971). Below 2, the column becomes unstable, and the turbulence will disperse both salt and heat; above 15, molecular processes no longer predominate. This phenomenon arises because of the difference, about a factor of 100, between the diffusion coefficients for salt and heat, which allows thermally driven motion within the gradient to lift the salt at the expense of the downward flow of heat. During much of our investigation, this ratio for the upper hypolimnion was below 15, reaching values down to 3 by August,

indicating that double diffusion was in large part responsible for the upward transport of salt to the halocline, and corroborating the higher diffusivities for this portion of the profile.

Heat

The flow of heat in the hypolimnion also indicates weak eddy diffusivity. Temperature profiles over the two months changed radically, but, nevertheless, heating of the water at the base of the halocline was evident. This implied that the upper hypolimnion was a strongly absorptive layer. In other systems, specifically, a meromictic lake in New York (Fry 1986), the Pettaquamscutt estuary (Jonathan Garber, Ken Hinga - pers. comm.), and a hypersaline lake in the Sinai desert (Cohen et al. 1977 a,b,c), sharp pycnoclines have been associated with dense populations of bacteria, photosynthetic phytoplankton, and zooplankton that all but obscure the transmission of light. Crandell and Horacek (1973) found that zooplankton populations in Big Lagoon concentrated in this zone, providing additional evidence for a particulate layer at the base of the halocline. Our data for trace gases, oxygen, and pH are further support for enhanced biological activity near the halocline (Figure 5.3).

We first assumed that the amount of light penetrating beyond this layer was insignificant and that any transfer of heat below it was strictly diffusive, then applied the heat equation (another analog of Fick's second law) to the observed changes in the temperature profiles, using a detailed temperature profile from August 13 to calclulate d^2T/dz^2 (Figure 5.4). As expected, our assumption led to a slight overestimate of the apparent diffusivity coefficient. The coefficient

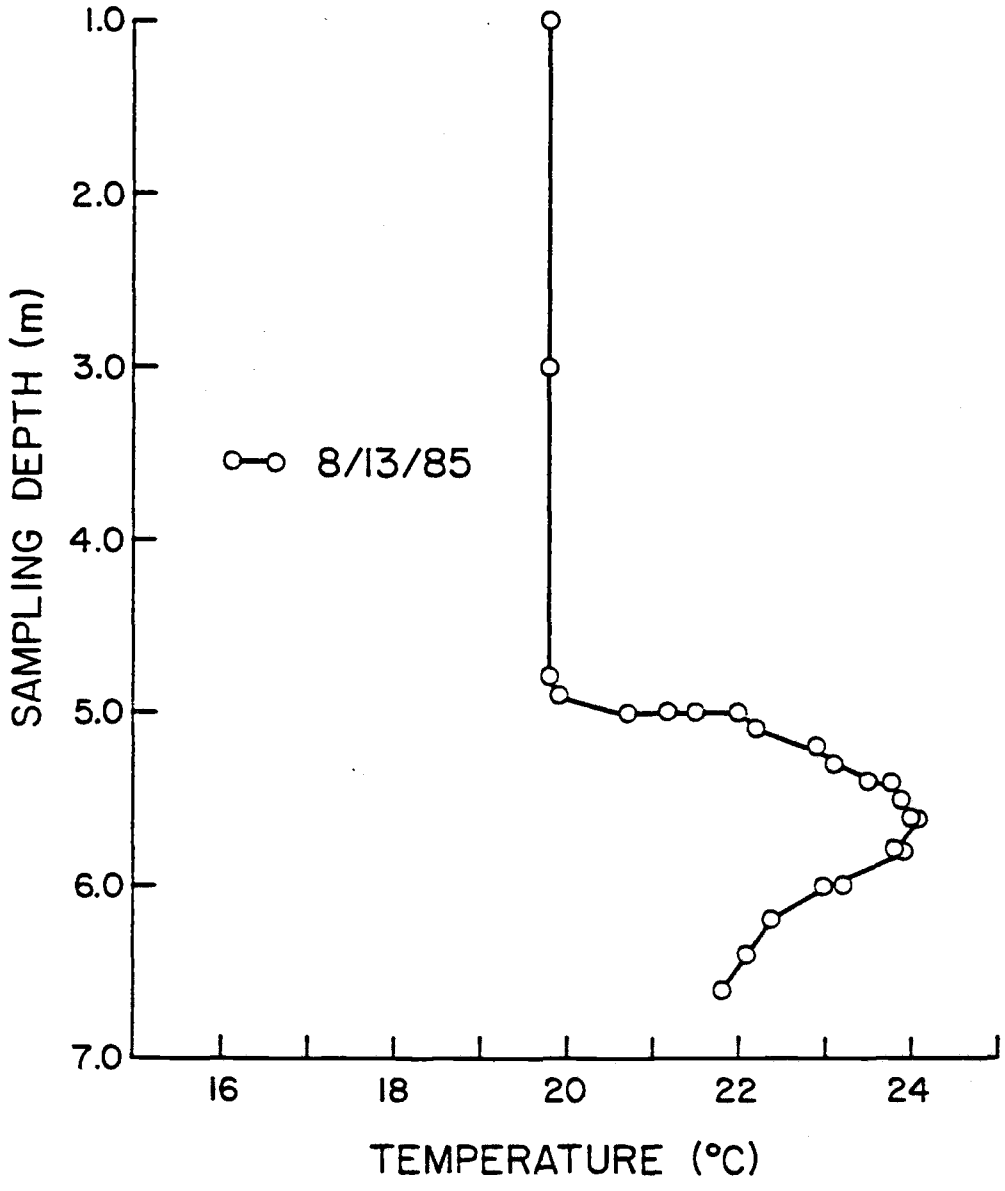

Figure 5.4. Detailed temperature profile taken on 13 August 1985.

of diffusivity was calculated at 2.5×10^{-3}, and, even when corrected for molecular heat flow (1.2×10^{-3}), was a little high for the lower hypolimnion. If we considered the lagoon sediments a reflective boundary and evaluated the flux of heat to the bottom of the lagoon (Fick's first law), we arrived at a K_z of 2.8×10^{-3}, a result in close agreement with that from the heat equation. These values are close to the coefficient for molecular diffusion of heat, but because diffusivities are not truly additive, we cannot derive a coefficient for salt from these results. However, they do verify our assumption of little light penetrating beyond the lower halocline, and they lend general support our calculations based on salt distributions, showing that the rates of diffusion below the halocline are slightly greater than would be expected for molecular diffusion.

Transport across the Halocline

Although double diffusion may have played a part in transporting salts and gases across the halocline, the primary mechanism operating for this process was vertical shear. This was evidenced by the reduction in height of the hypolimnion and by the sharpening of the halocline during the study. Were diffusion predominant, the halocline would have spread out, not narrowed (Turner 1968). The total amount of salt transported across the halocline can be accounted for by vertical shear, with most salt passing between the June 18 and July 15 samplings, when the lagoon height dropped significantly.

Cycling and Transport

On examination of the dissolved oxygen, pH, and nutrient profiles, it became apparent that biological activity was concentrated either in the sediments or near the base of the halocline in the upper hypolimnion (Figure 5.3, Table 5.4). In general, the surface layer was an oligotrophic conduit between the halocline and the atmosphere, and the lower hypolimnion served as a conduit between the halocline and the sediments. There was some biological activity in the lower hypolimnion, particularly with respect to the trace gases, but this was not reflected in other constituents. As inorganic nitrogen throughout the lagoon was low (Figure 5.3; Appendix, Table A.3), nitrogen cycling must have been particularly important within the upper hypolimnion to sustain the observed biological activity.

Where we needed to calculate fluxes, we assumed that internal consumption of biologically mediated compounds in the epilimnion and within the lower hypolimnion was small relative to the activity near the halocline and in the sediments. For the nutrients we used a diffusion model to calculate the fluxes into or out of these vertically distinct regions. However, a mass-balance approach was used to determine the oxygen, methane, and nitrous oxide fluxes, as these compounds showed consistent trends throughout the study. Direct chemical oxidation was invoked for hydroxylamine and microbial oxidation rates predominated in the CO flux calculations. For methane and nitrous oxide, gas effusion at the air-water interface was computed and compared with apparent fluxes across the halocline, so that we could estimate contributions from sediments adjacent to the epilimnion.

TABLE 5.4. VERTICAL DISTRIBUTION OF CHEMICAL AND BIOCHEMICAL PROCESSES IN BIG LAGOON

Zone	Processes	Evidence
Near Surface (Epilimnion)	Photochemical	NH_2OH & CO Peaks, CO oxidation rates
Surface Mixed Layer (Epilimnion)	Oligotrophic Conduit between atmosphere and deeper waters	Low nitrogen, well mixed, oxidative waters; gradients of O_2, PO_4^{-3}, N_2O
*Upper Halocline (Hypolimnion)	Photosynthesis Gas Production	O_2 & pH peaks; N_2O, CH_4, CO peaks
*Lower Halocline (Hypolimnion)	Decomposition, Remineralization	NO_2^-, NH_2OH peaks; O_2, pH, and N_2O (?) valleys
Bottom Layer (Hypolimnion)	Semi-passive conduit; Oxidation of reduced compounds from seds.; nitrification (?)	PO_4^{-3} distribution; Si, O_2, & N_2O gradients; N_2O peaks, NO_2^- and NH_2OH valleys; low O_2
Sediment Interface	Nitrif. in Spring; Denitrification in Summer; methanogenesis	N_2O, NO_2^-, and NH_2OH distributions; CH_4, CO dists.

* Distinctions of upper and lower halocline are only indicative. Whether biological activity below the halocline was stratified as indicated here is not certain; for computational purposes these were treated as a single layer.

Dissolved Oxygen and Net Productivity

Dissolved oxygen profiles show that O_2 was consumed in the sediments throughout the study, and that this oxygen was generated in the upper hypolimnion (Figure 5.3). The lower hypolimnion never became anoxic during our study, although other investigators have noted this in other years (Crandell and Horacek 1973). The concentration of O_2 increased near the lower halocline between the May 30 and the June 18 samplings, but remained reasonably constant (within 10%) and highly supersaturated from June 18 on. Net production of oxygen in the hypolimnion between samplings was computed from the integrated changes in mass within the zone of production and the diffusive losses to the epilimnion and the sediments (Table 5.5). Because of the apparently high microbial activity in this same zone, the gross rates of production must have been considerably higher.

Carbon fixation was estimated from the net production rates of oxygen, under the assumption that carbon fixation was proportional to net oxygen evolution. In these calculations, we used a photosynthetic quotient of 1.3, consistent with Redfield-Ketchum-Richards ratios, for lack of a more suitable, specific number for these populations. We also assumed that phytoplankton growth was confined to a depth range of 0.4 m, as evidenced by the dissolved oxygen and pH profiles, and that photosynthesis continued for an average of 12 hours per day. Our calculated production rates of 7 to 14 $mgC/m^3/h$ were about the same as those obtained by Brady (1977), who reported a range of productivities of 8 to 20 $mgC/m^3/h$ for Big Lagoon populations during the same time of

TABLE 5.5. OXYGEN FLUXES AND ESTIMATED NET CARBON FIXATION

Dates	$d(O_2)$	$J(O_2)$(sed)	$J(O_2)$(hal)	C_{fix}	
		($ml/m^2/d$)		(mg $C/m^2/d$)	(mg $C/m^3/h$)
5/30 - 6/18	64	11	21	40	8.3
6/18 - 7/25	9.9	8.8	59	32	6.7
7/25 - 8/13	18	5.9	135	65	14

$d(O_2)$ is the change in O_2 residing in the upper hypolimnion, and $J(O_2)$ represents the outward fluxes of O_2 from this zone. Hourly carbon fixation is based on a 12 hour day and a depth range of 0.4 m for plant activity.

year. However, Brady's work involved the measurement of C-14 uptake by Big Lagoon populations under controlled light and temperature, thus is an estimate of gross, rather than net, productivity. Nevertheless, considering the different approaches, we feel the data are in good agreement.

These findings indicate that, although a surplus of oxygen is ever-present within the upper hypolimnion, the supersaturation is not caused by extremely high net photosynthetic rates, but rather is the result of a lower production rate and subsequent, slow, outward transport. Our calculated net rates of carbon fixation are higher than those for the open ocean, but still represent a low productivity (Riley and Chester 1971). This comparison is not totally appropriate, however, as microbial populations in the Big Lagoon halocline were probably much more dense and active than those in the open ocean, and nitrogen cycling must have played an important part in sustaining phytoplanktonic and bacterial growth within the halocline. A daily consumption of about 1 uM would be needed to account for the oxygen evolved. Thus, gross production by phytoplankton probably was much greater in Big Lagoon than in the open ocean, but, nevertheless, limited by an overall nitrogen deficiency (Figure 5.3).

Nutrients

Ammonium and nitrite were the predominant forms of nutritive nitrogen in Big Lagoon, although both were low throughout most of the study. Nitrate was virtually absent, except near the sediments during the May sampling (Appendix, Table A.3). Although the apparent sedimentary fluxes of ammonium were higher than those of nitrite, both

were quite low throughout the study (Figure 5.3, Table 5.6). Significant ammonium concentrations near the halocline were found only on June 18, and a small nitrite peak was located just below the oxygen peak, but otherwise there was little evidence of inorganic nitrogen transport from the upper hypolimnion.

