1996

Oxidation Kinetics of manganese(II) in seawater at nanomolar concentrations

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Recommended Citation

Langen, Peter J. von, "Oxidation Kinetics of manganese(II) in seawater at nanomolar concentrations" (1996). *Master's Theses*. 1338.
DOI: https://doi.org/10.31979/etd.f8fz-a8hw
https://scholarworks.sjsu.edu/etd_theses/1338

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OXIDATION KINETICS OF MANGANESE(II) IN SEAWATER AT NANOMOLAR CONCENTRATIONS

A Thesis
Presented to
The Faculty of Moss Landing Marine Laboratories
San Jose State University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science
in
Marine Science

by
Peter J. von Langen
August, 1996

UMI Number: 1381449

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ABSTRACT

OXIDATION KINETICS OF MANGANESE(II) IN SEAWATER AT NANOMOLAR CONCENTRATIONS

by Peter J. von Langen

Manganese oxidation rates were determined at low (≈ 20 nM) concentrations in seawater by measuring dissolved manganese (Mn(II)) using flow injection analysis with chemiluminescence detection. Mn(II) was measured in samples that had been filtered (0.2 μm) and kept in the dark under controlled temperature and pH conditions. Eight carboys with mean pH values ranging from 8.17 to 8.75 were kept at 25°C, another carboy (pH = 9.32) was kept at 5°C. Oxidation followed Morgan's (1967) homogeneous rate equation ($d[Mn(II)]/dt = k_1[O_2]\{OH^-\}^2 [Mn(II)]$). Oxidation rate constants for all carboys were similar ($k_1 = 1.2 - 3.6 \times 10^{12}\ M^{-3} d^{-1}$) and in agreement with work by Morgan (1967; $k_1 = 4 \times 10^{12}\ M^{-3} d^{-1}$) and Davies and Morgan (1989; $k_1 = 1.1 \times 10^{12}\ M^{-3} d^{-1}$) in dilute solutions. Autocatalytic increases in Mn(II) oxidation rates, as predicted by a heterogeneous reaction mechanism (Morgan, 1967) ($d[Mn(II)]/dt = k_2'[Mn(II)][MnO_2]$) were not observed, indicating the homogeneous reaction dominates Mn(II) oxidation at low nM concentrations in seawater. These results were incorporated into a kinetic model (Johnson *et al.*, 1996) that suggests slow Mn oxidation kinetics and, consequently, reduced oceanic scavenging rates can account for the persistence of the Mn(II) maximum associated with the oxygen minimum at mid-ocean depths.

ACKNOWLEDGMENTS

I wish to sincerely thank Dr. Ken Johnson and Dr. Kenneth Coale for enthusiastically teaching their invaluable knowledge of marine chemistry, as well as their encouragement, assistance and funding which enabled me to complete this thesis project. I am grateful to Dr. Nicholas Welschmeyer for his insightful comments and allowing me the use of his laboratory facilities. I am also thankful to Dr. William Broenkow for his energetic, interesting, and humorous teachings of oceanography, which have helped me become more of a digital and less of an analog scientist. I wish to thank Dr. John Boothby for providing assistance and expertise in microbiology and Sara Tanner and Kurt Buck for teaching me epifluorescence microscopy techniques used in bacterial enumeration. Special thanks go to Ginger Elrod and Jocelyn Nowicki for teachings of flow injection analysis. I also with to thank them and the rest of the chemical oceanography lab for friendship and showing me what drawer things were in. I thank the librarians Sheila Baldridge, Sandi O'Neil, and Joan Parker for help in locating the most obscure references. Thanks to Gail Johnston, Sandy Yarborough, and Irene Chung for helping to guide me through home campus bureaucracy. I wish to thank the David and Lucille Packard Foundation for a grant which allowed me to present this work at the AGU/OSLO Ocean Sciences Meeting at San Diego in February, 1996. I am indebted to my mom and dad for support and encouragement during my education at Moss Landing Marine Laboratories I also wish to thank my girlfriend, Charlane DuFur, for being so helpful, supportive and loving.

PREFACE

In this thesis, I present a study of the oxidation rates of Mn(II) in seawater. Chapter 1 is an introduction to manganese biogeochemistry and its relationship to the marine environment and this study. Chapter 2 is the main body of this thesis work that is being submitted for publication in *Geochimica et Cosmochimica Acta*. This chapter is in a format for publication and includes an introduction which repeats some of the information already stated in Chapter 1, as well as methods, and results and discussion from this project. Chapter 3 ties in the results from this thesis work into a kinetic Mn model with which the formation of the secondary Mn(II) maximum associated with the oxygen minimum can be described. This model has already been published by Johnson *et al.* (1996) in *Geochimica et Cosmochimica Acta*, and this chapter is a summary of these results. For consistency, Chapters 1 and 3 are written in the same format and style as Chapter 2.

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CHAPTER 1

INTRODUCTION

IMPORTANCE OF MANGANESE

GENERAL

Manganese (Mn) comprises approximately 0.1% of the earth's crust by weight. This transition metal is found in natural environments in a variety of oxidation states. In oxygenated seawater at natural temperature and pH values, Mn(II) is in the dissolved state while Mn(III) and Mn(IV) are essentially insoluble as Mn oxides. Mn oxide particles (e.g. MnO_2) have negative surface charges and high specific surface areas (100 m^2g^{-1}; Santschi *et al.*, 1990) which facilitates scavenging of dissolved heavy metals from the water column (Balistrieri *et al.*, 1981). Scavenging of trace metals is thought to be a two-step process, whereby dissolved metals are first sorbed by particles. These particles, along with their associated metals, are then removed by settling.

The sorption of metals onto Mn oxides is an important process in ferromanganese nodule formation (Murray and Brewer, 1977). Abundances of these deep sea nodules have been proposed as future economically feasible mineral sources (Agarwal, 1979). The level of enrichment of trace metals in ferromanganese nodules over their seawater concentrations has been shown to be Co > Ni > Cu > Zn (Murray and Brewer, 1977). The enrichments result from interactions between these metals and Fe and Mn oxides. For example, studies have shown that a strong electric field at the MnO_2-solution interface allows Co(II) to oxidize to Co(III) at lower concentrations (Murray and Dillard, 1979) and pH (Murray, 1975) than it would otherwise, if it were in solution.

Dissolved metals are capable of being incorporated into living tissue while metals in particulate form generally are not. It is the concentration of free dissolved metal, and not the total metal concentration, that is bioavailable and perhaps, toxic to plants and animals (Sunda *et al.*, 1990). Binding of dissolved heavy metals by Mn oxides lowers the concentrations of these metals in solution. Under initially high concentrations of toxic metals, such as dissolved copper, the scavenging properties of Mn oxides may therefore decrease metal toxicity (Sunda *et al.*, 1981; Sunda and Huntsman, 1983; Sunda, 1987). Likewise, initially low dissolved metal concentrations may be lowered further by Mn oxide scavenging to levels that are insufficient for metabolic activity. Low concentrations of Mn(II) may be biologically limiting, as Mn(II) is an essential micro-nutrient (McClendon, 1976). Low concentrations of Mn(II) have been shown to limit reproductive rates of certain phytoplankton (Brand *et al.*, 1983; Coale, 1991).

THE OCEANOGRAPHIC BEHAVIOR OF MANGANESE

Mn(II) is used as an effective tracer for a variety of biogeochemical processes in the marine environment (Murray *et al.*, 1983; Martin *et al.*, 1985). The main inputs of Mn to the ocean are from rivers, atmospheric input and hydrothermal vents, while adsorption onto sinking particles (scavenging) is the major mechanism of Mn removal (Chester, 1990). Hydrothermal vents are a major source of Mn(II) to the deep ocean and may contribute more Mn(II) to the oceans than all other sources combined (Edmond *et al.*, 1979, 1982). Mn(II) is relatively easy to measure in hydrothermal fluids and exhibits conservative behavior, decreasing in concentration with distance from hydrothermal vents. These traits have resulted in Mn(II) being used as an effective tracer of hydrothermal plumes (Klinkhammer and Hudson, 1986; Coale *et al.*, 1991; Chin *et al.* 1994). Mn(II) is also observed to decrease in concentration with distance offshore (Fig. 1) (Martin *et al.*, 1985). The higher nearshore concentrations are the result of riverine, aeolian, and sedimentary inputs. Because distributions of scavenged elements, such as Mn(II), reflect the influences of sources, Mn(II) has been proposed as a tracer for lateral movements of water masses offshore (Martin and Knauer, 1982, 1983, 1985; Martin *et al.*, 1985).

Mn is a transition metal that undergoes a variety of redox transformations in the ocean environment. It may exist as soluble Mn(II) or insoluble Mn(III) or Mn(IV) oxides. Mn is biologically active in both dissolved and oxidized forms. The energy yield from various oxidants consumed per mole of organic carbon oxidized has been shown as O_2 > Mn oxides = nitrate > Fe oxides > sulfate (Froelich *et al.*, 1979). This order shows the importance of Mn oxide as a terminal electron acceptor during the oxidation of organic matter (Burdige and Nealson, 1986; Myers and Nealson, 1988a; Myers and Nealson, 1988b; Tebo *et al.*; 1991). Because of its biological utilization as a micro nutrient, it is thought that Mn(II) is incorporated and released in Redfield-like proportions to carbon (Morel and Hudson, 1985). The release of Mn(II) during remineralization of particulate organic matter (POM) may be an important source of Mn(II) in the deep-sea. The variety of sources, internal cycling, and complicated redox behavior exhibited by Mn results in a unique distribution that reflect sources, sinks, and changes in redox state. Understanding the complexities of Mn(II) biogeochemistry will enable more accurate modeling of oceanographic processes such as redox cycling, aeolian transport, scavenging, and hydrothermal inputs.

MANGANESE CHEMISTRY

THERMODYNAMICS

Much oceanographic interest in Mn relates to its ability to have several oxidation states in seawater. Mn may exist as Mn(II), Mn(III), or Mn(IV). In the highly oxidizing conditions typical of the ocean environment, pE-pH diagrams suggest that Mn should exist predominantly in the form of particulate $MnO_2(s)$ (Stumm and Morgan, 1981). Morgan (1967) summarized several studies which demonstrate that, at ordinary temperature and pressure, the initial product of Mn(II) oxidation in highly oxidizing environments is δ-MnO_2 (birnessite):

$$Mn^{2+} + 2H_2O \Longleftrightarrow \delta\text{-}MnO_2(s) + 4H^+ + 2e^- \qquad (1)$$

If we assume δ-MnO_2 is controlling Mn(II) concentrations in alkaline, well-oxygenated seawater and the equilibrium constant for Eqn. 1 is 2.5×10^{-44} (Stumm and Morgan, 1981), then at $pH = 8$ and $pE = 12.8$, which are typical of surface seawater, the predicted Mn(II) concentration is approximately 1.6×10^{-15} M. This is orders of magnitude lower than typical seawater Mn(II) concentrations ($\approx 0.1 - 10 \times 10^{-9}$ M; Klinkhammer and Bender, 1980; Landing and Bruland, 1980, 1987; Martin *et al.*, 1985). Thermodynamic equations, however, cannot be used to predict the rate at which Mn(II) concentrations approach the equilibrium state. Equilibrium calculations that predict concentrations of products that vary from observed values are often the result of slow reaction rates.