Phosphate concentrations were anomalously high in the hypolimnion, implying considerable diffusion from the sediments (Figure 5.5). High inorganic phosphorus concentrations have been reported for analagous bodies of water, notably the Pettaquamscutt River (Gaines and Pilsen 1972) and the Baltic Sea (Holm 1978, Shaffer and Ronner 1984), and are associated with anoxic conditions and low pH. Grasshoff (1975) noted that PO_4 concentrations in anoxic Baltic Sea waters were elevated dramatically (up to 10 uM) where the pH dropped to 7.1, but that no elevation was noted for the Black Sea, where the pH does not drop below 7.5, and the Cariaco Trench, where the bottom was probably too deep to accumulate much PO_4. During our study, the bottom waters of Big Lagoon never were anoxic and the pH correlating with high PO_4 (greater than 2.5 uM) ranged from 7.2 to 7.9. However, Big Lagoon is vertically compact relative to these other systems, hence dissolved substances diffusing from the sediments would be more likely to have an effect on the 2 m thick bottom layer. An elevated pH and the presence of dissolved oxygen do indicate that the PO_4 is not remineralizing in the bottom waters. Most likely, it is re-precipitating through the redox chemistry of iron, forming ferric oxide gel-phosphate complexes (Grasshoff 1975, Mortimer 1942). Phosphate accumulated in the epilimnion of Big Lagoon from June 18 to August 13, representing an average flux of 5 u-mol/m^2/d across the halocline. The average flux calculated from the PO_4 gradient in the

TABLE 5.6. NUTRIENT FLUXES FROM SEDIMENTS

Date	NH_4^+	NO_2^-	PO_4^{-3}	$Si(OH)_4$
		(u-moles/m^2/d)		
5/30/85	--	0.5	11	66
6/18/85	4.8	1.3	14	103
7/15/85	20	4.0	12	127
7/25/85	0.8	0.5	9.5	101
8/13/85	4.2	0.8	10	130

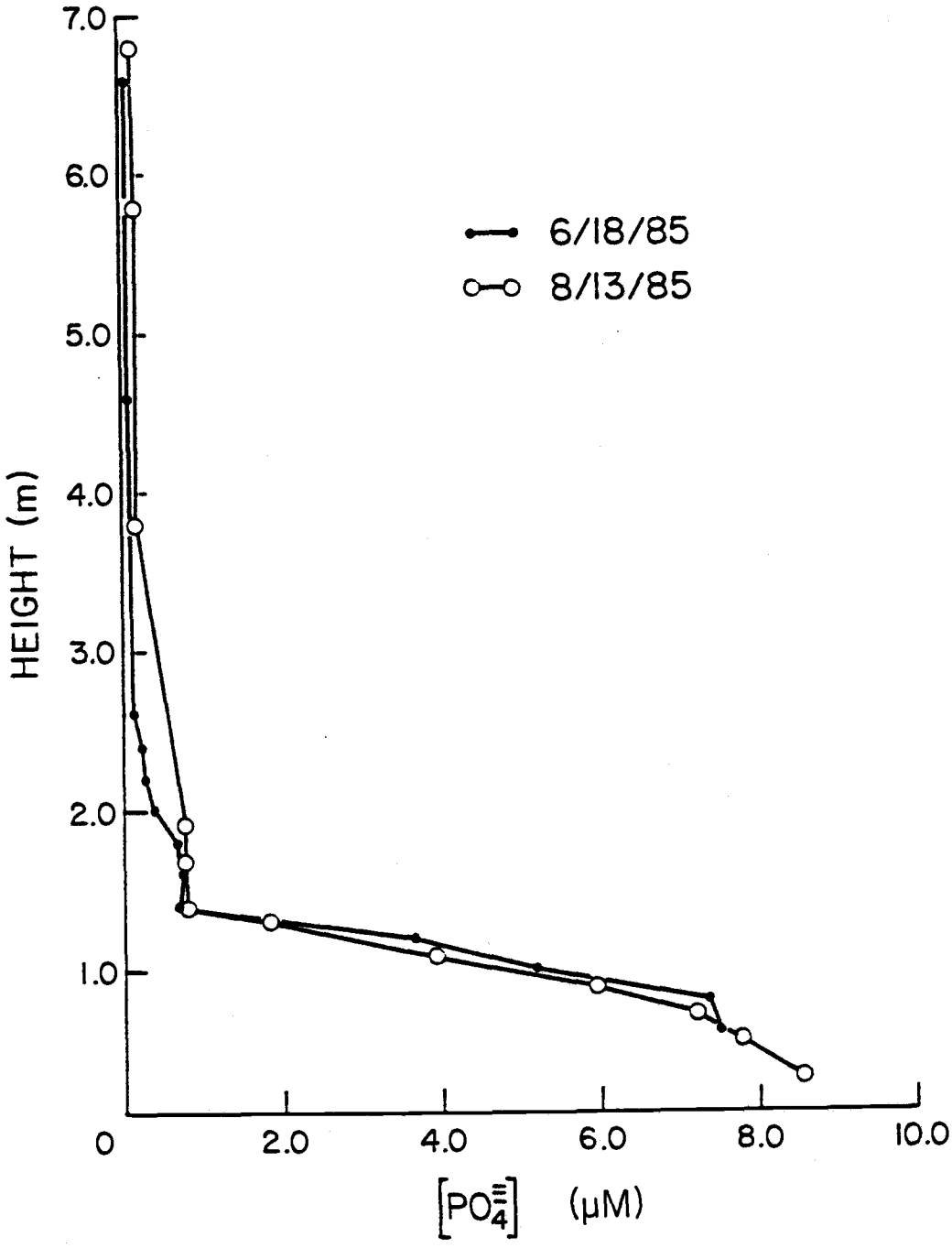

Figure 5.5. Phosphate concentration vs height for 18 June and 13 August 1985.

lower hypolimnion, which was constant during this time (Figure 5.5), was 11 u-mol/m^2/d, about twice that of the surface accumulation. This indicates that either biological or chemical re-precipitation of phosphorus was occurring in the hypolimnion, perhaps near the halocline.

Silicate distributions did not change much, although some loss in the hypolimnion over the summer is apparent (Figure 5.6). Fluxes of silicate from the sediments also were constant and low relative to the ambient concentrations (Table 5.6; Appendix, Table A.3); a continued flux of 100 u-mol Si/m^2/d would result in an increase of about 1 uM in the epilimnion over the entire study, a concentration that was much smaller than the variations in the epilimnion.

Trace Gases and Hydroxylamine

Methane. Methane concentrations in the hypolimnion increased over an order of magnitude from May to August, with the most significant gains apparent at the end of the study (Figure 5.7; Appendix, Table A.3). Production of methane in the hypolimnetic sediments was an expected result, but an even greater net production within and just below the halocline was not. Methanogenesis is associated with anaerobic processes, either the splitting of acetate by fermentative bacteria or the combining of H_2 and CO_2 by obligate anaerobes (Fenchel and Blackburn 1979, Kuivila and Murray 1984). Consequently, the occurrence of a significant peak of methane in what are clearly O_2 saturated and supersaturated waters is somewhat anomalous. In addition, even the lowest observed concentrations are extremely high relative the air-saturation value of about 2 nM (Wiesenburg and Guinasso 1979).

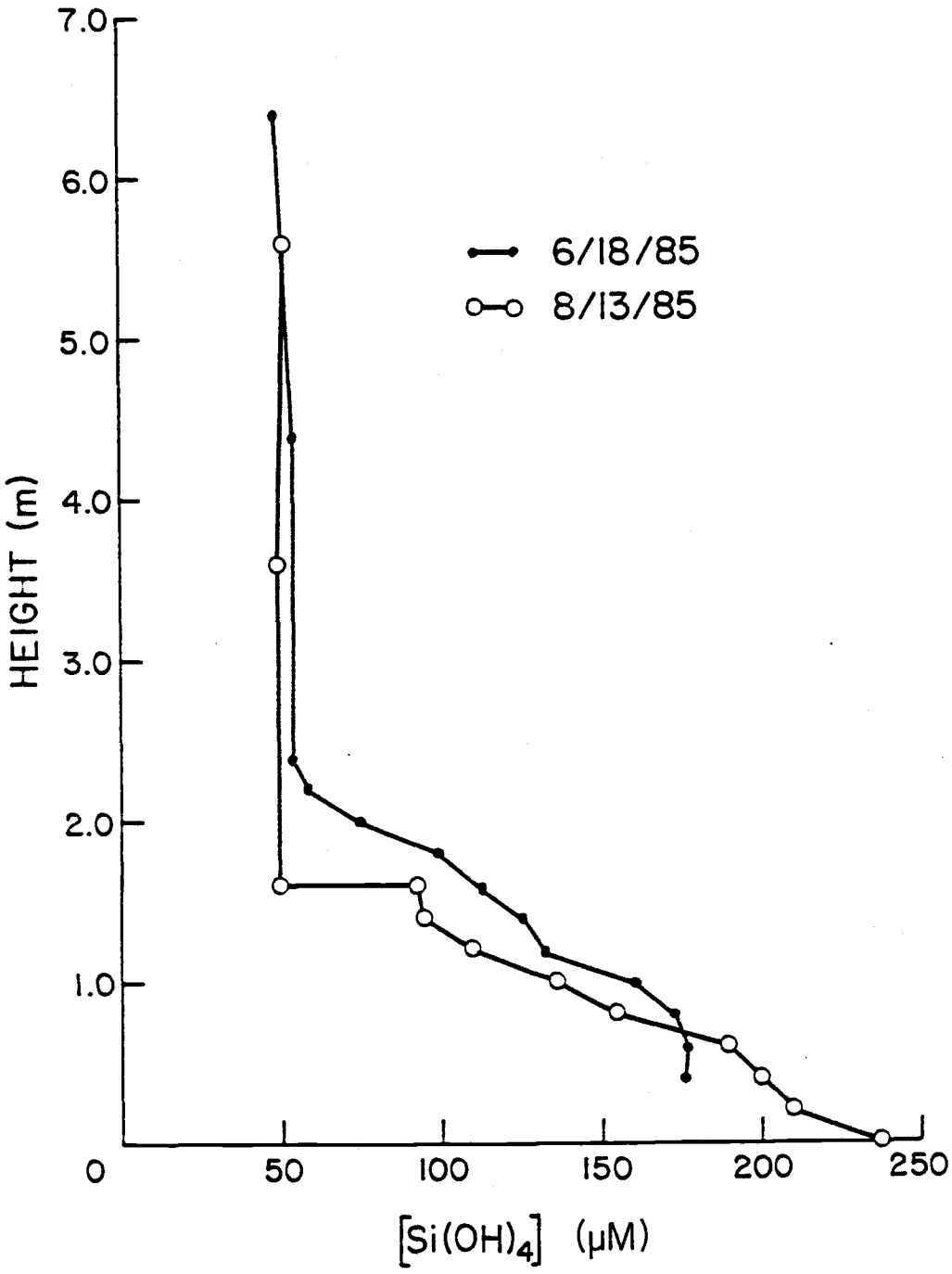

Figure 5.6. Silicate concentration vs height for 18 June and 13 August 1985.

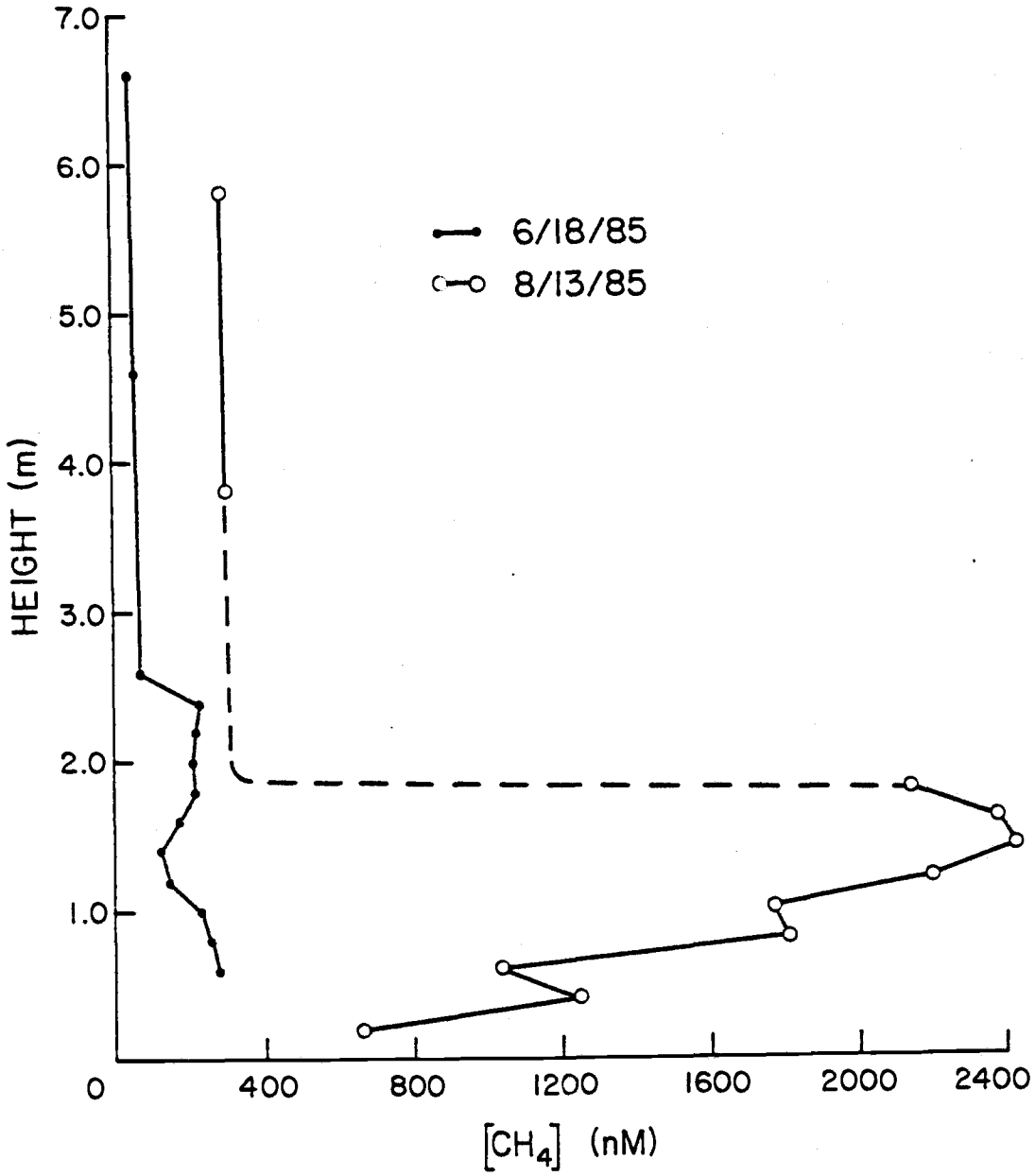

Figure 5.7. Methane concentration vs height for 18 June and 13 August 1985. Dashed line indicates probable distribution based on salinity profile.

Methane production within and just below the halocline could be supported by the formation of anoxic microenvironments associated with suspended detrital particles as suggested by Burke et al (1983), but methane also could be produced by enteric microbes inhabiting the guts of zooplankton (Oremland 1979, Traganza et al. 1979). Physical processes could enhance methane concentrations within the halocline, but do not provide explanations as probable as in situ production. For example, horizontal transport from adjacent, anoxic sediments would be supported by lower pH, higher microbial oxidation rates, and deficits of O_2 and N_2O, something we did not observe. Further, the concentrations of CH_4 were higher in the halocline than what we found for waters near the sediments, implying that the source sediments would have to be far richer than those above which we sampled. Ebullition from the sediments, as observed by Strayer and Tiedje (1978), followed by partial breakage and re-solution of bubbles owing to particulate matter in the halocline may be possible; however, such disruptive processes would tend to expand the halocline with time, not contract it, as was observed.