KINETICS

Kinetic models appear to be necessary to explain the persistence of relatively high Mn(II) concentrations in naturally oxic marine environments. The kinetics of Mn(II) oxidation in natural waters have been described by the following equation (Morgan, 1967):

$$-d[\mathrm{Mn(II)}]/dt = k_1' [\mathrm{Mn(II)}] + k_2' [\mathrm{Mn(II)}] [\mathrm{MnO_x}] \qquad (3)$$

where $k_1' = k_1 [O_2] \{OH^-\}^2$ with $k_1 = 4 \times 10^{12}\ M^{-3}\ d^{-1}$

and $k_2' = k_2 [O_2] \{OH^-\}^2$ with $k_2 = 10^{18}\ M^{-4}\ d^{-1}$

The rate constants were calculated from Morgan's (1967) data by Diem and Stumm (1984). This equation's first term (k_1' [Mn(II)]) represents homogeneous oxidation and the second term (k_2' [Mn(II)] [$\mathrm{MnO_x}$]) describes a heterogeneous, autocatalytic mechanism due to Mn oxide surfaces. Studies have shown that Mn(II) oxidation rates are also catalyzed by bacteria (Johnston and Kipput, 1988; Miyajima, 1992). Several papers have suggested that microbial oxidation is the principal pathway in the marine environment (Tebo and Emerson, 1986; Sunda and Huntsman, 1988; Moffett, 1994). Studies have shown that laboratory Mn(II) oxidation rates (Morgan, 1967) are orders of magnitude lower than those found in natural environments (e.g. Emerson *et al.*, 1982; Burdige and Kepkay, 1983; Burdige *et al.*, 1983; Tebo, 1991) due to the lack of bacterial catalysis in these experiments.

MANGANESE(II) DISTRIBUTION IN THE OCEAN

Coastal surface waters have relatively high Mn(II) concentrations that decrease with distance from shore (Fig. 1). Mn(II) profiles are considerably different from "nutrient like" trace metals such as Zn, Cd, and Ni (Bruland and Franks, 1983). Mn(II) profiles also do not exhibit "surface depletion, depletion at depth" characteristics of trace metals such as Fe and Cr, nor do Mn(II) concentrations have mid-depth concentration minima, as do scavenged elements such as Al (Donat and Bruland, 1995). Mn(II) profiles observed by Johnson *et al.* (1992) in the Pacific Ocean (Fig. 2) exhibit surface maxima, subsurface minima, deeper maxima associated with the oxygen minimum, and lowest levels in the deep sea, where oxygen is never completely depleted (Wyrtki, 1962). Observations of Mn(II) profiles by other investigators (e.g. Klinkhammer and Bender, 1980; Landing and Bruland, 1980, 1987; Martin and Knauer, 1985; Martin *et al.*, 1985) are consistent with these measurements and suggest steady state conditions. Steady state conditions reflect balances in Mn sources and sinks superimposed on internal biogeochemical and physical processes. Known Mn sources and sinks are explained in the next section and are followed by three theories proposed to explain Mn(II) profiles and, in particular, the occurrence of a secondary Mn(II) maximum associated with the oxygen minimum.

MANGANESE(II) SOURCES

Manganese is delivered to the ocean in oxidation states that reflect the source. Sources of Mn(II) to the ocean are rivers, hydrothermal vents (Klinkhammer *et al.*, 1985), upwelling of Mn(II) rich water, and Mn(II) ion dispersion from reducing sediments (Johnson *et al.*, 1992). The main supply of particulate Mn oxides to surface waters of the open ocean is thought to be from aeolian dust (Landing and Bruland, 1987). Photoreduction reactions of particulate Mn(III, IV) oxides to Mn(II) result in persistently high photic zone (Fig. 2) Mn(II) concentrations (Sunda *et al.*, 1983; Sunda and Huntsman, 1988, 1990). Ultraviolet light reduces Mn oxides through complex reactions whose mechanisms are still unknown. Sunda and Huntsman (1988) found a 12-fold increase in the dissolution rate of Mn oxides due to sunlight. Sunda and Huntsman (1990) also found that formation rates of Mn oxides during daylight hours were only 1.4 - 5% of rates at night. They attributed this to the combined effects of Mn oxide photodissolution and photoinhibition of Mn(II) oxidizing bacteria.

Sunda *et al.* (1983) suggested a combination of photoreduction and organic matter oxidation may be responsible for the persistence of Mn(II) surface maxima. They showed that additions of humic acid (5 mg/L) resulted in a two-fold increase in Mn(II) concentrations in the dark and a five-fold increase when exposed to light (290 μE $m^{-2}s^{-1}$). Laboratory studies by Xyla *et al.* (1992) found only slight effects on MnOOH and MnO_2 dissolution from light alone. Their studies showed a combination of light and a ligand/electron donor (oxalate) simulating natural organic acids substantially increased Mn oxide dissolution rates. Stone and Morgan (1984) found Mn(III,IV) oxide dissolution by fulvic acid was enhanced by light. The rapid decrease in Mn(II) concentration with depth is consistent with a decrease of light in the photic zone (Fig. 2).

MANGANESE(II) SINKS

Scavenging of metals is a function of both surface chemical properties and biological activity (Jannasch *et al.*, 1988). In the euphotic zone, primary producers may take up dissolved metals and, subsequent to their demise, sink below the photic zone. Chemical scavenging of Mn(II) from solution occurs by two processes. The first is by direct adsorption of Mn(II) on particle surfaces followed by oxidation to Mn(IV). The second is by direct oxidation of Mn(II) in colloidal form, which is then scavenged by larger particles. Adsorption of Mn(II) onto Mn oxide particle surfaces may be a strong mechanism for Mn(II) removal from the ocean water column (Balistrieri *et al.*, 1981). At pH = 8, hydrous Mn oxides are nearly twice as surface active as the most surface active clay minerals (Murray and Brewer, 1977). Martin and Knauer (1982) found that Mn(II) was rapidly scavenged from near shore surface waters on biogenic particles (2.4 nmol L^{-1} y^{-1}) and released slowly at depth (0.05 nmol L^{-1} y^{-1}).

Adsorption may occur primarily onto the surface of bacteria, as they comprise nearly one-half of the total amount of particulate organic matter. Bacteria are extremely small and therefore have high surface to volume ratios and an enormous total surface area for adsorption. Spores of a marine bacillus strain (SG-1) have been shown to passively catalyze Mn(II) oxidation without metabolic activity (Rosson and Nealson, 1982). Other studies have found certain strains of Mn(II) oxidizing bacteria contain plasmids, demonstrating active enzymatic oxidation of Mn(II) (Schuett *et al.*, 1986).

THEORIES TO EXPLAIN MANGANESE(II) PROFILES

The subsurface Mn(II) maximum is associated with the oxygen minimum (Fig. 2). Three main theories have been proposed to explain Mn(II) profiles and, in particular, the occurrence of a Mn(II) maximum associated with the oxygen minimum. These theories are termed the equilibrium theory, the lateral advection theory, and the kinetic theory.

EQUILIBRIUM THEORY

The order of oxidants consumed in the oxidation of organic carbon has been shown as O_2 > Mn oxides = nitrate > Fe oxides > sulfate (Froelich *et al.*, 1979). This order suggests that consumption, decomposition, and recycling of organic particles sinking through the water column results in remineralization of Mn(II). Areas of high productivity, such as coastal regions, have large quantities of sinking organic matter. Therefore, high coastal productivity results in nearshore Mn(II) concentrations that are much higher than Mn(II) concentrations found offshore (Fig. 1).

The equilibrium theory suggests Mn(II) concentrations are controlled by thermodynamic equilibrium with Mn oxides. As oxygen and pH change, the Mn(II) concentrations will respond to maintain the equilibrium. In the oxygen minimum, where pH and oxygen concentrations are low, the reaction (Eqn. 1) shifts, resulting in Mn oxide remineralization and the formation of Mn(II) to maintain equilibrium. Klinkhammer and Bender (1980) considered the equilibrium theory in detail. Their model, however, overestimated Mn(II) concentrations in strong oxygen minima by several orders of magnitude and failed to reproduce Mn(II) minima between primary and secondary Mn(II) maxima .

If Mn oxide dissolution occurs, decreasing Mn oxide concentrations with depth are expected. Landing and Bruland (1987) and Martin and Knauer (1984) reported evidence of *in situ* Mn oxide dissolution within the oxygen minimum zone of the eastern tropical North Pacific. However, with the exception of high productivity coastal regions where nitrate reduction is observed, Mn(II) remineralized from particles sinking through the oxygen minimum is not thought to be responsible for increased Mn(II) concentrations. At open ocean stations, contrary evidence of Mn oxide concentrations increasing with depth was found (Martin *et al.*, 1985). Increasing Mn oxide concentrations with depth suggest Mn(II) is scavenged onto particles sinking through the oxygen minimum. A sediment trap study by Landing and Bruland (1987) found short residence times (105 - 235 d) for settling particulate refractory Mn from the upper water column and long residence times for scavenging of Mn(II) (3 - 74 y). These works support the concept that large particles rapidly pass through the upper water column and result in very little Mn(II) remineralization. Martin and Knauer (1985) found Mn(II) removal (-0.027 nmol L^{-1} y^{-1}) onto sinking biogenic particles in the oxygen minimum zone (500 - 1,100 m) of the northeast Pacific Gyre without a decrease in Mn(II) concentration. This result was interpreted to mean advective horizontal transport was supplying the region with Mn(II).

LATERAL ADVECTION THEORY

Secondary Mn(II) maxima have been suggested to result from Mn(II) diffusion out of continental sediments intersecting the oxygen minimum, which is laterally advected offshore (Martin and Knauer, 1985). A prior paradigm suggested dissolved metals are released to the water column in regions where sediments intersect low oxygen bottom waters. Johnson *et al.* (1992) discovered lower fluxes of Mn(II) from sediments intersecting the oxygen minimum zone than from sediments in more oxygenated, shallower coastal waters. A new paradigm suggests organically associated Mn is remineralized in oxygenated sediments, resulting in a Mn(II) flux to the water column. The remineralization is thought to be the result of aerobic bacteria in the fluff layer of organic material at the sediment-water interface, and not in the sediments. Sediments do not account for the flux, possibly because high concentrations of surface sites result in Mn oxidation before Mn(II) can reach the sediment-water interface. The study by Johnson *et al.* (1992) showed Mn(II) fluxes from shallow coastal shelf regions could only account for local elevated Mn(II) concentrations. Sediments which intersect the oxygen minimum, however, could not be responsible for subsurface Mn(II) maximum in the open Pacific Ocean.