Extreme supersaturations of methane have been reported for lakes and other waters (e.g. - Kuivila and Murray 1984, Harrits and Hanson 1980, Strayer and Tiedje 1978). The recurrence of this phenomenon indicates that production rates are far in excess of the ability of these systems to remove the methane either microbially or via atmospheric exchange. We did find that microbial methane oxidation rates were relatively low in Big Lagoon, a result that concurs with our findings for Yaquina Bay (Chapter 2), as well as those reported for other aquatic systems (Jones 1984, Harrits and Hanson 1980, Rudd and Hamilton 1978). Calculated microbial turnover times for methane in

surface waters were on the order of tens to hundreds of years, whereas turnover rates within the halocline were on the order of years (Table 5.7). Only in the near-bottom waters did methane turnover rates come close to or exceed transport rates; by August, microbial methane consumption was considerable, reflecting the higher concentrations to which the populations had acclimated (Table 5.7, Figure 5.7).

Methane production was estimated from a numerical model that included considerations for changes in total mass, atmospheric loss, and microbial oxidation (Appendix). For each survey, methane concentrations were integrated over the height of the lagoon to estimate the total mass. Atmospheric losses were computed from a laminar layer model with a film thickness of 200 um, corresponding to a mean daily windspeed of 3 m/sec (Peng and Broecker 1980). As explained in Chapter 2, this choice likely leads to an underestimate of atmospheric transport, so our approach here has been conservative. Microbial oxidation was treated as first-order decay. Because microbial oxidation was not measured at all depths for every survey, values were interpolated to obtain the missing data points. Although this introduced some bias, the trends in the rate constants were reasonably consistent over space and time, thus minimizing the error.

The results of the model show that 75% of the methane produced escaped to the atmosphere, with increases in _in situ_ concentration and biological oxidation still accounting for the remaining 25% (Table 5.8). One interesting feature was that transport of methane across the halocline accounted for just over 10% of the methane reaching the surface layer. Rudd and Hamilton (1978) also noted an excess of methane

TABLE 5.7. PARTIAL RESIDENCE TIMES* FOR CH_4, CO, AND NH_4^+ BASED ON MICROBIAL OXIDATION RATES

Date	Depth (m)	T(CH_4) (d x 10^{-3})	T(CO) (h)	T(NH_4^+) (h)
5/30/85	2.0	7.1	9.9	--
	5.0	.68	23	--
	6.0	1.1	5.7	--
6/18/85	0	12	8.4	64
	3.0	--	44	385
	5.2	50	16	121
	5.8	.51	9.2	--
	6.8	.023	3.8	30
7/15/85	0	1.5	2.7	257
	1.0	17	21	257
	3.0	50	29	293
	5.2	2.1	23	245
	5.6	2.6	18	155
	5.8	.30	3.4	28
	6.0	.096	2.2	18
8/13/85	0	6.2	0.6	--
	3.0	8.3	6.8	--
	5.2	.70	2.9	24
	5.6	.24	2.1	19
	5.8	.033	2.3	21
	6.2	.011	1.2	9
	6.6	.006	0.9	7

*Residence time calculated as the inverse of the first-order rate constant for microbial oxidation.

TABLE 5.8. METHANE BUDGET FOR BIG LAGOON

	6/18	7/15	7/25	8/13
Reservoirs				
Total CH_4 (surface)	672	1520	[2082]	3380
Total CH_4 (bottom)	644	1126	1174	3463
Fluxes				
Across Halocline	--	275	304	2377
Biological Oxidation	--	330	303	1152
Atmospheric Flux	--	5831	3889	11736
Gross Methane Production	--	7491	4802	16475
(m-moles/m^2/d)	--	.09	.15	.29
Total Methane Production	28768			
(m-moles/m^2/d)	.17			

Units are moles unless otherwise indicated; brackets indicate interpolated value. Oxidative and atmospheric losses were computed as averages between sampling dates. Areal rates are for the lagoon surface, which decreased by about 7% during the study.

in the epilimnion of a eutrophic lake, and attributed it to methane production in the epilimnetic sediments. Methanogenesis in the epilimnetic sediments of Big Lagoon could be contributing to the observed excess. Introduction of methane from epilimnetic sediments would be enhanced by horizontal advection, which, by maintaining a sharp gradient at the sediment-water interface, would increase diffusion and restrict oxidation by sedimetary methylotrophs (Rudd and Hamilton 1978).

Even with the relatively high evasion rates, methane production in Big Lagoon was low compared to other, more eutrophic systems. Our results show that methane production, averaged over the entire lagoon surface, increased from 0.1 to 0.3 m-mol/m^2/d from June to mid-August, with the rate rising geometrically by the end of the study. As our nutrient and oxygen data indicated that Big Lagoon was oligotrophic, we would expect that methanogenesis would be lower than that found for more productive bodies of water. Indeed, Strayer and Tieje (1978) found methane production rates of 60 m-mol/m^2/d for a small hypereutrophic lake, Rudd and Hamilton (1978) noted a range of 0.02 to 32 m-mol/m^2/d for a eutrophic lake, and Kuivila and Murray (1984) reported a range of 0.34 to 1.1 m-mol/m^2/d for sediments of an oxic lake. Fallon et al. (1980) and Harrits and Hanson (1980) also noted that methane oxidation rates correlated with methane concentration, and found that microbial oxidation accounted for much of the methane loss in the lakes that they studied. Likely because of the oligotrophic character of Big Lagoon, we found that methane oxidation was low in comparison to accumulation and atmospheric loss. However, we did find that methane oxidation rates correlated spatially and temporally with methane concentration, being highest in the hypolimnion near the end of the summer (Table 5.7).

Carbon Monoxide. Although the concentration of CO below the halocline increased an average of about 5 nM/day, its distributions were far more erratic (Figure 5.8), most likely owing to high rates of biological turnover (Table 5.7). These distributions thus represented a dynamic balance between rapid formation and destruction, any buildup of CO being the result of processes occurring during the day of sampling. For example, the average increase of 5 nM/day was three orders of magnitude less than the average measured rates of microbial oxidation, 4800 nM/day. This means that production and consumption of CO were virtually in balance, cycling an average of 5.5 m-mol/m^2/d for the entire study, and about 8 m-mol/m^2/d at the end. Rapid cycling of CO also was reported by Conrad et al. (1983), who determined that the production of CO was related to light, whereas consumption predominated in the dark.

Although we found little evidence of photoproduction of CO from our concentration measurements (Appendix, Table A.3), the short turnover times for microbial oxidation in the near surface are indicative of populations that have acclimated to a higher input of CO (Table 5.7). CO is produced by the photolysis of carbonyl compounds, but by short wavelength light that attenuates rapidly near the surface (Redden 1983, Conrad et al. 1982); thus one would expect high production rates, and perhaps high concentrations at the very near surface. However, the highest concentrations of CO in Big Lagoon were found in the hypolimnion, below the light-absorbing particle layer, indicating that both production and consumption of CO in the hypolimnion were microbially controlled.

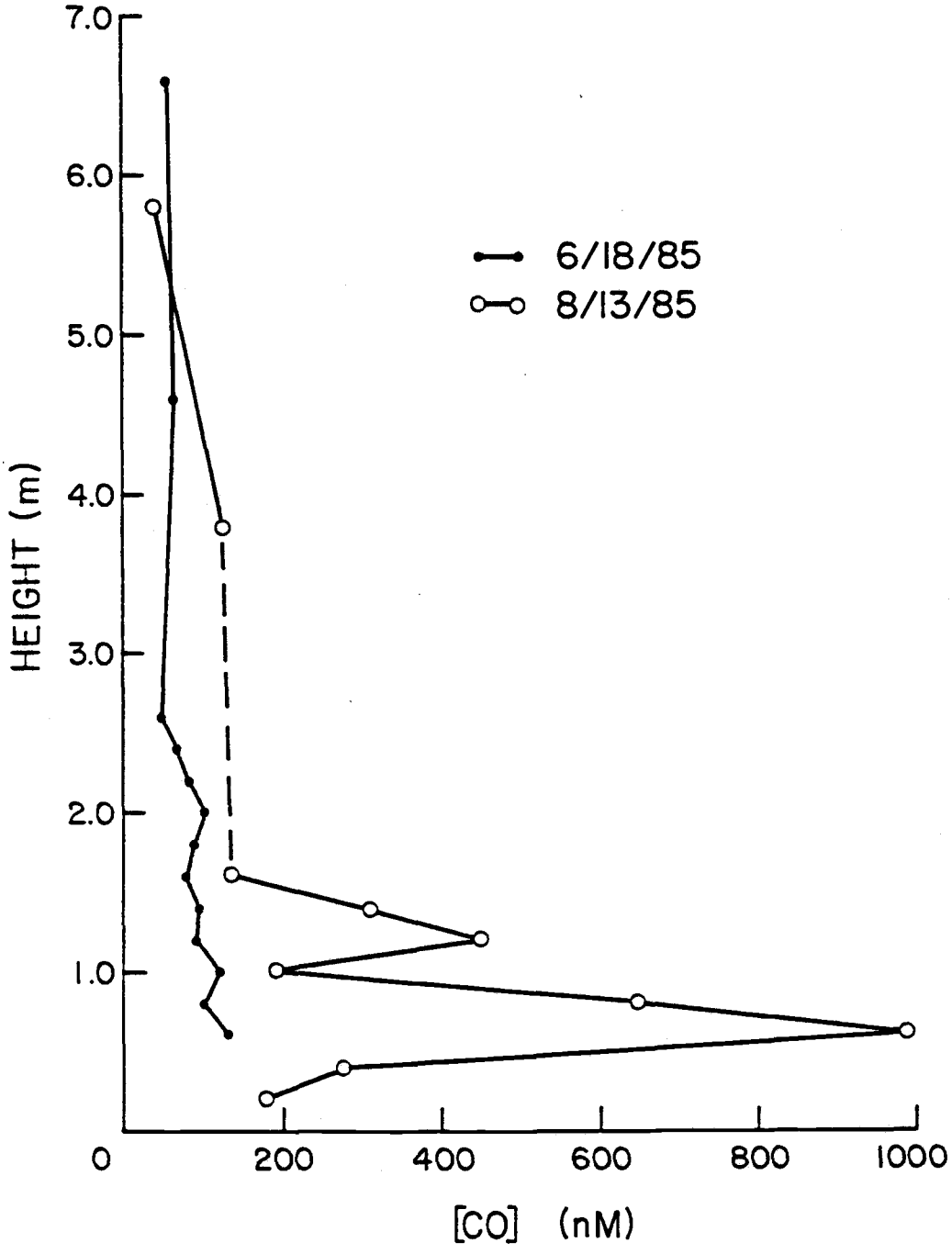

Figure 5.8. Carbon monoxide concentration vs height for 18 June and 13 August 1985. Dashed line indicates probable distribution based on salinity profile.

Nitrous Oxide and Hydroxylamine (Distributions). The relationship between nitrous oxide and hydroxylamine is not clear, although there is some evidence for a positive correlation. During the early part of the study, N_2O and NH_2OH both diffused from sediments of the hypolimnion, producing strong gradients (Figure 5.9). Later, as it became clear that nitrous oxide was being consumed in these sediments, presumably through denitrification, hydroxylamine was absent from the near-bottom waters. A hydroxylamine peak appeared in the upper hypolimnion during the first two samplings, but later in the study, as the sub-halocline N_2O peak was reduced to a mere positive anomaly in an otherwise negative gradient, hydroxylamine was barely detectable.

This correlation would be expected were nitrification the source of N_2O, although, alone, it does not imply cause and effect. For example, the June 18 profiles show a number of anomalous features that reflect a complex cycling scheme (Figure 5.9). At this time, the sediments below the hypolimnion had shifted from a mode of net N_2O production to one of net consumption. Whether the double peak in the N_2O profile was primarily the result of *in situ* production and consumption, or whether it was brought about by differential diffusion in the water column, with the sediments being the primary location of biological activity, cannot be discerned from these data. At a height of 2.0 m, a hydroxylamine peak was associated with a peak in nitrous oxide, but at 1.4 meters, hydroxylamine was absent where there was a peak of N_2O. Hydroxylamine still was being produced near the sediments during a time when they clearly were consuming N_2O. If NH_2OH coming from the sediments did result from nitrification, then nitrification and denitrification must have been occurring together at this time. The simultaneous occurrence

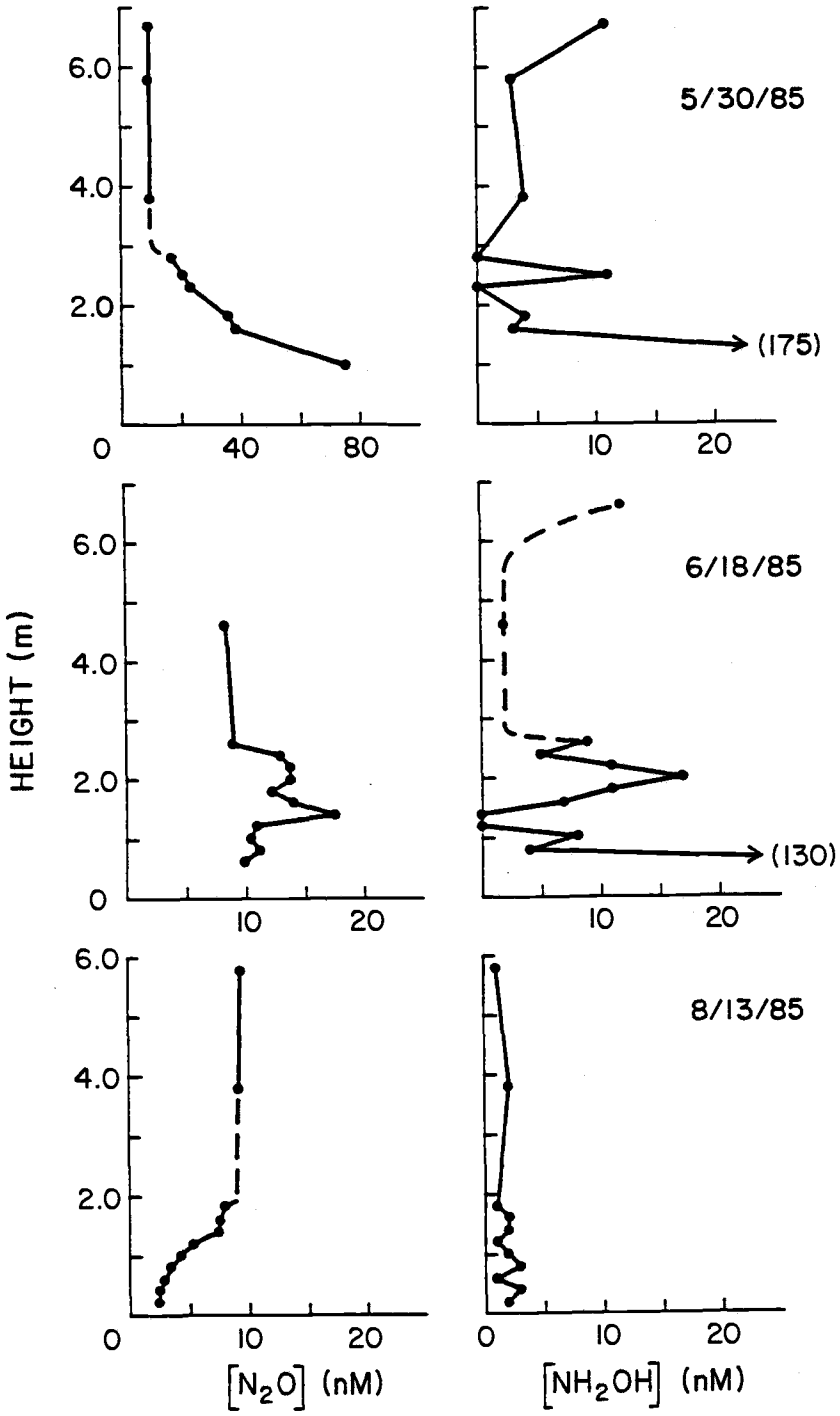

Figure 5.9. Nitrous oxide and hydroxylamine profiles on 30 May, 18 June and 13 August 1985. Dashed lines indicate probable distribution based on salinity profiles.

of nitrification and denitrification in sediments has been suggested by a number of investigators (Grundimanis and Murray 1977; Knowles 1978; Knowles et al. 1981), and must be taken into consideration in evaluating sedimentary N_2O fluxes (Seitzinger et al. 1983). Production of N_2O by nitrification and its concomitant consumption through denitrification also has been suggested as a mechanism for the removal of fixed nitrogen from oxygen minima of the open ocean (Codispoti and Christensen 1985).

However, it also is possible that NH_2OH was produced primarily by a dissimilatory reductive process leading to ammonium. Tanaka (1953) detected hydroxylamine in lake waters and attributed its presence to nitrate reduction. His reasoning, however, was deductive and not sufficient to rule out nitrification. Yordy and Ruoff (1981) discussed the possibility of NH_2OH production through nitrate reduction by facultative anaerobes, and Jorgensen and Sorensen (1985) showed that dissimilatory nitrate reduction accounted for much of the nitrate reduced in coastal sediments. On the other hand, Chen et al. (1972) concluded that dissimilatory reduction to ammonium was not significant in lake sediments. It is likely that this process is occurring in Big Lagoon, but where, and to what extent it produces hydroxylamine is, at this time, uncertain.

Also noteworthy were the high concentrations of hydroxylamine near the lagoon surface during the spring samplings (Figure 5.9; Appendix, Table A.3). Although NH_2OH is subject to photolysis in aqueous solution (Behar et al. 1972, Chapter 4), these data indicate that it also was produced either directly, by some photochemical reaction with dissolved organic matter, or indirectly, through some microbial response to light.

Nitrous Oxide and Hydroxylamine (Fluxes). N_2O was exported to the atmosphere at all times, apparently in quantities that bore little or no relation to activity in the hypolimnion (Table 5.9). N_2O saturation in the surface waters ranged from 104 to 118%, a range that is essentially identical to that reported by Cohen and Gordon (1979) for the world oceans. Export to the atmosphere continued throughout the late spring and summer as N_2O was being consumed in the hypolimnion (Table 5.9). Thus, there must have been a source of N_2O elsewhere in the lagoon. Nitrous oxide production in the epilimnion *via* aquatic nitrification as discussed by Wofsy *et al.* (1981) is unlikely, as ammonium concentrations were low at all times, and the entire epilimnion remained essentially oligotrophic. Import from streamflow also is unlikely (Lemon and Lemon 1981). However, nitrous oxide production in the epilimnetic sediments is not only possible, but virtually certain. Seitzinger *et al.* (1983, 1984) found sedimentary production rates in Narraganset Bay of 0.5 to 44 u-mol/m^2/d, DeAngelis (1980) noted production rates of about 3 u-mol/m^2/d for deep sea sediments, and Seitzinger and Nixon (1985) reported sedimentary production rates of 13 to 1200 u-mol/m^2/d in nutrient-amended MERL tanks. Simultaneous hypolimnetic consumption of N_2O during apparent atmospheric evasion also was noted by Knowles *et al.* (1981) for a eutrophic lake in Ontario. For the epilimnetic sediments of Big Lagoon to have generated all of the N_2O lost to the atmosphere during this study, they would have had to produce N_2O at a rate of 1.2 u-mol/m^2/d. This value is near the lower end of those reported by Seitzinger *et al.* and would be expected for an oligotrophic system, as N_2O production rates generally correlate with a system's overall production of organic matter (Lemon and Lemon 1981, Knowles *et al.* 1981).

TABLE 5.9. NITROUS OXIDE FLUXES

Dates	Losses from hypolimnion		Losses to atmosphere	
	(mol/d)	(u-mol/m^2/d)	(mol/d)	(u-mol/m^2/d)
5/30 - 6/18	4.6	2.4	2.4	0.74
6/18 - 7/25	0.24	0.18	1.8	0.58
7/25 - 8/13	0.22	0.13	2.7	1.1

Total loss from hypolimnion = 105 moles
Total loss to atmosphere = 166 moles

Losses from hypolimnion were computed from mass balance calculations, and therefore include in situ consumption, sedimentary consumption, and net transport across the halocline; atmospheric losses were computed from a laminar layer model (Broecker and Peng 1982).

Because hydroxylamine is both chemically and biochemically labile, its distribution, like that of CO, must be governed by fast production and consumption processes. Thus, the appearance of any profile under these conditions would reflect recent activity only. That the hydroxylamine peak below the halocline and the anomaly near the sediments were detected on two consecutive samplings suggests a continuous, high production rate during this time. Some of our kinetics work on natural waters shows that hydroxylamine is consumed rapidly at near-neutral pH, even in distilled water (Table 5.10). Its mean turnover time (1/k) in our laboratory tests was 5.5 hours. Evidence that high turnover rates also persisted in Big Lagoon waters was apparent in the dramatic NH_2OH gradient near the sediments on the May 30 and June 18 samplings. Unfortunately, the single data point showing extremely high NH_2OH at the bottom of each of the spring profiles is not sufficient for modelling the fluxes of NH_2OH from the sediments. We can only crudely predict that the in situ turnover time is on the order of hours, or days at the longest. Because the concentrations of metals, organics, and microbes would be much higher in near bottom waters, a short turnover time is most probable.

If the in situ oxidation rates of hydroxylamine in Big Lagoon fall within the range we have found in the laboratory, then hydroxylamine production, based on the June 18 data, would be 30 to 100 nM/d in the upper hypolimnion and, for either May 30 or June 18, up to 1.0 uM/d near the sediments. These production rates would account for 10 to 50% of the ammonium oxidized in the upper hypolimnion, and up to 30% of the ammonium oxidized near the sediments were ammonium oxidation the sole

TABLE 5.10. HYDROXYLAMINE OXIDATION RATES IN NEUTRAL (PH 6-8) WATERS

Water Type	Exper. Time (h)	k_o (h^{-1})	T_{NH_2OH} (h)
NSW & DDW	7	0.118	8.5
NSW & DDW	14	0.149	6.7
DDW	3	0.096	10
DW	3	0.316	3.2
ASW	3	0.266	3.8
NSW	3	0.125	8.0

NSW = natural seawater; DW = distilled water; DDW = deionized distilled water; ASW = artificial seawater

source of hydroxylamine (Table 5.7). Diffusive fluxes, calculated from the May 30 N_2O profile, indicate that nitrous oxide production near the sediments represented about 0.1% of the NH_2OH consumed. This is less than 0.1% of the ammonium oxidized near the sediments, although we were unable to account for ammonium oxidation within the sediments. Thus, most hydroxylamine apparently did not end up as nitrous oxide; it either was consumed by microbes or oxidized chemically to products other than N_2O.

Goreau et al. (1980) found that the production of N_2O in cultures of marine nitrifiers in the presence of oxygen accounted for about 0.25% of the ammonium oxidized, Seitzinger et al. (1983) reported a ratio ranging from 0.01% to 0.3% for Narragansett Bay sediments, and Elkins et al. (1978) suggested an average of 0.14% for a variety of aquatic environments. Our ratios of less than 0.1% for Big Lagoon fall within these ranges, and would be consistent with the production of nitrous oxide by nitrifiers. The concomitant production of hydroxylamine supports, but does not necessarily verify, this contention.

Whether the observed hydroxylamine production resulted from nitrification or from dissimilatory reduction with ammonium as an end product remains to be resolved. The close proximity of nitrous oxide and hydroxylamine peaks both in the halocline and near the sediments is a strong argument for nitrification as the source. Nitrification proceeds most rapidly at very low oxygen concentrations, and thus would be supported best just below the sediment interface, but it still could occur within the hypolimnion. Abiotic production of N_2O either in the water column or the sediments also is possible. When hydroxylamine autoxidizes, it gives rise to a variety of products, depending upon the

pH, salinity, temperature, and oxidant (Chapters 3, 4; Kolasa and Wardencki 1974, Moews and Audrieth 1959). One of these products is N_2O. If this is occurring, then no matter what the source of NH_2OH, one would expect to find a nitrous oxide peak. On the other hand, it is possible that, at these pH's, other compounds are favored, as in the oxidation by Fe(III), and that the concomitant occurrence of NH_2OH and N_2O then represents the presence of active nitrification, with N_2O being produced primarily by microbes (Anderson 1963, Yoshida and Alexander 1971, Poth and Focht 1985). This phenomenon certainly warrants additional study, as its resolution could lead to the estimation of either nitrification rates or dissimilatory reduction rates via measurement of hydroxylamine.

SUMMARY

Diffusion coefficients for the hypolimnion of Big Lagoon were computed from salinity profiles, supported by temperature data and salt transport calculations. Vertical transport in the hypolimnion was slow, but enhanced by apparent double diffusion near the halocline. Carbon fixation, estimated from these coefficients and from dissolved oxygen profiles, was similar to that measured by C-14 techniques in a previous year. Epilimnetic accumulation and atmospheric fluxes of CH_4 and N_2O exceeded transport across the halocline, invoking production of these gases in epilimnetic sediments. Although slow diffususion in the lower part of the lagoon allowed significant buildups of CH_4, CO, PO_4^{-3}, and, in a more restricted sense, dissolved oxygen, N_2O and NH_2OH, the lagoon essentially was oligotrophic. Productivity was low and limited by nitrogen, and production of trace gases was considerably less than for other lakes and coastal sediments.

Methane and carbon monoxide production in the hypolimnion apparently exceeded diffusion from the hypolimnetic sediments. Although both of these gases reached extreme levels of supersaturation, their concentrations were regulated differently. Methane was produced in the sediments and in the water, the latter presumably in anoxic micro-environments, but was lost through both diffusion and microbial oxidation. Much of the methane produced in or introduced into the water remained there throughout the study, allowing concentrations to build to

2400 nM (1200 % saturation). Carbon monoxide concentrations, on the other hand, were controlled almost exclusively by microbial processes. CO was present only by virtue of inferred high production rates, presumably microbial; its turnover time was on the order of hours.

Sediments of the hypolimnion initially produced N_2O, yet became a sink by late spring. Most nitrous oxide reaching the epilimnion, however, apparently resulted from production in the epilimnetic sediments. In the spring, hydroxylamine peaks were associated with N_2O near the sediments and in the water column, but throughout the summer, when N_2O was being consumed in the sediments, hydoxylamine was barely detected. This implies that the hydroxylamine excesses were a result of nitrification, but it also is possible for the hydroxylamine to have been produced *via* dissimilatory reduction of oxidized nitrogen to ammonium. The positive correlation between hydroxylamine and nitrous oxide could have been the result of the abiotic destruction of hydroxylamine, whether the hydroxylamine was derived from nitrification or dissimilatory nitrogen reduction, but further study is needed to evaluate the roles of these processes in cycling nitrous oxide and hydroxylamine. Nitrous oxide, like methane, was produced microbially and lost through microbial consumption and evasion to the atmosphere, but hydroxylamine, like carbon monoxide, was regulated primarily by microbial and abiotic, *in situ* processes.

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SUMMARY AND CONCLUSIONS

From the spatial and temporal distributions of trace gases in a dynamically controlled estuary and in a stratified coastal lagoon, it is apparent that each gas is regulated uniquely. All are produced by chemotrophic or heterotrophic microorganisms, but their losses are controlled by microbial consumption, by turbulent, diffusive, and advective transport, and by atmospheric evasion. Methane, for example, was slow to oxidize in both Yaquina Bay and Big Lagoon; hence its distributions were regulated in good part by physical transport and atmospheric evasion. Only after considerable time in a reasonably static environment, the hypolimnion of Big Lagoon, did methane oxidizers contribute significantly to the removal of methane. Nitrous oxide also appeared somewhat conservative in the water column of both environments; however, sedimentary nitrification and denitrification played an important part in determining its distributions.

Carbon monoxide, on the other hand, was controlled almost exclusively by microorganisms, as the partial residence times with respect to CO oxidation were on the order of hours, while the concentrations were at all times high. This rapid cycling led to erratic distributions which bore little or no relation to advective or diffusive processes in Yaquina Bay or Big Lagoon. Similarly, hydrogen, studied only in Yaquina Bay, appeared to be rapidly cycled, as its distributions were erratic and ill-defined. Although direct or indirect

photochemical processes probably contributed to carbon monoxide and hydrogen supersaturations in surface waters, both were found in high concentration where light had been absent or very low for some time.

The new method for measurement of hydroxylamine allowed for the acquisition of the first detailed profiles of NH_2OH in any aquatic environment. With a detection limit of 1 nM, it presently is the only technique that is suitable for measurement of hydroxylamine at nanomolar levels in fresh and saline waters. Previously, the best spectrophotometric methods had precisions of 20 nM or greater, and the von Breymann et al. (1982) method was accurate only to within about 30% in estuarine waters.

In both Big Lagoon, where the new method was used, and in Yaquina Bay, with the von Breymann et al. (1982) method, hydroxylamine was associated with apparent nitrous oxide production and with high ammonium oxidation rates. This implies that hydroxylamine was being produced by chemolithotrophic nitrification, although it does not rule out additional contributions via other oxidative and reductive pathways. Oxidation rates of hydroxylamine measured in the laboratory indicate that its half-life is on the order of hours. Thus, the mere presence of hydroxylamine in natural waters reflects a substantial rate of production.

Studies of the kinetics of hydroxylamine oxidation by Fe(III) indicate that the rate of nitrous oxide production depends strongly on salinity, pH, light, and temperature. Although this work was done primarily in support of the analytical method, it does indicate that the composition of nitrogenous products in the in situ oxidation of

hydroxylamine may depend as much on these properties as it does on the catalysts and oxidants present. Thus, the proportion of hydroxylamine oxidized abiotically to nitrous oxide, nitrite, nitrogen gas, or nitric oxide may depend not only on the composition of the water, but also on some very general properties of the system under study.