KINETIC THEORY

A kinetic theory to explain ocean Mn(II) concentrations has been suggested (Landing and Bruland, 1980, 1987) and, with recent knowledge of organic carbon cycling, is now quantified (Johnson *et al.*, 1996). In this model, subsurface Mn(II) maxima occur in regions where oxygen minima coincide with high carbon flux and resultant Mn(II) remineralization. The persistence of high Mn(II) concentrations in the subsurface secondary maximum may be related to slow Mn(II) oxidation kinetics in this region. In areas of low oxygen (< 100 μM) and pH (7.8 - 8.0), Mn(II) may take a long time (several years) to oxidize to Mn(IV), which allows relatively high Mn(II) concentrations to accumulate. The kinetic model requires the rate constant for Mn(II) oxidation rates, in natural seawater with nM concentrations of Mn(II), to calculate the ocean distribution of dissolved Mn(II). In this thesis project Mn(II) oxidation rates in seawater were determined. These rates were used to calculate a scavenging term in a quantitative model that accurately predicts open ocean Mn(II) concentrations (Johnson *et al.*, 1996).

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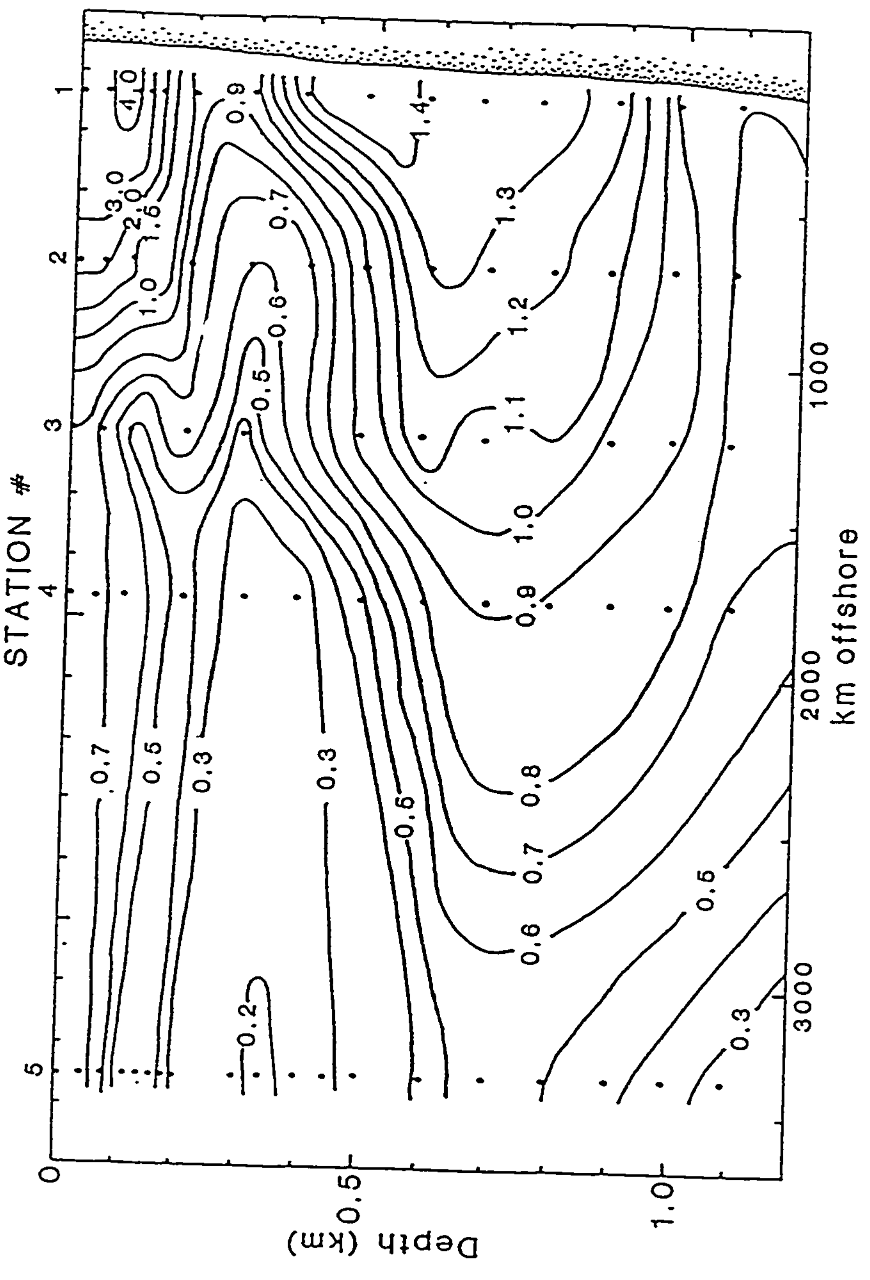
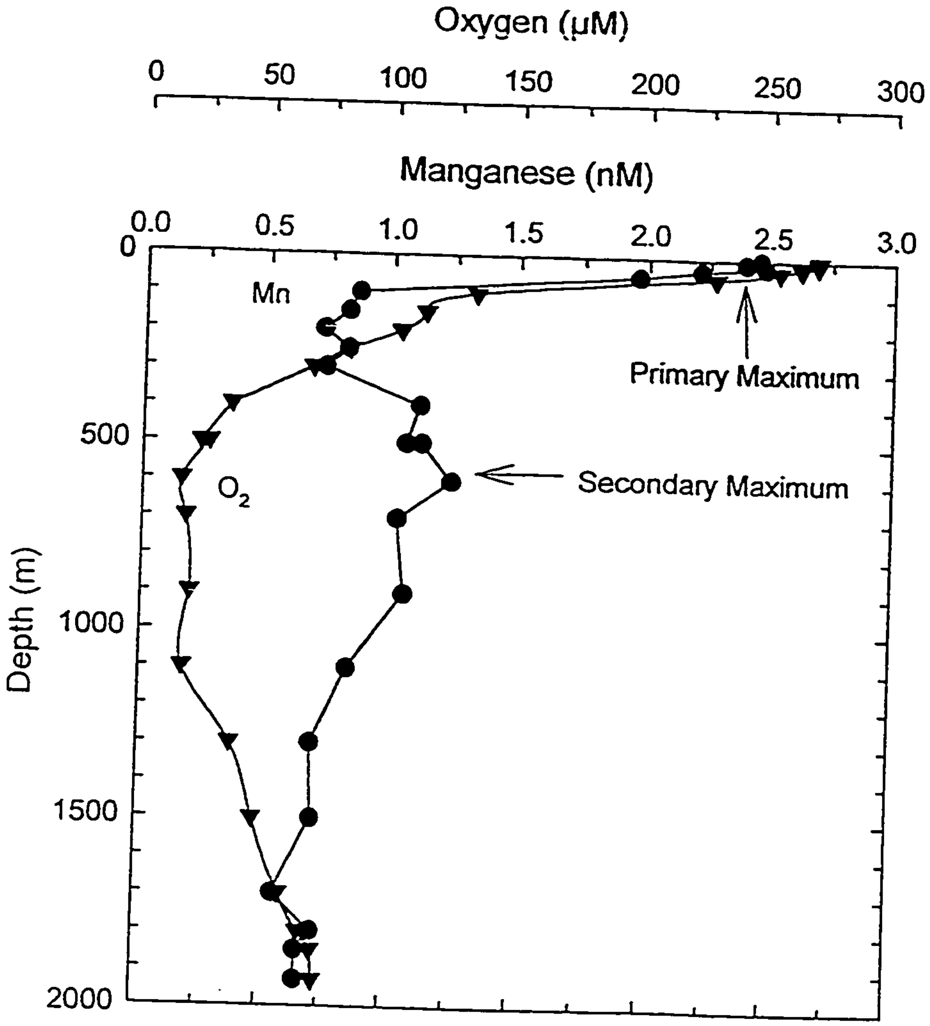
Figure Captions

Figure 1. Mn(II) concentrations vs. depth and distance offshore interpreted by Martin *et al.* (1985) for data from Vertex cruises IV and V stations 1 - 5 (figure copied with permission from Martin *et al.*, 1985).

Figure 2. Pacific Ocean Mn(II) (●) and oxygen (▼) profiles off the California coast at 35° 15'N and 121° 52'W (from Johnson *et al.*, 1992). The secondary Mn(II) maximum is associated with the oxygen minimum.


STATION #
1
2
3
4
5
km offshore
1000
2000
3000
Depth (km)
0
0.5
1.0
4.0
3.0
2.0
1.5
1.0
0.9
0.7
0.6
0.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.3
0.7
0.5
0.3
0.3
0.5
0.2


Oxygen (µM)
0
50
100
150
200
250
300
Manganese (nM)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
0
500
1000
1500
2000
Depth (m)
Mn
O₂
Primary Maximum
Secondary Maximum

CHAPTER 2

OXIDATION RATES OF MANGANESE(II) AT NANOMOLAR CONCENTRATIONS IN SEAWATER

ABSTRACT

Manganese oxidation rates were determined at low (≈ 20 nM) concentrations in seawater by measuring dissolved manganese (Mn(II)) using flow injection analysis with chemiluminescence detection. Mn(II) was measured in samples that had been filtered (0.2 μm) and kept in the dark under controlled temperature and pH conditions. Eight 20 L carboys with mean pH values ranging from 8.17 to 8.75 were held at 25°C, another carboy (pH = 9.32) was kept at 5°C. Oxidation followed Morgan's (1967) homogeneous rate equation ($d[Mn(II)]/dt = k_1[O_2]\{OH^-\}^2[Mn(II)]$). Rate constants for all carboys at 25°C were similar ($k_1 = 1.2 - 3.6 \times 10^{12}$ $M^{-3} d^{-1}$) and in agreement with work by Morgan (1967; $k_1 = 4 \times 10^{12}$ $M^{-3} d^{-1}$) and Davies and Morgan (1989; $k_1 = 1.1 \times 10^{12}$ $M^{-3} d^{-1}$) in dilute solutions. The rate constant at 5°C ($1.3 \pm 0.3 \times 10^{12}$ $M^{-3} d^{-1}$) was approximately 2-fold lower than the average rate constant ($2.1 \pm 0.5 \times 10^{12}$ $M^{-3} d^{-1}$) determined for samples at 25°C. Autocatalytic increases in Mn(II) oxidation rates, as predicted by a heterogeneous reaction mechanism (Morgan, 1967) ($d[Mn(II)]/dt = k_2'[Mn(II)][MnO_2]$) were not observed, indicating the homogeneous reaction dominates Mn(II) oxidation at low nM concentrations in seawater. Bacteria were enumerated by 4',6-diamidino-2-phenylindole (DAPI) staining during the experiments. No significant correlation between bacterial concentrations and Mn(II) oxidation rates was found.

INTRODUCTION

In natural waters, manganese (Mn) is found in the +II, +III, and +IV oxidation states (Stumm and Morgan, 1981). The primary dissolved form of Mn is thought to be Mn(II). Mn(III) and Mn(IV) are thought to be essentially insoluble as Mn oxides. Although recent work by Kostka *et al.* (1995) suggests that there may be some soluble Mn(III) complexes in natural waters, they are likely to be present only as meta-stable intermediates.