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APPENDIX

APPENDIX

Finite Increment Model for Big Lagoon

Changes in salt and heat, and production of oxygen, methane, and nitrous oxide in Big Lagoon were estimated with a simple, finite increment model. For salt and heat, this involved summing these properties for finite depth intervals from the bottom to the surface of the lagoon, and taking the difference over a specified time interval. Mathematically, this can be expressed as

$$\Delta M = \sum_{0,t_f}^{h} (C_j * V_j) - \sum_{0,t_i}^{h} (C_j * V_j) , \qquad (1)$$

where ΔM is the total change in mass, c_j is the concentration of the substance in question for the volume increment, v_j, h is the upper limit of the depth range being considered (in the case of salt and heat, the surface of the lagoon), and t_i and t_f represent specific sampling dates. (For a heat balance, ΔM would represent the total change in heat and c_j would be the temperature of volume element j.) Net oxygen production in the hypolimnion also was estimated with this equation, but with h adjusted accordingly.

Gross production of methane over a fixed time interval was estimated with a similar mass-balance model, but which included terms for biological consumption and atmospheric evasion. Biological decay was treated as a first-order reaction and atmospheric evasion was estimated with a laminar layer model. This can be expressed mathematically by modifying equation (1) to give

$$\Delta M = \sum_{0,t_f}^{h} (C_j * V_j) - \sum_{0,t_i}^{h} (C_j * V_j) + \frac{D}{z} * A * (C_s - C_a) * (t_f - t_i)$$

$$+ \sum_{0}^{h} [K_{b,j} * \overline{C_j} * V_j * (t_f - t_i)] \, , \qquad (2)$$

where ΔM this time is the total amount of methane produced, c_j, v_j, h, t_i, and t_f are as defined above, D is the coefficient of molecular diffusion for methane, z is the estimated thickness of the laminar layer at the lagoon surface, A is the surface area of the lagoon, c_s is the mean concentration of methane in the lagoon surface waters, c_a is the equilibrium solubility of methane at the temperature and salinity of the surface waters, $K_{b,j}$ is the mean, first-order decay constant for the *in situ* removal (in this instance, microbial oxidation) of methane in volume element, j, over the time interval, $(t_f - t_i)$, and $\overline{c_j}$ is the mean concentration of methane for the same volume element and time interval.

Consumption of nitrous oxide within the water column was considered insignificant. Consequently, the *in situ* decay term in the above equation was reduced to zero, resulting in an estimate of net, rather than gross, nitrous oxide production. For carbon monoxide and

hydroxylamine, the in situ term predominated over all others. Thus, under pseudo-steady state conditions, the in situ term, and hence ΔM, represented gross production.

Data Tables for Yaquina Bay and Big Lagoon

The following pages contain complete tables of the hydrographic, nutrient, trace gas, and hydroxylamine data collected on Yaquina Bay and Big Lagoon. Microbial oxidation rates, measured by Ron Jones, are tabulated as partial residence times in Chapter 2 for Yaquina Bay and in Chapter 5 for Big Lagoon. Likewise, the methods of analysis are described and sampling locations are mapped in Chapters 2 and 5.

In the study of Yaquina Bay, trace gases and microbial activities were not measured until the seventh survey (6 October 1983), although data from all cruises are reported here. The earlier surveys were conducted to obtain a reasonable hydrographic and dynamic picture of Yaquina Bay and to develop a suitable sampling regime for the remainder of the study. Consequently, some of our methods were altered and some analyses were added as the study progressed. Those changes are as follows:

Station designations for the first two surveys (15 June 1983 and 12 July 1983) differed slightly from those for the other ten surveys, although the exact locations are noted in the tables. Otherwise, all station designations represent the same positions for each cruise, with zero km located at the end of the jetties at the mouth of the bay. Samples were collected with a 1.5 liter NIO bottle on those surveys for

which gases were not measured, and with a 5.0 liter Niskin bottle for the remainder of the study. Salinity was measured with a hand-held refractometer for the first seven and the twelfth surveys (15 June 1983 - 6 October 1983, 15 August 1984), and with an Autosal^{R} for all other cruises. Measurements for suspended particulates were begun on the fifth survey (10 August 1983); elemental analyses of these and of dissolved organic matter have been directed by Jonathan Garber and will be reported elsewhere.

TABLE A.1a. HYDROGRAPHIC AND NUTRIENT DATA FOR YAQUINA BAY, 15 June 1983

Sample No	River Km	Samp Time	Hrs fr LT*	Sal o/oo	Temp C	pH	O_2 ml/l	O_2 % Sat	NO_3^- uM	NO_2^- uM	NH_4^+ uM	PO_4^{-3} uM	$Si(OH)_4$ uM	DIN uM	N/P
1s	1.7	1025	.0	32	15.0		5.50	94.9	1.3	.19	2.1	.92	20.6	3.5	3.8
1b		1042	.3	32	13.5		5.67	94.9	.9	.18	1.9	.76	17.8	3.0	3.9
2s	4.0	1118	.7	28	17.0		5.09	89.2	2.2	.28	2.5	.88	34.2	4.9	5.6
2b		1124	.7	29	14.8		5.21	87.9	1.5	.24	2.4	.80	24.2	4.2	5.2
3s	7.0	1205	1.1	27	16.9		4.83	84.0	3.2	.29	2.7	.85	45.4	6.2	7.3
3b		1211	1.2	28			4.95		2.1	.27	2.9	.89	33.6	5.2	5.9
4s	9.0	1243	1.7	22	18.4		5.00	86.9	5.1	.35	2.3	.75	58.0	7.8	10.4
4b		1251	1.7	24			4.70		3.2	.34	3.1	.86	46.1	6.7	7.7
6s	11.5	1324	2.2	21	18.2		4.84	83.3	5.5	.36	2.1	.67	63.9	7.9	11.8
6b		1329	2.3	20			4.78		5.4	.39	2.3	.70	62.3	8.1	11.6
8s	14.4	1353	2.5	19	18.5		5.07	86.7	7.0	.40	2.2	.56	73.9	9.6	17.2
8b		1358	2.6	18			4.99		6.4	.40	2.1	.59	69.1	8.9	15.0
10s	20.0	1448	3.2	10			6.40		12.1	.45	.3	.20	101.6	12.8	64.1
10b		1453	3.3	12			6.08		11.9	.41	.4	.15	100.4	12.7	84.4

* Delay of 3 min/km assumed (+ = after local low tide, - = before local low tide)

Low Tide at Newport = - 0.58 m at 1037

TABLE A.1b. HYDROGRAPHIC AND NUTRIENT DATA FOR YAQUINA BAY, 12 July 1983

Sample No	River Km	Samp Time	Hrs fr LT*	Sal o/oo	Temp C	pH	O_2 ml/l	O_2 % Sat	NO_3^- uM	NO_2^- uM	NH_4^+ uM	PO_4^{-3} uM	$Si(OH)_4$ uM	DIN uM	N/P
13	1.6	1316	-4.5	32	15.0		6.09	105.0	1.3	.02	.6	.37	8.6	1.9	5.1
1s	1.7	712	-1.7	32	15.8		5.21	91.4	2.0	.10	2.0	.78	17.8	4.1	5.3
1b		706	-1.7	32	15.8		5.39	94.5	2.0	.11	1.7	.77	17.1	3.8	5.0
2s	4.0	738	-1.3	30	17.0		5.04	89.4	2.0	.11	2.0	.80	25.5	4.1	5.1
2b		732	-1.3	31	16.0		4.88	85.4	1.6	.10	1.9	.82	21.8	3.6	4.3
3s	7.0	805	-1.0	24	18.7		4.76	84.2	3.4	.16	1.7	.78	41.9	5.3	6.7
3b		801	-1.0	26	18.2		4.67	82.8	3.1	.18	1.9	.81	39.3	5.2	6.4
4s	9.0	836	-.6	20	19.3		4.62	80.8	8.0	.20	2.5	.69	55.9	10.6	15.4
4b		830	-.6	20			4.64		7.5	.23	1.8	.70	55.4	9.5	13.6
5s	10.6	855	-.4	16	19.5		4.61	79.0	13.0	.28	2.4	.63	68.8	15.7	25.0
5b		850	-.4	16	19.4		4.56	78.0	12.7	.26	2.3	.65	67.4	15.3	23.5
6s	11.5	914	-.1	14	19.8		4.62	78.7	17.9	.29	3.5	.59	80.9	21.6	36.7
6b		910	-.1	14	19.8		4.58	78.0	17.4	.28	2.9	.58	80.0	20.6	35.5
7s	12.5	930	.1	12	19.8		4.65	78.3	19.7	.32	3.1	.58	87.0	23.2	39.9
7b		926	.1	12	19.7		4.61	77.5	19.3	.34	3.0	.57	85.8	22.6	39.6
8s	14.4	946	.3	10	19.9		4.72	78.7	24.4	.39	3.5	.56	104.0	28.3	50.5
8b		941	.3	12	19.7		4.61	77.5	20.3	.32	3.2	.56	88.7	23.9	42.6

TABLE A.1b. (continued)

Sample No	River Km	Samp Time	Hrs fr LT*	Sal o/oo	Temp C	pH	O_2 ml/l	O_2 % Sat	NO_3^- uM	NO_2^- uM	NH_4^+ uM	PO_4^{-3} uM	$Si(OH)_4$ uM	DIN uM	N/P
9s	18.0	1013	.6	5	19.1		4.90	78.1	37.7	.39	3.8	.52	154.0	41.9	80.6
9b		1010	.6	5	19.0		4.88	77.6	37.7	.36	3.3	.53	153.0	41.3	77.9
10s	20.0	1036	.9	2	18.6		5.27	81.6	43.4	.32	2.7	.55	174.0	46.4	84.3
10b		1031	.9	1	18.7		5.13	79.2	43.0	.33	3.2	.59	171.0	46.5	78.8
11s	25.0	1112	1.2	0	18.0		5.96	90.1	44.8	.25	1.4	.44	194.0	46.4	105.5
11b		1107	1.2	0	18.0		5.93	89.7	44.8	.27	1.4	.44	192.0	46.4	105.5
12		555		0			6.18		47.0	.21	.6	.37	214.0	47.8	129.1

* Delay of 3 min/km assumed (= after local low tide, - = before local low tide)

Low Tide at Newport = - 0.85 m at 0843

TABLE A.1c. HYDROGRAPHIC AND NUTRIENT DATA FOR YAQUINA BAY, 16 July 1983

Sample No	River Km	Samp Time	Hrs fr LT*	Sal o/oo	Temp C	pH	O_2 ml/l	O_2 % Sat	NO_3^- uM	NO_2^- uM	NH_4^+ uM	PO_4^{-3} uM	$Si(OH)_4$ uM	DIN uM	N/P
13	1.5	1546	3.8	33	15.0	7.90	6.09	105.8	7.1	.20	1.3	.90	11.6	8.6	9.6
1s	1.5	1051	-1.0	32	15.5	7.98	5.21	91.4	4.9	.20	2.3	.90	20.9	7.4	8.3
1b		1047	-1.0	32	15.4	7.98	5.39	94.5	4.0	.22	2.4	.90	18.8	6.6	7.3
2s	3.9	1114	-.9	28	17.3	7.96	5.04	88.4	4.5	.21	2.5	.94	31.9	7.2	7.7
2b		1109	-.9	32	15.6	7.97	4.88	85.9	3.2	.28	2.4	.93	21.5	5.9	6.4
3s	5.7	1130	-.7	26	18.1	7.87	4.76	85.2	6.2	.23	2.4	.89	40.5	8.9	10.0
3b		1127	-.7	30	16.5	7.98	4.67	84.8	3.5	.22	2.7	.95	27.1	6.3	6.7
4s	8.5	1150	-.5	23	19.0	7.81	4.62	82.2	8.2	.24	2.2	.81	49.8	10.5	13.0
4b		1145	-.5	25	18.5	7.83	4.64	81.4	6.5	.23	2.7	.89	43.5	9.3	10.5
5s	10.5	1207	-.3	19	19.5	7.72	4.61	80.4	12.9	.28	2.2	.71	64.1	15.3	21.6
5b		1204	-.3	20	19.2	7.75	4.56	79.9	11.4	.27	2.5	.76	59.8	14.2	18.7
6s	11.4	1223	-.1	16	19.8	7.68	4.62	79.6	16.7	.26	2.6	.66	76.4	19.6	29.6
6b		1219	-.1	18	19.2	7.71	4.58	79.9	13.6	.28	2.5	.70	66.4	16.4	23.5
7s	13.0	1234	.1	16	19.9	7.89	4.65	80.2	18.7	.26	3.0	.65	83.3	22.0	33.8
7b		1230	.1	16	19.6	7.67	4.61	79.3	16.8	.27	2.8	.68	76.8	19.8	29.2
8s	14.2	1249	.2	14	20.0	7.60	4.72	80.6	22.1	.30	3.4	.63	91.1	25.8	40.9
8b		1245	.2	15	19.5	7.64	4.61	78.9	17.7	.20	3.4	.69	81.5	21.3	30.8

TABLE A.1c. (continued)

Sample No	River Km	Samp Time	Hrs fr LT*	Sal o/oo	Temp C	pH	O_2 ml/l	O_2 % Sat	NO_3^- uM	NO_2^- uM	NH_4^+ uM	PO_4^{-3} uM	$Si(OH)_4$ uM	DIN uM	N/P
9s	16.0	1311	.4	9	20.1	7.62	4.90	79.9	29.7	.33	4.2	.59	119.0	34.2	58.0
9b		1306	.4	9	20.0	7.56	4.88	79.4	28.7	.32	4.4	.50	115.0	33.4	66.9
10s	17.0	1334	.7	2	19.4	7.37	5.27	81.6	42.6	.38	3.1	.60	168.0	46.1	76.9
10b		1330	.7	4	19.4	7.24	5.13	80.6	41.2	.38	3.3	.59	165.0	44.9	76.1
11s	25.0	1356	.8	0	18.9	7.50	5.96	90.1	45.3	.26	1.6	.58	179.0	47.2	81.3
11b		1351	.8	0	18.9	7.42	5.93	89.7	45.0	.26	1.7	.58	179.0	46.9	80.9
12	> 50	800		0		7.51	6.18		42.5	.20	.8	.36	201.0	43.5	120.8

* Delay of 3 min/km assumed (+ = after local low tide, - = before local low tide)