Mn(II) reacts with oxygen in basic solution to produce various forms of Mn oxides. In the highly oxidizing alkaline conditions typical of the ocean environment, pE-pH diagrams indicate that Mn should be found predominantly in the form of particulate $MnO_2(s)$ (Stumm and Morgan, 1981). At ordinary temperature and pressure, the initial product of Mn(II) oxidation in highly oxidizing environments is δ-MnO_2 (birnessite; Morgan, 1967).

$$Mn^{2+} + 2H_2O \Longleftrightarrow \delta\text{-}MnO_2(s) + 4H^+ + 2e^- \qquad (1)$$

The formation of Mn oxides in seawater is thermodynamically favored (Morgan, 1967). If we assume δ-MnO_2 is controlling Mn(II) concentrations in alkaline well oxygenated seawater and the equilibrium constant for Eqn. 1 is 2.5×10^{-44} (Stumm and Morgan, 1981), then at $pH = 8$ and $pE = 12.8$, the calculated Mn(II) concentrations are $\approx 1.6 \times 10^{-15}$ M. Vertical profiles of dissolved Mn(II) in the open ocean (Johnson *et al.*, 1992; Landing and Bruland, 1980, 1987; Martin and Knauer, 1982, 1985; Martin *et al.*, 1985, 1987) exhibit nM ($\approx$ 0.1 - 20) Mn(II) concentrations with surface maxima rapidly decreasing with depth, and secondary Mn(II) maxima associated with the oxygen minimum (Fig. 1). With respect to δ-MnO_2, equilibrium calculations for Mn(II) concentrations are orders of magnitude lower than observed seawater Mn(II) concentrations. Observed non-equilibrium Mn(II) concentrations suggest that slow kinetic Mn(II) oxidation rates are controlling ocean Mn(II) distribution. Many studies of Mn(II) distribution have focused on non-equilibrium processes (Landing and Bruland, 1980; Martin and Knauer, 1982, 1985; Martin *et al.*, 1985; Johnson *et al.*, 1996). These past studies were not able to quantify Mn(II) distributions because of insufficient knowledge of the rates of the relevant processes. With recent advances in the understanding of carbon cycling, it is now possible to quantify Mn uptake and remineralization rates. Inorganic Mn(II) oxidation rates have not been measured in seawater. Kinetic studies of Mn oxide formation rates in seawater are needed to quantify the rates of transformations as a factor in a kinetic model for ocean Mn(II) distributions (Johnson *et al.*, 1996).

The kinetics of Mn(II) oxidation in natural waters have been described by the following equation from Morgan (1967):

$$-d[\mathrm{Mn(II)}]/dt = k_1' [\mathrm{Mn(II)}] + k_2' [\mathrm{Mn(II)}] [\mathrm{MnO_x}] \qquad (2)$$

$$\text{where} \qquad k_1' = k_1 [O_2] \{OH^-\}^2 \ \text{ with } k_1 = 4 \times 10^{12}\ M^{-3}\ d^{-1}$$

$$\text{and} \qquad k_2' = k_2 [O_2] \{OH^-\}^2 \ \text{ with } k_2 = 10^{18}\ M^{-4}\ d^{-1}$$

This equation's first term (k_1' [Mn(II)]) represents homogeneous oxidation and the second term (k_2' [Mn(II)] [MnO_x]) describes a heterogeneous autocatalytic mechanism due to Mn oxide surfaces. Mn(II) oxidation may, therefore, be autocatalytic as Mn oxide formation exponentially increases additional binding of Mn(II) to the particulate surfaces. Landing and Bruland (1980) found open ocean concentrations of particulate Mn to be less than 0.4 nM. If we assume all of the Mn in particles are Mn oxides, then $k_2 \times [MnOx] < 2 \times 10^9\ M^{-3}\ d^{-1}$. The upper limit on the pseudo third order heterogeneous Mn oxidation rate in open ocean seawater is three orders of magnitude less than the homogeneous rate constant in Eqn. 2. Inorganic Mn(II) oxidation in open ocean seawater with low particle concentrations is therefore assumed to proceed by Morgan's (1967) homogeneous reaction:

$$-d[Mn(II)]/dt = k_1' [Mn(II)] = k_1 [Mn(II)] [O_2] \{OH^-\}^2 \qquad (3)$$

Although Mn(II) oxidation in seawater is assumed to proceed by a homogeneous mechanism (Eqn. 3), it is necessary to consider bacterial catalysis of the reaction rate. Mn(II) oxidation rates have been shown to increase by at least 3 to 5 orders of magnitude in the presence of Mn(II) oxidizing bacteria (Hastings and Emerson, 1986) and several papers have suggested that microbial oxidation is the principal pathway in the marine environment (Tebo and Emerson, 1986; Sunda and Huntsman, 1988; Moffett, 1994). Catalytic oxidation of Mn(II) by bacteria has been suggested in a variety of aquatic environments including lakes (Johnston and Kipphut, 1988; Miyajima, 1992), rivers (Ponter *et al.*, 1992), estuaries (Sunda and Huntsman, 1987), sediments (Burdige and Kepkay, 1983; Burdige *et al.*, 1983), hydrothermal vents (Cowen *et al.* 1986, 1990), suboxic regions (Tebo, 1991; Tebo *et al.*, 1991) and in coastal seawater (Sunda and Huntsman, 1990). Studies have shown that laboratory Mn(II) oxidation rates (Morgan, 1967) are orders of magnitude lower than those found in natural environments (e.g. Emerson *et al.*, 1982; Burdige and Kepkay, 1983; Burdige *et al.*, 1983; Tebo, 1991). These studies have generally been conducted in environments with high Mn(II) concentrations and may not be typical of the open ocean. Accurate measurements of the inorganic Mn(II) oxidation rate in seawater are needed to fully assess the role of bacteria in Mn(II) removal.

Previous work on Mn(II) oxidation kinetics (Morgan, 1967; Davies and Morgan, 1989) has been done on low ionic strength samples with high initial Mn(II) concentrations (μM - mM). This work was designed to determine inorganic Mn(II) oxidation rates in seawater at natural nM Mn(II) concentrations under controlled conditions of varying pH and temperature. The results are used as a parameter in a kinetic model which accurately predicts open ocean Mn(II) concentrations (Johnson *et al.*, 1996).

METHODS

SAMPLE COLLECTION

Seawater samples were collected on two separate cruises. Santa Barbara Channel Seawater (SBCS) was collected while aboard the R/V Point Sur during March of 1994. Samples were collected at 50 m depth by 10 liter General Oceanics Niskin bottles mounted on a General Oceanics rosette. Previous measurements have demonstrated that this system does not contaminate samples with Mn(II) (Chapin *et al.*, 1991; Johnson *et al.*, 1992). Samples were drawn into acid cleaned polycarbonate carboys (25 L). Monterey Bay surface seawater (MBSS) was collected from the bow of an inflatable boat while heading upwind. Long plastic gloves were worn while filling acid cleaned polycarbonate carboys (25 L) held over the side. Carboys and spigots were covered with plastic bags and plastic gloves, respectively, to avoid possible trace metal contamination.

EXPERIMENTAL PARAMETERS

Studies of Mn(II) oxidation kinetics at nM seawater concentrations were performed under conditions of varying pH and temperature in a similar fashion to studies of Fe(II) oxidation kinetics (Millero *et al.*, 1987; King *et al.*, 1995). Figure 2 shows a schematic representation of methods explained in the following paragraph. Carboys of seawater (25 L) were spiked to initial Mn(II) levels (≈ 20 nM). Seawater pH was adjusted (8.17 - 9.32) by 7.4 M ammonium hydroxide (NH_4OH) additions. When a desired pH level was attained, seawater was filtered (0.2 μm) into microwave-sterilized (Keller *et al.*, 1988) carboys (11 L). Eight carboys with pH values ranging from 8.17 - 8.75 were stored at 25°C in an incubator, and one carboy with a pH value of 9.32 was refrigerated at 5°C. All carboys were covered by three dark plastic bags to inhibit Mn oxide photo-dissolution (Sunda *et al.*, 1983; Sunda and Huntsman 1988, 1990) and were shaken every few days to ensure homogeneity. Salinity measurements were determined by a bench top inductive salinometer (Beckman Instruments, Inc.) for MBSS (33.3 PSU) and SBCS (33.6 PSU). Equations from Benson and Krause (1984) were used to calculate oxygen concentrations in samples that were in atmospheric equilibrium. To make certain calculated oxygen concentrations were correct, oxygen concentrations were also measured by Winkler titration. All plastic-ware used in the experiment was initially cleaned by soaking for at least one week in a MICRO® detergent (International Products Corporation) and deionized water solution. Plastic-ware was then rinsed three times with Milli-Q and placed in a 0.01 M hydrochloric acid (HCl) bath for a minimum of one week. After the acid bath, plastic-ware was thoroughly rinsed with Milli-Q.

MANGANESE(II) DETERMINATION

Flow Injection Analysis

Samples were drawn into volumetric flasks approximately once a month for analysis. For each pH range, standards (+5, +7.5, and +10 nM Mn(II)) were made by adding 25 μL, 37.5 μL, and 50 μL of 10 μM Mn(II) respectively, to 50 mL seawater samples. Mn(II) concentrations were determined by flow injection analysis (FIA) with chemiluminescence detection (Chapin *et al.*, 1991). Mn(II) catalyzes the oxidation of 7,7,8,8-tetracyanoquinodimethane (TCNQ), releasing photons at a rate proportional to the concentration of Mn(II). The application of FIA enabled relatively quick, easy, and inexpensive Mn(II) determinations with minimal sample handling. The FIA manifold was set up generally as described by Chapin *et al.* (1991). Modifications to optimize the system are noted in the following text. Reagent R1 (5 mL Eosin Y, 1.85 g DDAB, 0.05 g TCNQ, 1 liter Milli-Q) supplied TCNQ which mixed with a 0.5 M solution of NH_4OH. In this study more TCNQ (0.05 g) was used than that reported (0.01 g) by Chapin *et al.* (1991). NH_4OH reduced blanks associated with pH shifts during sample injection, without reducing sensitivity. Therefore, NH_4OH was used instead of sodium hydroxide as in Chapin *et al.* (1991). The use of NH_4OH resulted in the system being very sensitive to pH. The system was optimal when the pH of

NH_4OH and the waste effluent were 11.4 ± 0.1 and 11.0 ± 0.1, respectively. This alkaline NH_4OH-reagent R1 blend mixed with samples in the detection cell. An automated multi-port stream selection valve controlled the flow of sample load, Milli-Q, and 0.0025 M HCl. The flow and subsequent mixing of seawater samples and reagents was driven by a Rainin Rabbit Plus® peristaltic pump. Unlike the technique utilized by Chapin *et al.* (1991), the sample line was extended and rerouted around the pump to reduce blanks associated with column back pressure effects. Samples were pumped (2.7 mL min^{-1}) for 4 minutes through 0.8 mm i.d. Teflon tubing into a chelator column of immobilized 8-hydroxyquinoline (8-HQ). The procedure determined by Landing *et al.* (1986) was used to immobilize 8-HQ with the exception that Toyopearl® resin (Tosohaas) replaced Fractogel-TSK. The 8-HQ column acts as a ligand to bind Mn(II), concentrating it from the sample. The 8-HQ column only weakly binds other cations such as calcium (Ca^{2+}) and magnesium (Mg^{2+}), which in natural seawater concentrations interfere with Mn(II) determinations. For example, Mg^{2+} at seawater concentrations (53 mM) was found to give a signal equivalent to 1 nM Mn(II) (Chapin *et al.*, 1991). The stream selection valve immediately turned following the sample injection and allowed a Milli-Q rinse to flow (2.7 mL min^{-1}) through the column and remove these other cations for 120 seconds. The injection valve then switched to the elute position and 0.0025 M HCL flowed (2.7 mL min^{-1}) through the column in the reverse direction for 120 seconds. The acid eluted Mn(II) from the column and immediately mixed with the TCNQ-NH_4OH solution in the flow cell. The oxidation of TCNQ produced light which was measured and recorded. During the period of column elution, the multi-port stream selection valve rotated so that the 0.0025 M HCL filled the line between the two valves. This acid washed any remaining metals from the 8-HQ column when the injection valve switched back to the load position for the next sample.

Signal Detection

The detector flow cell was constructed of 25 cm long 1.27 mm i.d. clear PVC tubing coiled into a grey PVC holder. The PVC holder was bolted onto the shutter of a Pacific Instruments Model 3547 photomultiplier tube (PMT) housing which contained a Hamamatsu R268 PMT. The photomultiplier output signal was amplified by a Pacific Instruments Model 126 laboratory photometer, and the analog output was converted to a digital signal with a Metrabyte Dascon-1, 12 bit analog-to-digital converter. The analog signal was digitized every 0.3 seconds and stored on disk in a microcomputer. A strip chart recorder was used for backup records.

Mn(II) Seawater Standard

Variations in reaction efficiency were monitored by using an acidified seawater sample that was analyzed with each batch of samples. This standard was filtered SBCS acidified to pH 2. All Mn was in the dissolved phase (Mn(II)) and, because of the highly acidic condition, remained in solution. Therefore, Mn(II) concentrations in this standard did not vary with time. Measurements of this standard were used to check for system chemistry variations. Each day of sample analysis, 25 μL of tris(hydroxymethal)aminomethane buffer (TRIS) (J.T. Baker Chemical Co.) was added to 20 mL of the seawater standard. The TRIS increased the pH of the seawater standard to 8.2, so that it was alkaline enough for analysis by FIA (Chapin *et al.*, 1991).

MEASUREMENTS OF pH

Measurements of pH were made by both potentiometric (Bates, 1964) and spectrophotometric (Byrne *et al.*, 1988; Byrne and Breland, 1989) methods. The potentiometric method used the National Bureau of Standards (NBS) scale of hydrogen ion activity while the spectrophotometric method measured free hydrogen ion concentration. Byrne *et al.* (1988) reported that seawater pH measurements at 25°C determined by the spectrophotometric method were within 0.02 pH units of those determined by the potentiometric method using the NBS scale. Measurements of pH by both techniques were made at 25°C in this experiment, including the samples from the 5°C experiment. The *in situ* pH of the 5°C sample was estimated by correcting for the effect of temperature on carbonate dissociation constants (Millero, 1979). The 5°C sample was also corrected for the high total alkalinity ($\approx 3600 \mu Eq/L$) and dissociation of ammonium that resulted from adding 2 mL of 7.4 M NH_4OH to 11 L of seawater (Millero, 1995). The ammonium dissociation constants were converted to the NBS pH scale (Millero, 1979). Variations in sample pH, due to carbon dioxide exchange with the atmosphere, were minimized by immediately placing samples into airtight reaction cells along the circulating temperature control bath. To be consistent with Morgan (1967), all results were calculated using potentiometric method calibrated with NBS buffers.

BACTERIAL ENUMERATIONS

Bacteria were counted by 4',6-diamidino-2-phenylindole (DAPI) staining (Coleman, 1980; Porter and Feig, 1980). DAPI stains DNA so that bacteria appear bright white under an epifluorescence microscope. Samples (20 mL) were fixed with 10% gluteraldehyde (1 mL) resulting in 0.5% gluteraldehyde concentrations. After a few minutes, samples were poured into glass filter chimneys and passed through 0.2 μm polycarbonate and 1 μm Millipore backing filters with a vacuum pump (127 - 152 mm Hg). Filter chimneys were rinsed with Milli-Q and a small volume (1 - 2 mL) of solution left above the filters was stained for 3 - 4 minutes with 0.5 mL DAPI. Filter chimneys were again rinsed with Milli-Q and the solution carefully pulled through, so filters would not dry out. Filters were placed on labeled microscope slides and a small drop of Type B immersion oil was added. Slides were then secured with glass cover slips and stored in a refrigerator. Within one week, bacterial concentrations were determined by counting individual bacteria at 1000 x total magnification with a Zeiss Axiovert 10 epifluorescent microscope. Bacteria were counted in 10 randomly spaced squares in 10 x 10 grids with surface areas of 0.01 mm^2 $grid^{-1}$. These grids were subsamples of the total filter area (201 mm^2). After counting bacteria in a grid, slides were randomly moved and the process repeated until at least 400 bacteria and 4 grids were counted. The numbers of bacteria were extrapolated to the sample size and converted to densities of bacterial cells/mL.

RESULTS AND DISCUSSION

MANGANESE(II) OXIDATION RATES

Decreases in Mn(II) concentration may result from Mn(II) oxidation or from adsorption of Mn(II) on container walls. A mass balance equation for Mn is as follows:

$$Mn_{total} = Mn_{dissolved} + Mn_{oxides} + Mn_{adsorbed\ to\ container} \qquad (4)$$

It was not possible to determine the Mn adsorbed to container walls directly without sacrificing each experiment to perform a mass balance. A control experiment was, therefore, run to ascertain any surface adsorption effects of carboy interiors. This experiment used two different sized (60 mL and 11 L) containers. 60 mL bottles were filled with SBCS adjusted to pH levels of 8.23 and 8.69. Measurements of Mn(II) in the 60 mL bottle control samples were made on the same days as SBCS samples from 11 L carboys. If there were significant surface adsorption effects, higher surface to volume ratios in smaller containers (60 mL) would have resulted in lower Mn(II) concentrations than in larger containers (11 L). The control experiment showed no effect of Mn(II) adsorption on carboy walls (data not shown). We assume, therefore, that no adsorption occurred over the course of the experiments.

At constant pH and oxygen, the homogeneous reaction of Mn(II) can be considered as pseudo first order. The solution to Eqn. 3 is then:

$$Mn_t = Mn_0\, e^{-k_1't} \qquad (5)$$

A least squares fit of ln[Mn(II)] versus time can be used to obtain Mn(II) oxidation rate constants (k_1'). In each case (Figs. 3-5), the data are consistent with a linear relationship between ln[Mn(II] and time. The linear decrease of ln[Mn(II)] with time indicates that autocatalytic oxidation or bacterial catalyzed Mn(II) oxidation did not occur. These results are consistent with the heterogeneous term in Eqn. 2 not being significant in filtered or open ocean seawater because of extremely low Mn oxide concentrations.

We have treated our results as being entirely due to homogeneous Mn(II) oxidation. The slope of the semi-log plot for each experiment corresponds to the pseudo first order rate constant ($k_1' = k_1 [O_2] \{OH^-\}^2$). The homogeneous rate constant (k_1) was determined by correcting k_1' for the observed oxygen and hydroxide ion concentrations. Oxygen concentrations measured by Winkler titration (205 - 217 μM) were consistent with concentrations calculated (213 μM at 25°C) for samples in atmospheric equilibrium (Benson and Krause, 1984). Samples at 5°C were not measured but were assumed to be in atmospheric equilibrium ($O_2 = 320\,\mu$M).

Unlike results reported by Byrne *et al.* (1988), large differences in measured pH were found between potentiometric and spectrophotometric methods. On average, pH measurements determined by potentiometer were 0.15 ± 0.1 pH units higher than those determined by spectrophotometer. Both potentiometric and spectrophotometric pH measurements detected decreases in sample pH over the duration of each experiment. Decreases in measured pH with time were larger for the spectrophotometric method than for the potentiometric method. On the potentiometric scale, pH decreases were approximately 0.1 - 0.2 pH units over 6 months. Monthly pH measurements were averaged to estimate a mean pH for each experiment (Table 1). The pH changes were probably due to changes in laboratory air pCO_2. Other possibilities which could contribute to the drops in pH include HCl leaching out of acid washed carboys and bacterial respiration. Two Monterey Bay samples at pH = 8.17 and 8.28 (Fig. 3) showed large decreases (0.9 pH units) in observed pH during their experimental runs which then increased (0.6 pH units) approaching the end of the experiment. The large decreases in pH measured in these two samples were too large to be accounted for by the previous explanations and we did not arrive at any other plausible answers. The lowest pH measurements were, therefore, assumed to have been in error and were not included in mean pH calculations for these carboys (Table 1, Fig. 3). To be consistent with the NBS scale, hydroxide ion activities were calculated using values for pKw of 14.00 and 14.73 for samples at 25°C and 5°C, respectively (Harned and Owen, 1958).

Confidence intervals (CI) for the rate constants (k_1) were determined by combining the 95% CI of the pseudo first order rate constants (k_1') with the 95% CI of the potentiometric pH measurements. For each experiment, the change in ln[Mn(II)] with time was used to calculate an average pseudo first order rate constant (k_1') and pseudo first order rate constant 95% CI ($\delta\, k_1'$). Variations in sample pH over time were converted to average ($\{OH^-\}$) and 95% CI ($\{\delta\, OH^-\}$) hydroxide activities. Because of the second order effect of {OH-} on Mn oxidation rate constants (k_1), 95% confidence intervals ($\delta\, k_1$) in the rate constants are calculated from the following equation (Daniels *et al.*, 1970):

$$\delta\, k_1/k_1 = [[\delta\, k_1'/k_1'] + 2\,\{\delta OH^-/OH^-\}] \qquad (6)$$

PARAMETERS AFFECTING MANGANESE(II) OXIDATION

Effects of pH on Mn(II) Oxidation Rates

Samples with higher pH values generally exhibited faster pseudo first order oxidation rate constants (k_1') (Table 1). Figure 6 shows the $\log_{10}$ of the pseudo first order rate constants (log k_1') plotted versus pH for the eight experiments at 25°C and $pO_2 = 0.22$ atm. The slope is equivalent to the reaction rate dependence on hydroxide concentration. The calculated slope of 1.5 ± 0.3 is near the predicted value of 2 if there is second order hydroxide concentration dependence, as in Morgan's (1967) homogeneous rate Eqn. (5). A line which represents second order dependence on pH is shown for clarity (Fig. 6).