Low Tide at Newport = 0.03 m at 1151

TABLE A.1d. HYDROGRAPHIC AND NUTRIENT DATA FOR YAQUINA BAY, 26 July 1983

Sample No	River Km	Samp Time	Hrs fr LT*	Sal o/oo	Temp C	pH	O_2 ml/l	O_2 % Sat	NO_3^- uM	NO_2^- uM	NH_4^+ uM	PO_4^{-3} uM	$Si(OH)_4$ uM	DIN uM	N/P
13	1.5	1220	3.4	33	13.0	8.00	6.83	113.8	2.0	.09	.3	.50	.0	2.4	4.8
1s	1.5	645	-2.1	32	14.0	7.92	5.53	93.5	4.2	.20	1.9	.96	7.8	6.3	6.6
1b		641	-2.2	32	13.8	7.91	5.53	93.1	4.2	.21	2.1	.98	7.5	6.5	6.6
2s	3.9	704	-1.9	30	15.2	7.88	5.11	87.5	4.3	.22	1.6	1.00	16.1	6.1	6.1
2b		701	-2.0	32	14.8	7.89	5.19	89.2	3.7	.17	1.7	1.00	11.7	5.6	5.6
3s	5.7	733	-1.6	28	17.0	7.81	4.88	85.6	4.4	.22	.9	.90	24.1	5.6	6.2
3b		730	-1.6	29	16.1	7.83	4.83	83.6	4.0	.21	1.2	.95	18.8	5.5	5.7
4s	8.5	753	-1.4	25	18.5	7.79	4.72	83.7	4.9	.23	.8	.73	35.4	5.9	8.1
4b		750	-1.4	26	18.0	7.79	4.68	82.7	4.7	.23	.9	.79	32.0	5.8	7.3
5s	10.5	811	-1.2	20	19.5	7.70	4.69	82.3	8.5	.28		.62	44.3		
5b		808	-1.2	21	19.2	7.74	4.64	81.4	8.4	.27	.7	.62	43.6	9.4	15.2
6s	11.4	827	-.9	18	20.0	7.66	4.68	82.0	8.7	.29	.9	.60	57.5	9.8	16.4
6b		824	-1.0	18	20.0	7.68	4.67	81.8	11.5	.29	.6	.58	56.9	12.4	21.3
7s	13.0	840	-.8	16	20.3	7.61	4.55	79.2	14.0	.32	.9	.56	58.5	15.3	27.3
7b		836	-.9	16	20.2	7.61	4.57	79.5	13.9	.31		.55	60.0		
8s	14.2	900	-.5	14	20.6	7.58	4.55	78.7	17.3	.34	1.3	.54	67.6	19.0	35.1
8b		856	-.6	18	20.0	7.63	4.36	76.4	12.7	.30	1.4	.55	54.8	14.4	26.2
8As	16.0	920	-.3	12	20.7	7.54	4.58	78.5	21.3	.34	1.6	.49	78.4	23.3	47.5
8Ab		918	-.3	12	20.5	7.49	4.54	77.5	21.2	.36	1.6	.48		23.1	48.1

TABLE A.1d. (continued)

Sample No	River Km	Samp Time	Hrs fr LT*	Sal o/oo	Temp C	pH	O_2 ml/l	O_2 % Sat	NO_3^- uM	NO_2^- uM	NH_4^+ uM	PO_4^{-3} uM	$Si(OH)_4$ uM	DIN uM	N/P
9s	17.0	937	-.1	10	20.6	7.59	4.76	80.4	23.6	.35	1.3	.49	88.2	25.3	51.6
9b		933	-.1	11	20.5	7.60	4.57	77.5	22.6	.35	2.0	.50	83.3	24.9	49.8
10s	20.5	1001	.2	3	20.0	7.42	5.01	80.3	36.2	.23		.53	147.9		
10b		957	.1	3	20.0	7.40	4.95	79.3	35.9	.24	1.5	.54	145.6	37.6	69.7
11s	25.0	1032	.5	0	19.4	7.40	5.32	82.8	38.4	.21	.7	.54	169.9	39.2	72.6
11b		1029	.4	0	19.3	.38	5.37	83.4	38.8	.21	.8	.54	169.4	39.8	73.7
12	>50	540		0	16.5	7.50	6.15	90.1	34.7	.23	1.4	.50	187.0	36.3	72.6

* Delay of 3 min/km assumed (+ = after local low tide, - = before local low tide)

Low Tide at Newport = - 0.27 m at 0817

TABLE A.1e. HYDROGRAPHIC AND NUTRIENT DATA FOR YAQUINA BAY, 10 August 1983

Sample No	River Km	Samp Time	Hrs fr LT*	Sal o/oo	Temp C	pH	O_2 ml/l	O_2 % Sat	NO_3^- uM	NO_2^- uM	NH_4^+ uM	PO_4^{-3} uM	$Si(OH)_4$ uM	DIN uM	N/P	Partic mg/l
13	1.5	1308	4.7	33.4			6.14		4.2	.10	.5	.95	10.4	4.8	5.0	3.6
1s	1.5	652	-1.7	33.0	13.6	7.95	5.44	91.8	3.2	.15	2.3	1.24	13.4	5.7	4.6	12.1
1b		648	-1.7	33.2	13.5	7.86	5.45	91.9	3.4	.18	2.5	1.13	11.7	6.0	5.3	18.5
2s	3.9	730	-1.1	32.0	15	7.76	4.95	85.4	3.9	.21	2.7	1.17	19.8	6.8	5.8	11.7
2b		726	-1.1	32.8	14.2	7.83	4.85	82.8	3.1	.18	2.9	1.13	16.5	6.2	5.5	18.6
3s	5.7	745	-0.9	30.0	16.9	7.70	4.35	77.0	3.2	.15	3.4	1.28	31.0	6.7	5.2	20.7
3b		745	-0.9	30.4	16.5	7.71	4.53	79.8	3.1	.21	3.3	1.29	27.8	6.6	5.1	52.9
4s	8.5	813	-0.6	26.0	18.8	7.62	3.85	69.1	4.4	.28	4.0	1.21	42.8	8.7	7.2	29.1
4b		811	-0.6	26.8	18.3	7.58	3.86	68.9	4.3	.26	4.0	1.31	39.8	8.6	6.6	56.8
5s	10.5	831	-0.4	21.7	19.9	7.46	3.68	65.7	6.0	.32	4.6	1.25	53.2	10.9	8.7	55.6
5b		828	-0.4	21.8	19.9	7.56	3.72	66.5	5.9	.31	4.5	1.24	52.5	10.7	8.6	54.1
6s	11.4	851	-0.1	19.5	20.4	7.41	3.61	64.3	7.5	.33	4.9	1.08	56.8	12.7	11.8	28.4
6b		848	-0.2	19.7	20.2	7.32	3.74	66.4	7.7	.33	4.9	1.03	56.7	12.9	12.5	32.3
7s	13	903	0.0	18.8	20.7	7.35	3.60	64.2	8.6	.35	5.0	1.11	60.0	14.0	12.6	32.1
7b		900	0.0	19.0	20.6	7.28	3.60	64.1	8.4	.37	5.0	1.07	59.6	13.8	12.9	40.0
8s	14.2	920	0.2	18.7	20.9	7.26	3.65	65.3	9.9	.37	5.2	1.03	64.3	15.4	15.0	27.3
8b		917	0.2	18.1	20.7	7.35	3.62	64.3	8.8	.39	5.2	.97	61.3	14.4	14.8	28.0
8As	16.2	943	0.5	16.0	20	7.29	3.68	63.7	11.3	.37	4.8	.92	69.3	16.5	17.9	25.6
8Ab		939	0.5	15.9	21	7.25	3.70	65.2	11.5	.31	4.9	.89	69.6	16.8	18.8	43.7

TABLE A.1e. (continued)

Sample No	River Km	Samp Time	Hrs fr LT*	Sal o/oo	Temp C	pH	O_2 ml/l	O_2 % Sat	NO_3^- uM	NO_2^- uM	NH_4^+ uM	PO_4^{-3} uM	$Si(OH)_4$ uM	DIN uM	N/P	Partic mg/l
9s	17	958	0.7	14.8	21.2	7.25	4.06	71.4	13.2	.37	4.5	.88	76.8	18.1	20.5	15.2
9b		954	0.7	14.2	21	7.16			12.8	.37	4.9	.80	73.6	18.0	22.5	27.4
9As	20.3	1022	1.0	10.1	21.2	7.15	4.16	71.1	19.4	.34	3.2	.79	102.3	22.9	28.9	13.0
9Ab		1018	0.9	10.2	21.2	7.20	4.15	71.0	19.2	.33	3.4	.80	102.7	22.9	28.7	18.1
10s	20.5	1039	1.2	8.0	21.2	7.15	4.65	78.6	23.7	.30	2.7	.82	121.3	26.7	32.6	14.5
10b		1035	1.2	9.9	21.2	7.15	4.15	70.9	20.9	.32	3.6	.77	109.4	24.9	32.3	26.0
10As	22.4	1055	1.4	5.0		7.26	4.83		28.2	.22		.81	145.4	28.4	35.0	13.9
10Ab		1052	1.3	8.0	21	7.10	4.28	72.0	23.4	.29	3.1	.76	121.5	26.8	35.2	19.7
11s	25	1120	1.7	1.9	21	7.22	4.85	78.8	32.1	.18	1.6	.81	173.9	33.8	41.8	17.4
11b		1116	1.6	1.8	20.9	7.16	4.95	80.2	31.9	.18	1.5	.76	176.7	33.6	32.9	24.4
12	>50	500		0.7	18	7.23	5.96	90.5	27.9	.27	1.7	.82	--	29.9	36.5	1.3

* Delay of 3 min/km assumed (+ = after local low tide, - = before local low tide)

Low Tide at Newport = - 0.61 m at 0823

TABLE A.1f. HYDROGRAPHIC AND NUTRIENT DATA FOR YAQUINA BAY, 15 September 1983

Sample No	River Km	Samp Time	Hrs fr LT*	Sal o/oo	Temp C	pH	O_2 ml/l	O_2 % Sat	NO_3^- uM	NO_2^- uM	NH_4^+ uM	PO_4^{-3} uM	$Si(OH)_4$ uM	DIN uM	N/P	Partic mg/l
13	1.5	1758	4.0	34.0	11.5		5.02	81.5	9.7	.25	3.7	1.34	16.2	13.6	10.2	3.39
1s	1.5	1105	-2.9	33.8	12.8		5.60	92.8	5.2	.19	3.5	1.22	11.5	8.9	7.3	11.11
1b	1.5	1101	-2.9	34.0		7.89	5.40	87.4	7.0	.22	3.8	1.25	12.3	11.0	8.8	3.95
2s	3.9	1138	-2.4	32.4	15.3		5.31	92.4	2.9	.17	2.5	1.02	22.2	5.5	5.4	14.99
2b	3.9	1133	-2.5	33.8	12.0	7.89	6.03	98.9	5.6	.19	3.3	1.09	9.7	9.1	8.4	4.35
3s	5.7	1158	-2.2	32.2	15.6		5.44	95.1	3.5	.17	2.2	1.09	21.1	5.8	5.3	5.39
3b	5.7	1154	-2.3	33.8	12.6	7.91	5.36	89.0	5.6	.20	3.5	1.20	11.6	9.3	7.8	6.75
4s	8.5	1223	-1.9	30.5	17.2		5.13	92.2	6.2	.25	1.9	1.29	35.0	8.4	6.5	7.57
4b	8.5	1220	-2.0	32.2	16.2	7.83	5.27	93.3	2.5	.19	2.2	1.05	25.5	4.9	4.6	6.59
5s	10.5	1243	-1.7	27.8	18.3		5.05	90.7	7.6	.32	2.2	1.08	47.4	10.1	9.4	7.62
5b	10.5	1239	-1.8	31.0	17.4	7.70	4.77	85.8	3.9	.25	2.4	1.15	36.0	6.6	5.7	5.63
6s	11.4	1301	-1.4	27.0	19.2		4.96	90.3	7.3	.33	2.3	1.02	51.6	9.9	9.7	5.99
6b	11.4	1257	-1.5	30.0	18.0	7.63	4.92	89.1	5.8	.28	1.6	1.06	40.6	7.7	7.2	7.03
7s	13.0	1317	-1.2	26.2	19.1		4.07	73.6	8.4	.37	2.9	1.06	55.5	11.6	11.0	5.67
7b	13.0	1313	-1.3	27.8	18.5	7.59	3.70	66.8	6.2	.32	2.2	1.03	47.2	8.6	8.4	8.67
8s	14.2	1332	-1.1	25.5	19.3		4.71	85.0	9.0	.38	3.5	1.00	59.4	12.8	12.8	5.39
8b	14.2	1328	-1.1	29.0	18.2	7.55	4.49	81.0	5.5	.30	3.0	1.13	44.2	8.8	7.8	6.07
8As	16.2	1356	-.8	22.5	19.7		4.55	81.3	11.6	.41	4.6	1.01	68.0	16.6	16.4	7.94
8Ab	16.2	1352	-.8	24.0	19.5	7.42	4.54	81.6	9.5	.39	4.0	1.01	61.9	13.8	13.7	7.81

TABLE A.1f. (continued)

Sample No	River Km	Samp Time	Hrs fr LT*	Sal o/oo	Temp C	pH	O_2 ml/l	O_2 % Sat	NO_3^- uM	NO_2^- uM	NH_4^+ uM	PO_4^{-3} uM	$Si(OH)_4$ uM	DIN uM	N/P	Partic mg/l
9s	17.0	1411	-.6	20.3	19.9		4.51	79.9	14.3	.44	5.6	.99	76.3	20.3	20.5	7.71
9b	17.0	1408	-.6	24.2	19.0	7.41	4.20	74.8	9.4	.39	4.6	1.04	61.0	14.4	13.8	6.11
10s	20.5	1440	-.2	16.0	20.2		4.53	78.7	19.3	.47	6.3	.85	98.3	26.0	30.6	6.33
10b	20.5	1435	-.3	22.0	19.4	7.25	3.77	75.3	13.3	.43	7.0	1.06	73.8	20.7	19.5	10.19
10Bs	(24)	1513	.0	10.2	20.2		5.02	84.1	25.1	.37	3.8	.69	125.8	29.3	42.4	6.43
10Bb	(24)	1507	-.1	15.2	19.6	7.18	4.15	75.3	20.4	.47	6.2	.87	101.6	27.1	31.1	7.81
11s	25.0	1533	.4	8.0	20.0		5.04	83.1	26.9	.32	3.4	.67	135.5	30.5	45.6	6.07
11b	25.0	1529	.4	13.9	19.3	7.20	4.10	69.1	21.4	.43	5.7	.85	109.3	27.4	20.9	5.95
11As	(27)	1558	.4	3.9	20.0		5.16	83.1	28.8	.22	2.2	.65	160.2	31.2	47.9	7.03
11Ab	(27)	1553	.4	6.0	19.4		4.67	75.2	28.2	.27	3.1	.65	146.9	31.5	48.5	4.91

* Delay of 3 min/km assumed (+ = after local low tide, - = before local low tide)

Low Tide at Newport = 1.16 m at 1353

TABLE A.2a. HYDROGRAPHIC, NUTRIENT, TRACE GAS AND HYDROXYLAMINE DATA FOR YAQUINA BAY, 6 October 1983

Sample No	River Km	Samp Time	Hrs fr LT*	Sal o/oo	Temp C	pH	O_2 ml/l	O_2 % Sat	NO_3^- uM	NO_2^- uM	NH_4^+ uM	PO_4^{-3} uM	$Si(OH)_4$ uM	DIN uM	N/P	Partic mg/l	H_2 nM	CH_4 nM	CO nM	N_2O nM	NH_2OH nM
13	1.5	1319	6.4	34	10.1		5.81	91.6	14.6	.36	1.3	1.43	20.6	16.4	11.5			15	17.7	14.0	18
2s	3.9	558	-1.0	33	11.2		5.69	91.2	10.1	.36	2.7	1.43	28.4	13.3	9.3		2.3	61	5.5	13.6	49
2b	3.9	543	-1.2	34	10.9		5.22	83.7	10.4	.30	2.8	1.42	25.9	13.6	9.6		.5	21	52.2	12.4	38
4s	8.5	654	-.3	30	13.6		5.13	85.0	9.5	.36	3.4	1.34	47.0	13.4	10.0			103	14.3	12.0	19
4b	8.5	644	-.4	30	13.4		5.06	83.5	9.5	.33	3.4	1.34	46.0	13.3	9.9		3.4	102	18.6		
6s	11.4	732	.2	24	14.2		4.97	80.4	12.8	.42	4.0	1.15	66.4	17.4	15.1			306	22.8	12.3	58
6b	11.4	724	.1	24	14.2		4.99	80.6	12.8	.38	4.0	1.16	66.2	17.4	15.0			300	17.3	13.0	35
8s	14.2	804	.6	23	14.5		5.04	81.5	14.2	.36	4.5	1.12	71.8	19.2	17.1		3.2	392	12.2	14.2	109
8b	14.2	754	.4	23	14.4		4.91	79.2	14.2	.38	4.4	1.13	70.8	19.1	16.9		3.6	367	20.7	13.6	59
8As	16.2	834	1	22	14.5		4.97	80.0	15.0	.36	4.7	1.09	75.2	20.2	18.6		3.5	458	22.2	14.5	40
8Ab	16.2	826	.9	22	14.2		4.97	79.3	15.3	.35	4.7	1.09	75.6	20.5	18.8						
9s	17.0	903	1.4	22	14.5		4.98	80.0	15.2	.39	4.7	1.10	75.4	20.4	18.6			469	20.9	13.8	50
9b	17.0	853	1.3	22	13.5		4.94	77.7	15.5	.36	4.7	1.10	75.8	20.7	18.8		5.6	467	15.4	14.7	25
10s	20.5	939	1.9	20	14.8		5.02	80.2	16.9	.36	5.2	.98	85.9	22.5	23.0		5.3	743	21.3	15.3	188
10b	20.5	930	1.7	19	14.6		4.99	78.9	16.7	.36	5.1	1.00	85.9	22.3	22.3		5.0	727	25.8	15.6	
11s	25.0	1020	2.3	11	14.4		5.67	85.0	22.8	.32	4.5	.69	125.6	27.8	40.3		.6	949	81.9	26.9	141
11b	25.0	1009	2.2	10	14.3		5.48	81.5	22.9	.32	4.1	.66	130.4	27.5	41.7		3.0	612	27.6	17.7	63
11As	(27)	1057	2.9	6	14.6		5.60	81.7	24.4	.21	3.2	.57	152.8	27.9	48.9		6.2	394	26.4	18.9	42
11Ab	(27)	1046	2.7	5	14.5		5.58	80.8	24.4	.21	3.1	.56	155.5	27.8	49.6		.3	375	32.9	19.1	40

* Delay of 3 min/km assumed (+ = after local low tide, - = before local low tide)

Low Tide at Newport = - 0.21 m at 0603

TABLE A.2b. HYDROGRAPHIC, NUTRIENT, TRACE GAS AND HYDROXYLAMINE DATA FOR YAQUINA BAY, 8 November 1983

Sample No	River Km	Samp Time	Hrs fr LT*	Sal o/oo	Temp C	pH	O_2 ml/l	O_2 % Sat	NO_3^- uM	NO_2^- uM	NH_4^+ uM	PO_4^{-3} uM	$Si(OH)_4$ uM	DIN uM	N/P	Partic mg/l	H_2 nM	CH_4 nM	CO nM	N_2O nM	NH_2OH nM
13	1.5	1306	5.0	32.26	12.9	8.11	6.10	101.4	2.8	.28	.9	.57	8.5	4.1	7.1	1.80	17.7	15	27.6	12.4	48
2s	3.9	721	-.8	27	12.1	7.99	5.89	93.4	16.5	.31	3.5	.81	41.4	20.3	25.0	4.71	7.1	71	42.0	12.3	244
2D		658	-1.2	31.58	13.0		6.07	100.5	4.3	.24	1.5	.63		6.0	9.5	3.21	24.8	32	23.7	10.1	184
4s	8.5	807	-.3	17.94	11.5	7.76	5.77	91.5	47.6	.38	4.8	.84	92.9	52.8	62.8	6.63	26.6	169	35.9	19.9	59
4D		802	-.4	25.4	12.6	7.95	5.78	84.7	20.9	.34	4.1	.85	50.5	25.3	29.7	7.53	10.1	105	26.7	13.9	362
5s	10.5	836	.1	11.75	11.2	7.51	5.91	83.1	77.2	.44	4.8	.77	126.2	82.4	107.0	7.23	20.9	269	25.0	27.9	214
5D		832	.0	19.34	12.1	7.79	5.68	85.6	42.4	.38	4.9	.87	83.9	47.7	54.8	7.63				19.6	226
6s	11.4	905	.5	9.79	11.2	7.43	5.82	80.8	86.9	.49	4.5	.73	137.5	91.8	125.8	8.53	7.0	315	44.8	31.2	130
6D		858	.4	17.29	12.3	7.72	5.65	84.4	51.0	.42	4.9	.84	97.0	56.4	67.1	7.82	12.9	177	29.0	21.5	172
8s	14.2	934	.9	6.25	11.1	7.26			105.8	.49	4.1	.66	159.8	110.3	167.1	9.80	7.1	434	37.3	35.8	102
8D		926	.7	22.18	12.2	7.86	5.61	86.0	31.2	.38	4.6	.89	69.1	36.2	40.7	10.96	21.9	135	36.2	18.6	58
8As	16.2	1008	1.3	5.09	10.7	7.18	6.18	82.5		.47	4.1	.64	166.7	4.5	7.1	11.17	16.2	445	20.0	40.6	155
8Ab		1000	1.2	15.68	11.9	7.68	5.70	83.1	60.2	.47	4.9	.82	104.9	65.6	80.0	24.58	9.9	222	32.1	24.1	18
9Xs	18	1047	1.9	4.63	10.7	7.18	6.25	83.0	113.5	.54	4.0	.64	169.1	118.0	184.4	9.83	14.5	451	80.7	41.2	141
9Xb		1040	1.8	9.23	11.3	7.36	5.82	80.9	89.1	.45	4.5	.72	141.6	94.1	130.6	16.58	11.2	354	33.8	36.4	218
10s	20.3	1138	2.6	2.21	10.5	7.02	6.37	82.9	122.1	.49	3.1	.63	189.9	125.7	199.6	15.98	16.4	641	40.2	45.8	102
10b		1130	2.5	3.25	10.7	7.09	6.22	82.1	116.9	.56	3.6	.63	179.9	121.0	192.1	10.46	16.8	576	40.0	46.3	39

* Delay of 3 min/km assumed (+ = after local low tide, - = before local low tide)

Low Tide at Newport = 1.07 m at 0758

TABLE A.2c. HYDROGRAPHIC, NUTRIENT, TRACE GAS AND HYDROXYLAMINE DATA FOR YAQUINA BAY, 7 January 1984

Sample No	River Km	Samp Time	Hrs fr LT*	Sal o/oo	Temp C	pH	O_2 ml/l	O_2 % Sat	NO_3^- uM	NO_2^- uM	NH_4^+ uM	PO_4^{-3} uM	$Si(OH)_4$ uM	DIN uM	N/P	Partic mg/l	H_2 nM	CH_4 nM	CO nM	N_2O nM	NH_2OH nM
13	1.5	1345	5.0	29.60	11.2	8.16	6.62	104.6	5.2	.36	.6	.60	22.6	6.1	10.2		7.3	22	26.2	11.2	5
2s	3.9	758	-.9	23.22	11.0	8.10	6.52	92.3	27.3	.39	1.6	.71	68.4	29.3	41.3	6.12	14.7	109	24.3	13.6	5
2b		749	-1.1	29.90	11.0	8.16	6.42	100.9	6.3	.35	.9	.64	21.7	7.6	11.8	6.44	13.6	36	28.4	11.6	4
4s	8.5	846	-.3	12.96	10.4	7.30	6.74	94.3	61.0	.25	2.0	.61	135.2	63.3	103.7	6.04	5.5	283	25.1	18.3	7
4b		839	-.5	23.83	11.0	8.10	6.41	91.7	25.4	.36	1.7	.72	64.3	27.5	38.1	9.64	19.7	147	36.9	14.7	0
6s	11.4	928	.2	5.70	10.1	7.36	7.03	92.9	86.3	.18	1.8	.48	181.0	88.2	183.8	10.80	11.5	432	21.9	22.9	1
6b		920	.1	13.90	10.5	7.87	6.65	93.5	58.1	.20	2.0	.62	129.0	60.3	97.3	12.30	7.8	321	10.8	19.2	7
8s	14.2	1004	.7	3.19	10.1	7.19	7.17	93.1	95.0	.27	1.6	.50	197.4	96.9	193.8	25.00	2.1	514	10.2	22.6	20
8b		954	.5	18.97	10.5	8.02	6.45	93.9	40.5	.39	2.1	.68	94.9	43.0	63.3	17.70	1.8	231	16.5	17.1	7
8As	16.2	1036	1.1	1.18	10.0	7.05	7.23	92.8	100.0	.18	1.3	.45	198.8	101.5	225.5	15.60	17.5	626	48.3	24.5	17
8Ab		1027	1.0	5.59	10.2	7.34	7.00	92.3	100.8	.20	1.8	.49	177.9	102.8	209.8	18.80				22.2	8
9Xs	18.0	1120	1.8	1.02	10.1	6.96	7.18	92.1	101.1	.23	1.3	.44	217.4	102.6	233.1	37.00		754	31.9	25.2	16
9Xb		1130	1.9	5.59	10.0	7.26	6.94	91.4	86.4	.21	1.9	.49	181.0	88.4	180.5	16.90		575		25.1	0
10s	20.3	1204	2.6	.30	10.0	6.83	7.28	92.5	102.3	.15	1.2	.46	219.3	103.6	225.3	22.70	15.4	879	45.6	23.0	7
10b		1215	2.4	.19	10.0	6.83	7.20	91.3	102.8	.19	1.2	.47	218.8	104.2	221.8	17.40	19.8	887	29.3	22.3	17

* Delay of 3 min/km assumed (+ = after local low tide, - = before local low tide)

Low Tide at Newport = 1.31 m at 0841

TABLE A.2d. HYDROGRAPHIC, NUTRIENT, TRACE GAS AND HYDROXYLAMINE DATA FOR YAQUINA BAY, 5 April 1984

Sample No	River Km	Samp Time	Hrs fr LT*	Sal o/oo	Temp C	pH	O_2 ml/l	O_2 % Sat	NO_3^- uM	NO_2^- uM	NH_4^+ uM	PO_4^{-3} uM	$Si(OH)_4$ uM	DIN uM	N/P	Partic mg/l	H_2 nM	CH_4 nM	CO nM	N_2O nM	NH_2OH nM
13	1.5	1348	5.0	32.08	11.0	8.12	6.53	104.7	1.2	.20	.6	.56	5.7	2.0	3.6	2.96	7.9	9		11.6	
2s	3.9	646	-2.1	23.21	11.0	8.11	6.48	97.7	24.1	.22	1.7	.59	70.1	26.0	44.1	3.56	5.9	100	32.5	13.7	10
2b		632	-2.4	29.14	11.0	8.15	6.46	101.5	7.0	.27	1.4	.57	25.1	8.6	15.2	3.61	6.5	42	22.2	12.0	18
4s	8.5	742	-1.4	15.03	10.7	7.96	6.61	94.2	36.3	.23	1.7	.58	118.9	38.3	65.9	6.97	4.2	201	43.3	15.1	24
4b		733	-1.6	18.16	10.9	8.04	6.54	95.5	37.2	.21	1.8	.62	100.0	39.2	63.3	8.90					
6s	11.4	833	-.7	8.75	10.8	7.28	6.84	94.0	60.7	.21	1.3	.57	160.2	62.2	109.1	7.28	5.7	392	19.2	15.6	21
6b		820	-.9	9.20	10.4	7.71	6.83	93.2	59.4	.28	1.3	.50	156.9	61.0	122.0	7.85	6.8	364	22.4	18.6	16
8s	14.2	925	.0	3.16	10.3	7.19	6.94	94.6	76.0	.19	.9	.42	194.3	77.0	183.3	12.82	5.7	674	46.4	19.9	18
8b		906	-.3	6.47	10.5	7.69	7.22	92.4	67.0	.23	1.2		175.1	68.4		15.99	4.5	509	35.6	18.2	
10s	20.3	1030	.7	.08	10.0	7.05	7.68	97.6	83.3	.17	.7	.36	209.4	84.2	233.8	3.33	9.0	1054	8.5	19.1	12
10b		1022	.8	.12	10.0	7.01	7.66	97.5	82.3	.18	.8	.33	209.9	83.3	252.4	3.44	5.9	1017	13.5	19.3	5
11s	25.0	1128	1.5	.01	10.5	7.22	7.75	99.7	85.1	.17	.7	.30	201.4	86.0	286.6	4.05	4.6	932	10.2	17.7	25
11b		1119	1.4	.01	10.2		7.77	99.3	85.3	.15	.7	.28	200.0	86.1	307.4	2.55	4.2	899		17.2	7

* Delay of 3 min/km assumed (+ = after local low tide, - = before local low tide)