Davies and Morgan (1989) tabulated Mn(II) oxidation rates in the absence of metal oxides at 25°C and $pO_2 = 1.0$ atm. for their own data as well as that from Morgan (1967). Davies and Morgan (1989) and Morgan (1967) ran their experiments at higher initial levels of Mn(II) (50 μM and 450 μM, respectively), higher pH levels (9 - 9.5), and lower ionic strength (0.1 M $NaClO_4$ and $[HCO_3^-] + [CO_3^{2-}] = 1.6$ mM, respectively) than our experiments. When our rates are converted to values expected at $pO_2 = 1.0$ atm and then compared to those determined by Morgan (1967) and Davies and Morgan (1989), it is apparent that there is remarkable agreement between them (Fig. 7). Over a pH range of 8.17 to 9.5, Mn(II) oxidation rates exhibit linear ($R^2 = 0.95$), second order behavior (slope = 2.3 ± 0.3) with respect to pH or hydroxide activity. We have, therefore, assumed that all of the Mn(II) oxidation rates can be modeled as a process second order in hydroxide activity.

Rate constants derived from our data were similar for all samples at 25°C (average = $2.1 \pm 0.5 \times 10^{12}$ $M^{-3}d^{-1}$) and were the same for SBCS and MBSS (Table 1). Diem and Stumm (1984) report that Morgan (1967) found a homogeneous Mn(II) oxidation rate constant of 4×10^{12} $M^{-3}d^{-1}$. A rate constant of 1.1×10^{12} $M^{-3}d^{-1}$ is derived from the data reported by Davies and Morgan (1989) if oxidation with respect to $\{OH^-\}$ is assumed to be second order (Fig. 7). The average Mn(II) oxidation rate constant determined from the combined data sets (n = 14) is $2.4 \pm 0.6 \times 10^{12}$ $M^{-3}d^{-1}$. The excellent agreement with our data at high ionic strength (0.7 M) and low Mn(II) concentrations (nM) suggests that neither ionic strength nor Mn(II) concentrations significantly affect Mn(II) oxidation rate constants (k_1). In a like manner, Fe(II) oxidation rate constants have been found to be similar in experiments that utilized nM (King *et al.*, 1995) and μM (Millero, 1985; Millero *et al.*, 1987) dissolved iron (Fe(II)) concentrations. As we show below, transition state theory would suggest little or no ionic strength effect on Mn(II) oxidation rates.

Effects of Salinity on Mn(II) Oxidation Rates

Transition state theory can be used to predict how the rate of a reaction is affected by variations in ionic strength (Morel and Hering, 1993). Electrostatic interactions between reactants and ions in solution may increase, decrease, or have no effect on a reaction's rate constant in comparison to the rate constant determined for infinitely dilute solutions. Inherent in the transition state theory is the assumption that an activated complex is formed in the rate limiting step, which dissociates to form the products. The concentration of this activated complex is proportional to the reaction rate.

Variations in ionic strength change the equilibrium constant for the formation of the activated complex, thereby altering rate constants. Debye-Huckel theory can be used to predict how ionic strength (I) will change activity coefficients (γ):

$$\log \gamma = -AZ^2\sqrt{I} \tag{7}$$

In Eqn. 7, Z is the charge on the reactant, and A is a constant that depends on the dielectric constant and absolute temperature. Activity coefficients are solved for each reactant in the rate limiting equation. The Debye-Huckel rate law works well in predicting activity coefficients in low ionic strength solutions ($I < 0.01$); however, it does not work well at higher ionic strengths. The Davies equation, a modification of the Debye-Huckel equation, is more accurate at predicting activity coefficients in higher ionic strength solutions such as seawater ($I = 0.7$):

$$\log \gamma = -AZ^2((\sqrt{I} / (1 + \sqrt{I})) - 0.3I) \tag{8}$$

Changes in activity coefficients (γ) results in a revised rate constant (k) in accordance with the following relationship

$$k = k_0 \gamma A \ \gamma B / \gamma^{\dagger} \tag{9}$$

where k_0 is the known rate constant in infinitely dilute solution, γ_A and γ_B are activity coefficients of reactants, and $\gamma^\dagger$ is the activity coefficient of the rate limiting activated complex. Substituting Eqn. 8 into Eqn. 9 gives:

$$\log k = \log k_0 + 1.02 Z_A Z_B((\sqrt{I}/(1+\sqrt{I})) - 0.3I) \qquad (10)$$

In Eqn. 10, k_0 is the rate constant in infinitely dilute solution, k is the rate constant in a solution of known ionic strength (I), and Z_A and Z_B are the charges of the first and second reactants. Positive and negative values for $Z_A Z_B$ increase and decrease reaction rates in higher ionic strength solution, respectively. If one of the reactants in the rate limiting step is neutral charged ($Z_A Z_B = 0$), we predict by transition state theory that there would be no change in rate constants resulting from variations in ionic strength. Therefore, if oxygen is a reactant in the rate limiting step ($Z_A Z_B = 0$), according to transition state theory, the Mn(II) oxidation rate constant will not differ due to changes in ionic strength. Mn(II) oxidation rates in freshwater (k_0) would be similar to rates found at higher ionic strength solutions (k), such as in seawater ($I = 0.7$).

The effects of salinity on reaction rates in seawater have been investigated in several studies (Johnson, 1982; Millero, 1985). In each case, transition state theory was found to provide a good estimate of the ionic strength effect on reaction rates in seawater. Rate constants determined in this experiment ($2.1 \pm 0.5 \times 10^{12}$ $M^{-3} d^{-1}$) were not significantly different from the mean of the low ionic strength results determined by Morgan (1967, 4×10^{12} $M^{-3} d^{-1}$) and Davies and Morgan (1989, 1.1×10^{12} $M^{-3} d^{-1}$). Millero (1985) reported Fe(II) oxidation rates in seawater that were approximately 30% slower than those in freshwater due to the formation of chloride and sulfate ion pairs. This small effect would be within the uncertainties of the low ionic strength data and agree with transition state theory predictions. Further research is needed to determine if there is a small (< 30%) effect on Mn(II) oxidation rates due to complexation of Mn(II) in seawater.

Effects of Temperature on Mn(II) Oxidation Rates

The pH of the cold sample (5°C) measured at 25°C was 8.95 ± 0.3. Using the dissociation constants for ammonium (Millero, 1995) and the carbonate system (Millero, 1979), and a titration alkalinity of 3600 μEq/kg (1300 μEq/kg from addition of NH_4OH), the pH was estimated as 9.32 at the temperature of the experiment (5°C). At first glance, the pseudo first order oxidation rate constant ($k_1' = 0.0064 d^{-1}$) of the 5°C sample (Fig. 5) is lower than expected in comparison to other samples with similar pseudo first order oxidation rate constants (k_1') but lower pH values (Figs. 3 - 4, Table 1). This is because oxygen concentration (Benson and Krause, 1984) and the ion product of water (Kw) change with temperature. Kw at 5°C (0.18×10^{-14}) is lower than at 25°C (1.01×10^{-14}). Reductions in the ion product of water (Kw) correspond to matching reductions in hydroxide activity $\{OH^-\}$:

$$\{OH^-\} = Kw / \{H^+\} \tag{11}$$

Using oxygen concentration and hydroxide activity for the 5°C sample of 320 μM and 3.8 μM, respectively, the oxidation rate constant was calculated as

$1.3 \pm 0.3 \times 10^{12}$ M^{-3} d^{-1}. Morgan (1967) found a two fold reduction of the reaction rate constant with an 11°C decrease in temperature. Morgan's (1967) results suggest that samples at 5°C should have a Mn(II) oxidation rate constant 4 times lower than samples at 25°C. Our results indicate approximately a 2-fold change from 25°C to 5°C. The experimental errors are large enough to include a 4-fold difference, however, so both data sets are compatible. Activation energies for Mn(II) oxidation are temperature dependent in seawater as well as in low ionic strength solution. A two fold reduction in Mn(II) oxidation rate constants with a decrease in temperature from 25°C to 5°C is identical to findings by Millero (1987) for Fe(II) oxidation. Millero (1987) reported Fe(II) oxidation rate constants in both seawater and freshwater at 5°C ($k = 2.2 \times 10^{14}$ mol^{-3} kg H_2O^3 min^{-1} and $k_0 = 6.0 \times 10^{15}$ mol^{-3} kg H_2O^3 min^{-1}, respectively) were one half of those at 25°C ($k = 4.5 \times 10^{14}$ mol^{-3} kg H_2O^3 min^{-1} and $k_0 = 11.7 \times 10^{15}$ mol^{-3} kg H_2O^3 min^{-1}, respectively). Because of the low sample size (one experiment at 5°C), our data may not adequately quantify the effects of temperature on seawater Mn(II) oxidation rates. Further studies with samples at varying temperatures are necessary to describe these changes in Mn(II) oxidation rates.

Effects of Bacterial Concentrations on Mn(II) Oxidation Rates

Substantial numbers of bacteria were found in our experiments immediately after filtering ($0.4 - 0.8 \times 10^6$ cells mL^{-1}) and bacterial densities increased to values typical of open ocean seawater by the end of our experiments ($1.0 - 3.3 \times 10^6$ cells mL^{-1}). The sterilization techniques were incomplete, therefore, and it is necessary to consider whether bacterial oxidation of Mn(II) may have biased the results. No significant correlation between bacterial densities and oxidation rates (Fig. 8) was found. There was also good agreement with the Mn(II) oxidation rates measured by Morgan (1967) and Davies and Morgan (1989). If bacterial catalysis of Mn(II) oxidation occurred, it must have been the same in all three experiments, which is unlikely. We therefore believe Mn(II) oxidizing bacteria were only a minor component of the total measured bacteria in these experiments. The kinetic oxidation rate results were therefore interpreted as inorganic.

Although our inorganic oxidation rates are consistent with other studies (Morgan, 1967; Davies and Morgan, 1989), work by Diem and Stumm (1984) suggests that inorganic Mn(II) oxidation does not occur over a time span of years. Diem and Stumm (1984) reported Mn(II) concentrations, measured by atomic absorption spectrometry, did not change until five years in filtered (0.45 μm) solutions undersaturated with respect to rhodochrosite. We now understand that metal oxides form organic and inorganic colloids (Wells and Goldberg, 1992). Recent work (e.g. Baskaran *et al.*, 1992; Wells and Goldberg, 1992, 1993) has reported that colloids easily pass through 0.45 μm filters. Atomic absorption spectrometry has been reported to not only measure the truly dissolved phase of metals, but also inorganic (e.g. OH^-) and organic complexes (Donat *et al.*, 1994). Mn(II) does not normally form organic complexes, but inorganic Mn oxides (Kostka *et al.*, 1995) in colloidal form may pass through 0.45 μm filters and, therefore, they may be included with truly dissolved Mn(II) in measurements by atomic absorption spectrometry. If this were the case, it is plausible that no decrease in Mn(II) concentrations would be observed after a period of five years (Diem and Stumm, 1984). It is possible that, after this period, colloids aggregated into particles large enough to be retained by 0.45 μm filters and resulted in decreasing Mn(II) concentrations.

A short-term (≈ 1 month) experiment by Diem and Stumm (1984) found Mn(II) concentrations rapidly decreased with increasing additions of Mn(II) oxidizing bacteria (*metallogenium*), while no decrease in Mn(II) concentrations were observed in the control (no bacteria additions). Slow inorganic oxidation may form Mn oxides differently than bacterially-mediated oxidation (Mandernack *et al.*, 1995). Bacterial Mn(II) oxidation results in extracellular Mn deposition on polymer matrices (Nealson and Tebo, 1980; Cowen and Silver, 1984; Hastings and Emerson, 1986; Mandernack et al., 1995) that would be retained by 0.45 μm filters. Higher additions of Mn(II) oxidizing bacteria resulted in higher Mn(II) oxidation rates and possibly increased the rate of Mn oxide mat formation. These mats would be removed by filtration and therefore samples with increasing additions of Mn oxidizing bacteria would have lower measured Mn(II) concentrations.

MECHANISM OF MANGANESE(II) OXIDATION

Both Fe(II) and Mn(II) oxidize with a second order dependence on hydroxide concentration. Millero (1985) demonstrated that the second order dependence for Fe(II) oxidation occurs because $Fe(OH)_2$ complexes oxidize much faster than do the Fe^{2+} or $Fe(OH)^+$ ions. Mn^{2+} also reacts with water, forming hydrolyzed Mn(II) species:

$$Mn^{2+} + H_2O \rightarrow Mn(OH)^+ + H^+ \qquad (12)$$

$$Mn^{2+} + 2H_2O \rightarrow Mn(OH)_2 + 2H^+ \qquad (13)$$

The equilibrium relationship between Mn^{2+} and hydrolyzed Mn(II) species are given by the following hydrolysis constants:

$$\beta_1 = [Mn(OH)^+]\,[H^+]\ /\ [Mn^{2+}] = 1.1 \times 10^{-11} \qquad (14)$$

and $$\beta_2 = [Mn(OH)_2]\,[H^+]^2\ /\ [Mn^{2+}] = 2.3 \times 10^{-23} \qquad (15)$$

The values of these equilibrium constants are changed by variations in ionic strength. The values shown above were calculated at seawater ionic strength according to Turner *et al.* (1981). The hydrolysis products $Mn(OH)^+$ and $Mn(OH)_2$ are lower in concentration than that of Mn^{2+} by many orders of magnitude. These species all have the potential to react with oxygen and form insoluble Mn oxides:

$$Mn^{2+} + O_2 \xrightarrow{k_{10}} \text{Products} \qquad (16)$$

$$Mn(OH)^+ + O_2 \xrightarrow{k_{11}} \text{Products} \qquad (17)$$

$$Mn(OH)_2 + O_2 \xrightarrow{k_{12}} \text{Products} \qquad (18)$$

Observed pseudo first order rate constants are related to these values by the following equation:

$$-d[Mn(II)]/dt = k_1'[Mn(II)]_T = k_{10}[Mn^{2+}] + k_{11}[Mn(OH)^+] + k_{12}[Mn(OH)_2] \qquad (19)$$

Substituting the equilibrium constants into Eqn. 19:

$$k_1'/\alpha_{Mn} = k_{10} + k_{11}\beta_1/[H^+] + k_{12}\beta_2/[H^+]^2 \qquad (20)$$

In Eqn. 20, the extent to which Mn(II) complexes hydroxide is given by the hydrolysis coefficient (α_{Mn}). The hydrolysis coefficient is defined as:

$$\alpha_{Mn} = (1 + \beta_1/[H^+] + \beta_2/[H^+]^2)^{-1} \qquad (21)$$

Data from this study, Davies and Morgan (1989), and Morgan (1967) were combined to determine which hydrolyzed species is controlling Mn(II) oxidation. From Eqn. 20, a regression was performed with k_1'/α_{Mn} values plotted against $1/[H^+]$ and $1/[H^+]^2$ over the entire pH range (8.17 -9.5). The slopes $k_{11}\beta_1 = -8.3 \pm 2.7 \times 10^{-10}$ d^{-1} and $k_{12}\beta_2 = 9.0 \pm 0.9 \times 10^{-19}$ d^{-1} were determined from the least squares fit with the intercept given by $k_{10} = 0.17 \pm 0.14$ d^{-1}. Because a negative value for $k_{11}\beta_1$ is unrealistic, we assumed that k_{11} was zero. A least squares fit to Eqn. 20 with $k_{11} = 0$ gave $k_{12}\beta_2 = 6.4 \pm 0.3 \times 10^{-19}$ d^{-1} and $k_{10} = -0.17 \pm 0.09$ d^{-1}, respectively. The negative intercept k_{10} was also unrealistic and likewise, this term was set to zero. This indicates that rate constants for Mn^{2+} (k_{10}) and $Mn(OH)^+$ (k_{11}) reacting with oxygen were negligible. The value for $k_{12}\beta_2$ was therefore, determined by the equation $k_1'/\alpha_{Mn} = k_{12}\beta_2 \times 1/[H^+]^2$ as $6.1 \pm 0.3 \times 10^{-19}$ d^{-1} (Fig. 9). By dividing this slope ($k_{12}\beta_2 = 6.1 \pm 0.3 \times 10^{-19}$ d^{-1}) by the $Mn(OH)_2$ hydrolysis constant ($\beta_2 = 2.3 \times 10^{-23}$), we calculated a value of $2.7 \pm 0.4 \times 10^4$ d^{-1} for the

$Mn(OH)_2$ oxidation rate constant (k_{12}). These results suggest that in this pH range (8.17 -9.5), Mn^{2+} and $MnOH^+$ do not react significantly with oxygen, and virtually all Mn(II) oxidized is hydrolyzed $Mn(OH)_2$. Second order dependence of reaction rates on pH (Figs. 6 - 7) are also consistent with Mn(II) oxidation being controlled by the Mn(II) dihydroxide species.

The Haber-Weiss mechanism for metal oxidation reactions predicts a sequence of steps, with the slowest step limiting the reaction rate. The reaction kinetics for most transition metals predicts the rate limiting step is with neutrally charged divalent oxygen. Evidence that $Mn(OH)_2$ is the oxidized Mn(II) species is consistent with the following reaction scheme predicted by the Haber-Weiss mechanism:

$$\begin{array}{llr}
\text{slow} & Mn(OH)_2(aq) + O_2 \longrightarrow Mn(OH)_2^{+} + O_2^{\cdot -} & (22)\\
 & Mn(OH)_2(aq) + O_2^{\cdot -} + 2\,H^+ \longrightarrow Mn(OH)_2^{+} + H_2O_2 & (23)\\
 & Mn(OH)_2(aq) + H_2O_2 + H^+ \longrightarrow Mn(OH)_2^{+} + OH\cdot + H_2O & (24)\\
 & Mn(OH)_2(aq) + OH\cdot + H^+ \longrightarrow Mn(OH)_2^{+} + H_2O & (25)\\
\hdashline
\text{Total} & 4\,Mn(OH)_2(aq) + O_2 + 4\,H^+ \longrightarrow 4\,Mn(OH)_2^{+} + 2\,H_2O & (26)
\end{array}$$

Because $Mn(OH)_2$ and O_2 are neutrally charged, the above rate limiting step (Eqn. 22) is consistent with observations, and predictions by transition state theory, that Mn(II) oxidation rate constants will not significantly change with variations in ionic strength. The dependence of Mn(II) oxidation on the hydrolyzed form $Mn(OH)_2$ can be explained by frontier molecular orbital theory (Luther, 1990). Because of increased electron density donated by the hydroxide ligands, the hydrolyzed form of Mn(II) has expanded basicity which will facilitate electron transfer from Mn(II) to oxygen (Luther, 1990). Hem and Lind (1983) proposed that Mn(II) oxidation is a two step process where Mn(II) first oxidizes to a metastable solid which subsequently oxidizes to Mn(IV). The Mn(III) formation predicted by Eqn. 26 is consistent with findings that inorganic (Murray *et al.*, 1985) and organic (Hastings and Emerson, 1986) Mn(II) oxidation initially involves an Mn(III) mineral end product.

OPEN OCEAN MANGANESE(II) OXIDATION RATES

Mn(II) oxidation rates reported in open ocean seawater studies are generally in agreement with inorganic oxidation rates found here. Sunda and Huntsman (1988) found particulate Mn scavenging rates of 0.01 nM d^{-1} at sites in the upper 40 m and at 500 m in the Sargasso Sea. At *in situ* pH, oxygen, and Mn(II) concentrations, the sum of heterogeneous and homogeneous rate constants ($k_1' + k_2'[MnO_x]$) ranges from $2 - 10 \times 10^{12}$ M^{-3} d^{-1} (Sunda and Huntsman, 1988). This agrees well with values from laboratory Mn(II) oxidation experiments (Morgan, 1967; Davies and Morgan, 1989; this study) and suggests the heterogeneous mechanism does not overwhelm the homogeneous inorganic reaction in surface or deep waters of the Sargasso Sea. Cowen *et al.* (1990) measured scavenging rates of Mn(II) in water above hydrothermal vents and found biological scavenging rates accounted for less than 50% of total scavenging rates. Spores of marine bacillus have been found in seawater (Rosson and Nealson, 1982) and they have been shown to catalyze Mn(II) oxidation (Hastings and Emerson, 1986). However, spore-forming bacteria are not a major component of the marine environment's bacterial composition

(Cowen and Bruland, 1985). Studies of Mn(II) oxidation show that the bacterial catalyzed reaction follows Michaelis-Menton kinetics with half saturation constants of 190 - 500 nM (Tebo and Emerson, 1986; Sunda and Huntsman, 1987). Open ocean seawater Mn(II) concentrations (≈ 1 nM) may be too low for bacteria binding sites to adequately compete for Mn(II). We, therefore, believe that Mn(II) oxidation is not overwhelmed by bacterial oxidation in most of the deep sea where concentrations of Mn(II) and spore forming bacteria are low. The results reported here may, therefore, have general applicability to studies of Mn scavenging in the deep-sea. Homogeneous Mn(II) oxidation rates are used as a scavenging parameter in a kinetic model that predicts open ocean Mn(II) distributions (Johnson *et al.*, 1996).

CONCLUSIONS

The average homogeneous Mn(II) oxidation rate constant at natural (nM) concentrations in seawater was $2.1 \pm 0.5 \times 10^{12}$ $M^{-3} d^{-1}$. This is in good agreement with results from experiments performed using μM Mn(II) concentrations in low ionic strength solution by Morgan (1967) and Davies and Morgan (1989). Morgan (1967) reported a homogeneous reaction rate constant value of 4×10^{12} $M^{-3} d^{-1}$. A rate constant of 1.1×10^{12} $M^{-3} d^{-1}$ is derived from Davies and Morgan (1989) if oxidation with respect to $\{OH^-\}$ is second order. Combined results from this work, Morgan (1967), and Davies and Morgan (1989) suggests that at high pH levels (8-9.5), Mn(II) oxidation is controlled by $Mn(OH)_2$ complexes reacting with oxygen. The lack of a strong ionic strength effect on Mn(II) oxidation rates is in agreement with the predictions of transition state theory.