Low Tide at Newport = 0.00 m at 0842

TABLE A.2e. HYDROGRAPHIC, NUTRIENT, TRACE GAS AND HYDROXYLAMINE DATA FOR YAQUINA BAY, 13 June 1984

Sample No	River Km	Samp Time	Hrs fr LT*	Sal o/oo	Temp C	pH	O_2 ml/l	O_2 % Sat	NO_3^- uM	NO_2^- uM	NH_4^+ uM	PO_4^{-3} uM	$Si(OH)_4$ uM	DIN uM	N/P	Partic mg/l	H_2 nM	CH_4 nM	CO nM	N_2O nM	NH_2OH nM
13	1.5	1155	4.7	32.96		7.89	4.72	78.6	18.1	.35	1.4	2.61	30.8	19.8	7.6		3.8	80		18.2	
2s	3.9	608	-1.2	20.37	14.0	7.87	6.10	96.8	31.5	.34	1.7	.96	93.9	33.6	35.0		2.9	112	17.1	14.8	
2b		551	-1.5	26.23	13.0	7.92	5.50	88.7	21.5	.41	2.1	1.13	62.2	24.0	21.3		7.0	66	26.5	16.3	
4s	8.5	709	-.4	11.13	14.6	7.60	6.23	94.4	49.9	.43	1.7	.73	144.6	52.1	71.3		5.5	286	65.6	17.4	
4b		650	-.7	12.29	14.8	7.66	6.20	95.3	47.1	.37	1.6	.77	137.4	49.1	63.8		5.7	269	46.6	17.0	
6s	11.4	750	.1	2.59	15.0	7.19	6.70	96.6	70.5	.53	1.5	.61	193.2	72.5	118.9		6.7	550	24.9		
6b		737	-.1	3.45	14.9	7.25	6.90	99.2	68.0	.47	1.4	.58	187.3	69.9	120.5		7.0	504	19.2	18.2	
8s	14.2	830	.8	.41	14.3	7.02	7.07	99.9	77.2	.34	.8	.57	205.0	78.3	137.4		11.1	797	23.4	20.2	
8b		817	.4	1.95	14.7	7.13	6.73	96.3	72.1	.80	1.5	.57	196.4	74.4	130.5		> 40	14		19.3	
10s	20.3	922	1.2	.04	13.7	7.00	7.16	98.8	79.6	.31	.9	.50	203.9	80.8	161.5		11.5	1096	25.6	18.2	
10b		911	1	.05	13.3	6.94	7.14	97.7	77.1	.26	1.1	.49	210.6	78.5	160.1		4.0	84	13.4	19.4	
11s	25	1002	1.7	.01	13.0	7.12	7.51	101.9	82.0	.26	.9	.43	200.6	83.1	193.3		6.2	654	15.8	16.5	
11b		950	1.4	.02	13.0	7.13	7.69	104.4	83.8	.71	1.0	.44	199.7	85.5	194.3		28.8	665	38.8	20.7	

* Delay of 3 min/km assumed (+ = after local low tide, - = before local low tide)

Low Tide at Newport = - 0.73 m at 0708

TABLE A.2f. HYDROGRAPHIC, NUTRIENT, TRACE GAS AND HYDROXYLAMINE DATA FOR YAQUINA BAY, 15 August 1984

Sample No	River Km	Samp Time	Hrs fr LT*	Sal o/oo	Temp C	pH	O_2 ml/l	O_2 % Sat	NO_3^- uM	NO_2^- uM	NH_4^+ uM	PO_4^{-3} uM	$Si(OH)_4$ uM	DIN uM	N/P	Partic mg/l	H_2 nM	CH_4 nM	CO nM	N_2O nM	NH_2OH nM
13	1.5	1526	6	34.3	14.5	8.10	6.85	118.7	3.8	.25	1.4	.71	9.9	5.5	7.7	14.83		14	21.6		
2s	3.9	846	-.8	33.0	15.3	7.89	5.29	92.5	5.4	.31	2.8	1.19	31.9	8.5	7.2	16.08		73	24.6	14.5	9
2b		836	-1	33.8	14.8	7.83	4.84	84.2	4.0	.26	2.9	1.25	30.9	7.2	5.8	54.93		110	50.9	14.6	8
4s	8.5	941	-.1	29.7	18.8	7.65	4.60	84.4	6.7	.31	1.3	1.01	45.9	8.3	8.2	34.63		82	35.5	11.9	12
4b		932	-.3	30.0	18.0	7.58	4.57	82.6	6.3	.32	1.9	1.05	44.9	8.6	8.2	37.02		99	75.2		
6s	11.4	1023	.4	25.0	21.0	7.54	4.38	81.4	9.4	.32	1.6	.79	52.6	11.3	14.3	29.15		95	42.7	12.3	11
6b		1013	.2	25.5	20.4	7.54	4.22	77.8	8.5	.33	1.8	.87	52.6	10.7	12.3	12.08		115	102.0	12.3	7
8s	14.2	1103	.9	22.5	21.8	7.49	4.35	80.8	11.1	.35	2.1	.75	55.7	13.6	18.1	17.75		187	103.0		
8b		1053	.8	23.3	20.1	7.44	4.17	75.4	10.8	.38	2.5	.78	55.5	13.6	17.5	15.40		169	37.4	13.2	1
9s	17	1137	1.4	18.7	22.0	7.32	4.12	75.3	14.9	.41	3.3	.72	61.1	18.6	25.8	31.55		245	114.0	14.6	16
9b		1145	1.5	19.8	22.4	7.44	4.19	77.7	14.6	.39	3.2	.71	60.6	18.2	25.7	27.08		255	46.4	16.4	8
10Am	22.4	1226	1.9	14.3		7.25	4.28	76.9	21.5	.40	3.2	.61	79.5	25.1	41.2	54.08		509	41.7	17.9	53
11As	27	1313	2.9	6.3	23.0	7.28	4.79	83.0	32.2	.36	2.2	.53	121.5	34.8	65.6	33.55		316	49.2	18.9	100
11Cs	35	1341	2.1	.4	22.6	7.22	4.72	78.2	33.1	.35	2.3	.86	171.4	35.7	41.5	43.63		233	9.5	16.9	65

* Delay of 3 min/km assumed (+ = after local low tide, - = before local low tide)

Low Tide at Newport = 0.12 m at 0924

TABLE A.3a. HYDROGRAPHIC, NUTRIENT, TRACE GAS, AND HYDROXYLAMINE DATA FOR BIG LAGOON, 30 MAY 1985*

Depth** (m)	Temp (C)	Sal (o/oo)	pH	O_2 (ml/l)	NH_4^+ (uM)	NO_2^- (uM)	NO_3^- (uM)	PO_4^{-3} (uM)	$Si(OH)_4$ (uM)	(N/P)	CH_4 (nM)	CO (nM)	N_2O (nM)	NH_2OH (nM)
1.0	17.9	6.54	7.21	6.31		.10	.1	.18	51.8		56	21	9.6	11
2.0	17.8	6.52	7.91	6.33		.08	.0	.18	48.5		69	24	10.3	3
3.0	17.8	6.57	7.90	6.70		.10	1.0	.17	53.1		69	23	10.3	
4.0	17.8	6.58	7.79	6.33		.07	.3	.22	53.2		68	22	10.2	4
5.0	17.8	12.13	7.89	7.41		.22	.8	.33	49.3		211	29	17.2	0
5.3	17.8	18.02	7.95	8.42		.35	.0	.42	57.0		177	30	20.4	11
5.5	16.3	25.32	7.89	7.84		.40	.1	.42	101.4		98	37	22.7	0
6.0	16.2	26.48		7.09		.73	.6	1.22	125.1		58	47	36.2	4
6.2	16.2	26.79	7.76	6.96		.59	.0	1.77	133.9		56	49	38.4	3
6.8	16.1	27.78	7.50	1.73		1.24	12.3	10.70	145.0		141	59	74.7	175

*Samples were collected on 30 May with a Van Dorn bottle, hence the data are integrated values

**Relative Height = 7.8 - Depth (Relative heights are estimated from measured changes in lagoon height and salinity profiles)

TABLE A.3b. HYDROGRAPHIC, NUTRIENT, TRACE GAS, AND HYDROXYLAMINE DATA FOR BIG LAGOON, 18 JUNE 1985

Depth* (m)	Temp (C)	Sal (o/oo)	pH	O_2 (ml/l)	NH_4^+ (uM)	NO_2^- (uM)	NO_3^- (uM)	PO_4^{-3} (uM)	$Si(OH)_4$ (uM)	(N/P)	CH_4 (nM)	CO (nM)	N_2O (nM)	NH_2OH (nM)
1.0	19.8	6.32	7.66	6.17	.8	.08	.1	.10	49.5	9.8	54	54	8.5	12
3.0	19.5	6.34	7.91	6.35	.7	.08	.1	.09	54.0	9.8	65	64	8.3	2
5.0	19.7	8.75	8.08	7.11			.1	.16	53.6		78	44	8.9	9
5.2	19.5	16.97	8.07	9.69	1.1	.33	.0	.25	57.5	5.7	231	66	12.9	5
5.4	19.2	22.49	7.79	10.25			.0	.29	76.1		218	81	13.8	11
5.6	19.0	24.65	7.97	9.85	3.0	.49	.0	.38	99.4	9.2	207	102	13.8	17
5.8	18.6	25.56	7.73	7.58			.0	.68	112.8		214	89	12.2	11
6.0	18.0	26.12	7.20	7.31	1.3	.54	.0	.73	125.0	2.5	168	78	14.1	7
6.2	17.8	26.49	7.81	7.96			.0	.67	132.7		124	95	17.5	0
6.4	17.2	26.91		4.92	1.5	.76	.0	2.86	160.8	.8	149	92	10.8	0
6.6	17.0	27.13	7.49	3.35			.0	5.20	172.5		230	119	10.4	8
6.8	17.1	27.26	7.33	1.90	2.9	.82	.0	7.40	177.5	.5	262	100	11.2	4
7.0	16.9	27.26	7.27	1.47	3.8	1.60	.0	7.50	176.7	.7	282	130	9.9	130

*Relative Height = 7.6 - Depth

TABLE A.3c. HYDROGRAPHIC, NUTRIENT, TRACE GAS, AND HYDROXYLAMINE DATA FOR BIG LAGOON, 15 JULY 1985

Depth* (m)	Temp (C)	Sal (o/oo)	pH	O_2 (ml/l)	NH_4^+ (uM)	NO_2^- (uM)	NO_3^- (uM)	PO_4^{-3} (uM)	$Si(OH)_4$ (uM)	(N/P)	CH_4 (nM)	CO (nM)	N_2O (nM)	NH_2OH (nM)
1.0		6.67	8.35	6.27	.1	.04	.1	.08	50.1	2.5	112	76	9.6	1
3.0		6.75	8.35	6.09	.2	.02	.0	.05	43.6	4.5	121	8	9.1	3
4.8		7.16	8.41	6.05	.4	.24	.1	.27	46.4	2.7	152	13	9.2	5
5.0		21.62	8.16	9.11	.3	.27	.0	.35	62.9	1.7	353	98	10.1	1
5.2		25.92	7.87	7.76	.4	.37	.0	.63	95.0	1.3	397	176	8.8	4
5.4		25.99	7.91	7.62	.4	.25	.0	.60	114.8	1.2	428	150	9.3	2
5.6		26.12	7.85	7.16	.4	.26	.0	.73	120.8	.8	407	125	9.3	0
5.8		26.54	7.54	4.67	.7	.64	.0	3.54	144.2	.4	508	139	4.7	0
6.0		26.64	7.34	2.08	3.9	1.53	.0	4.50	147.4	1.2	614	157	3.2	0

*Relative Height = 7.0 - Depth

TABLE A.3d. HYDROGRAPHIC, NUTRIENT, TRACE GAS, AND HYDROXYLAMINE DATA FOR BIG LAGOON, 25 JULY 1985

Depth* (m)	Temp (C)	Sal (o/oo)	pH	O_2 (ml/l)	NH_4^+ (uM)	NO_2^- (uM)	NO_3^- (uM)	PO_4^{-3} (uM)	$Si(OH)_4$ (uM)	(N/P)	CH_4 (nM)	CO (nM)	N_2O (nM)	NH_2OH (nM)
1.0	19.0	6.91	8.36	5.64			.3	.09	31.7	3.3				
3.0	19.0	6.89	8.47	6.21	.8	.04	.1	.16	51.9	6.2	60	21	9.1	4
5.0	21.0	23.06	8.29	10.10	.6	.28	.0	.35	70.7	2.4	856	252	10.3	2
5.2	21.8	24.93	8.06	9.12	.8	.32	.0	.47	81.1	2.3	734	214	8.6	3
5.4	22.0	25.87	8.00	8.59	.6	.28	.0	.44	100.5	1.9	738	212	9.2	0
5.6	21.8	26.44	7.97	7.90	.2	.18	.0	.63	108.5	.6	524	317	10.3	2
5.9	20.8	27.03	7.88	7.52	.1	.19	.0	2.98	135.2	.1	470	97	7.7	3
6.2	20.1	27.24	7.55	4.99	.4	.36	.0	5.20	151.5	.1	376	205	4.0	3
6.4	20.5	27.22	7.46	3.97	.8	.58	.0	6.25	132.4	.2	367	80	3.7	2

*Relative Height = 6.9 - Depth

TABLE A.3e. HYDROGRAPHIC, NUTRIENT, TRACE GAS, AND HYDROXYLAMINE DATA FOR BIG LAGOON, 13 AUGUST 1985.

Depth* (m)	Temp (C)	Sal (o/oo)	pH	O_2 (ml/l)	NH_4^+ (uM)	NO_2^- (uM)	NO_3^- (uM)	PO_4^{-3} (uM)	$Si(OH)_4$ (uM)	(N/P)	CH_4 (nM)	CO (nM)	N_2O (nM)	NH_2OH (nM)
.0		7.50	8.46		.1	.07	.6	.18	51.7	4.4				
1.0	19.8	7.50	8.59	6.08	.2	.09	.1	.17	49.1	2.0	303	38	9.4	1
3.0	19.8	7.47	8.60	6.09	.0	.07	.1	.18	51.9	.9	311	137	9.2	2
5.0	22.0	23.97	8.09	9.34	.3	.28	.0	.81	83.8	.7	2146	204	8.0	1
5.2	22.9	24.83	8.04	9.30	.3	.28	.0	.82	93.7	.7	2378	136	7.6	2
5.4	23.8	25.79	7.97	8.72	.3	.28	.0	.79	110.3	.7	2428	311	7.4	2
5.6	24.1	26.86	7.82	7.40	.5	.40	.0	1.86	141.4	.5	2208	452	5.3	1
5.8	23.9	26.98	7.65	6.10	.6	.46	.0	3.96	154.5	.3	1775	191	4.3	2
6.0	23.2	27.13	7.65	5.75	.5	.46	.0	5.95	178.7	.2	1812	646	3.3	3
6.2	22.4	27.22	7.48	4.17	.6	.54	.0	7.20	198.0	.2	1037	989	2.8	1
6.4	22.1	27.27	7.49	3.40	1.1	.66	.0	7.80	209.0	.2	1253	348	2.6	3
6.6	21.8	27.29	7.39	2.46	1.9	.89	.0	8.60	238.0	.3	670	178	2.6	2

*Relative Height = 6.8 - Depth