In regions with low Mn(II) and particulate matter concentrations, the homogeneous reaction of Mn(II) dominates oxidation. The inorganic reaction rate is comparable to measured rates of Mn(II) oxidation in deep-sea samples, which indicates there is little bacterial Mn(II) oxidation. The reaction rate is significantly decreased in regions of low pH and oxygen concentration. Slow inorganic Mn(II) oxidation kinetics and, consequently, reduced scavenging rates at mid-depths, can account for the persistence of the Mn(II) maximum associated with the oxygen minimum (Johnson *et al.*, 1996).

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Figure Captions

Figure 1. Pacific Ocean Mn(II) (●) and oxygen (▼) profiles off the California coast at 35° 15'N and 121° 52'W (from Johnson *et al.*, 1992). The secondary Mn(II) maximum is associated with the oxygen minimum.

Figure 2. Schematic diagram of experimental procedure for determination of Mn(II) oxidation rates in seawater. Monterey Bay Surface Seawater (MBSS) and 50 m Santa Barbara Channel Seawater (SBCS) were initially spiked with ≈20 nM Mn(II). Ammonium hydroxide (NH_4OH) was added to change seawater pH before filtering into 11 L carboys. One carboy at pH = 9.32 was kept at 5°C and eight carboys at pH values ranging from 8.17 - 8.75 were stored at 25°C. All carboys were kept in the dark and analyzed by flow injection analysis (FIA) at approximately monthly intervals.

Figure 3. Change in [Mn(II)] (■, left axis) and ln[Mn(II)] (●, right axis) as a function of time in filtered (0.2 μm) seawater kept in the dark at temperature 25°C. Slope of the natural log data and the resulting Mn(II) oxidation rate constant are shown. Monterey Bay surface seawater (MBSS) samples were at pH 8.17, 8.28, and 8.46. A 50m Santa Barbara Channel seawater (SBCS) sample was at pH 8.23.

Figure 4. Change in [Mn(II)] (■, left axis) and ln[Mn(II)] (●, right axis) as a function of time in filtered (0.2 μm) seawater kept in the dark at temperature 25°C. Slope of the natural log data and the resulting Mn(II) oxidation rate

constant are shown. Monterey Bay surface seawater (MBSS) samples were at pH 8.53, 8.69, and 8.75. An experiment was also run for approximately 110 days with a sample of 50m Santa Barbara Channel seawater (SBCS) at pH 8.69.

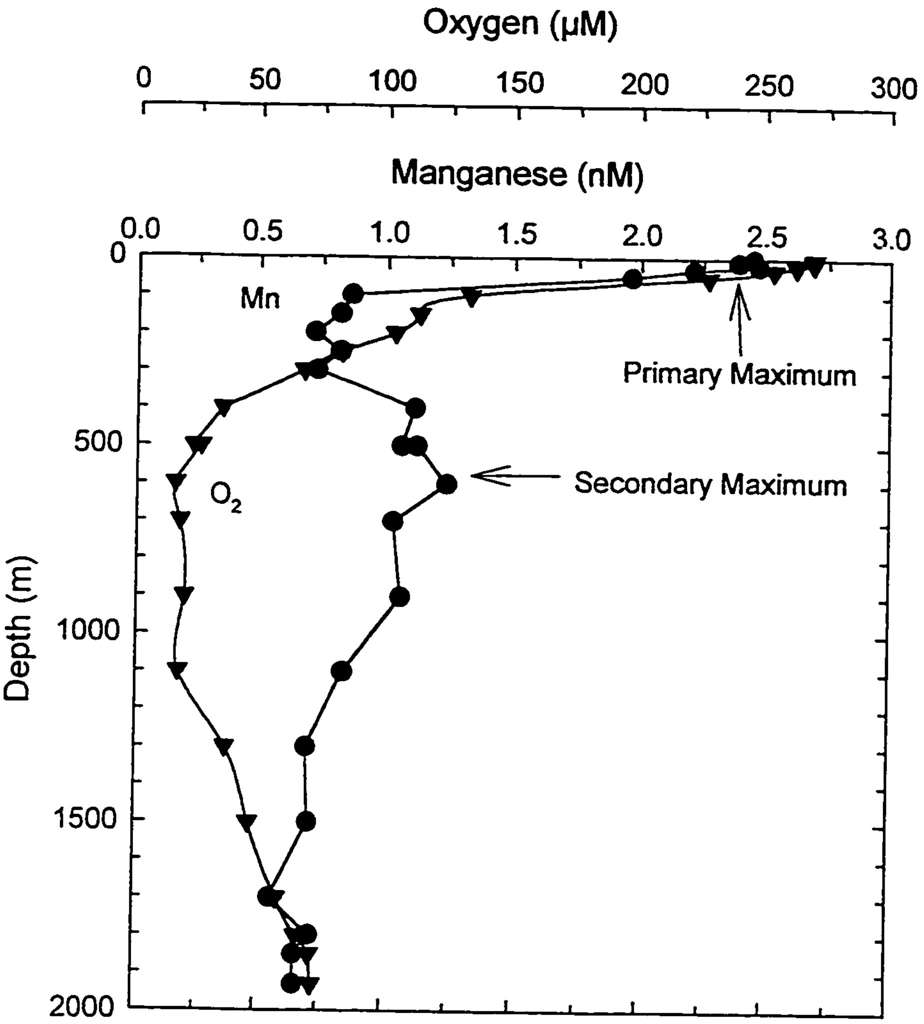
Figure 5. Change in [Mn(II)] (■, left axis) and ln[Mn(II)] (●, right axis) as a function of time in filtered (0.2 μm) Monterey Bay Surface Seawater (MBSS) kept in the dark at pH 9.32 and temperature 5°C . Slope of the natural log data and the resulting Mn(II) oxidation rate constant are shown.

Figure 6. The $\log_{10}$ of pseudo first order rate constants (k_1') vs. pH for eight seawater samples at 25°C and $pO_2 = 0.22$ atm. The slope (1.5 ± 0.3) is near the expected value (2), if dependence on hydroxide is second order, as predicted by Morgan's (1967) homogeneous rate equation ($d[Mn(II)]/dt = k_1 [O_2] \{OH^-\}^2 [Mn(II)]$). Error bars are 95% confidence intervals for plotted pH and rate constant values.

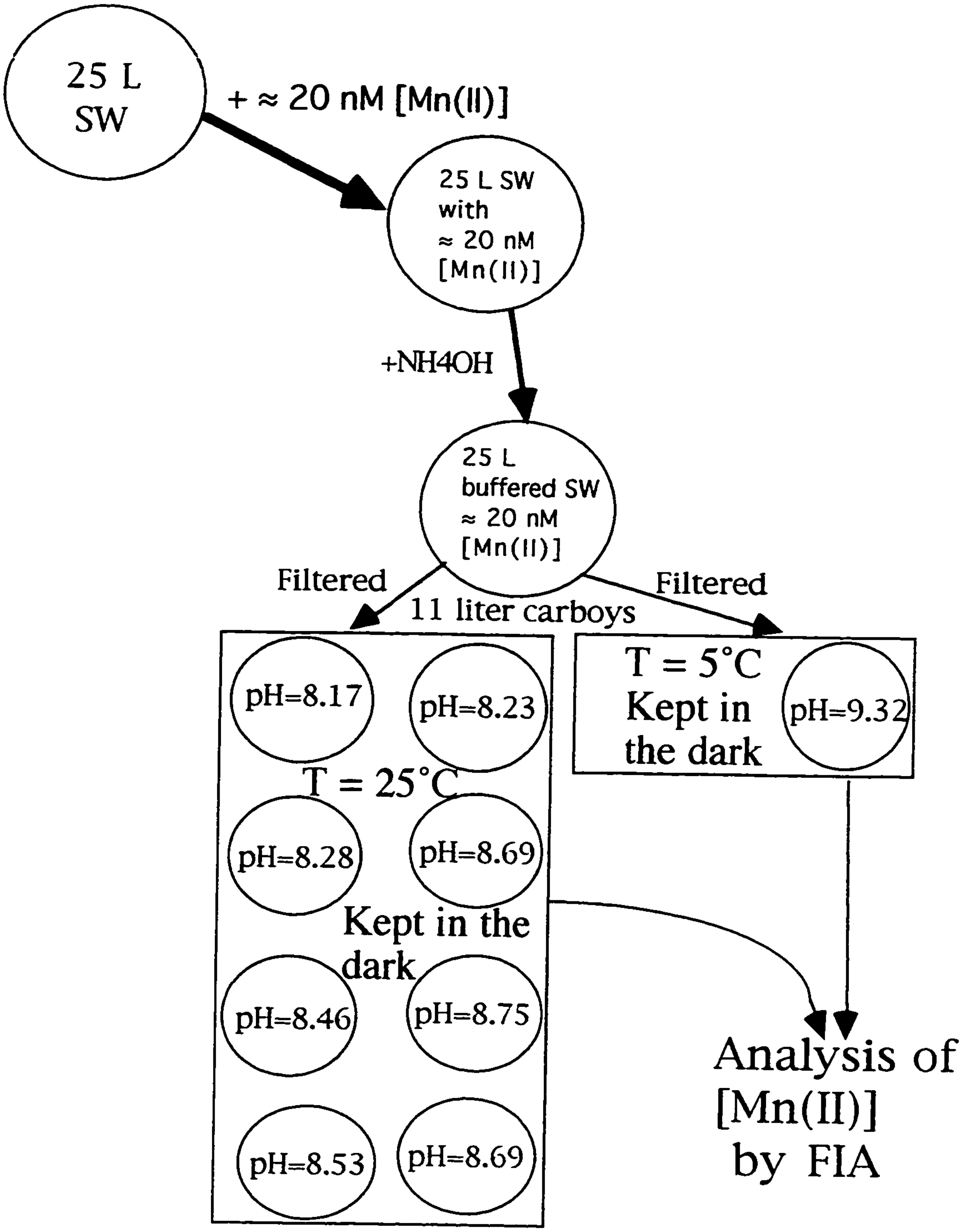
Figure 7. The $\log_{10}$ of pseudo first order rate constants (k_1') vs. pH for samples at 25°C from this work (■), Davies and Morgan (1989, ●), and Morgan (1967, ▲). To be consistent with Mn(II) oxidation rates determined by Morgan (1967) and Davies and Morgan (1989), rates determined in this work with $pO_2 = 0.22$ atm have been converted to expected rates with $pO_2 = 1$ atm. The slope (2.3 ± 0.3) is essentially the expected value (2), if dependence on hydroxide is second order, as predicted by Morgan's (1967) homogeneous rate equation ($d[Mn(II)]/dt = k_1 [O_2] \{OH^-\}^2 [Mn(II)]$). Error bars are 95% confidence intervals.

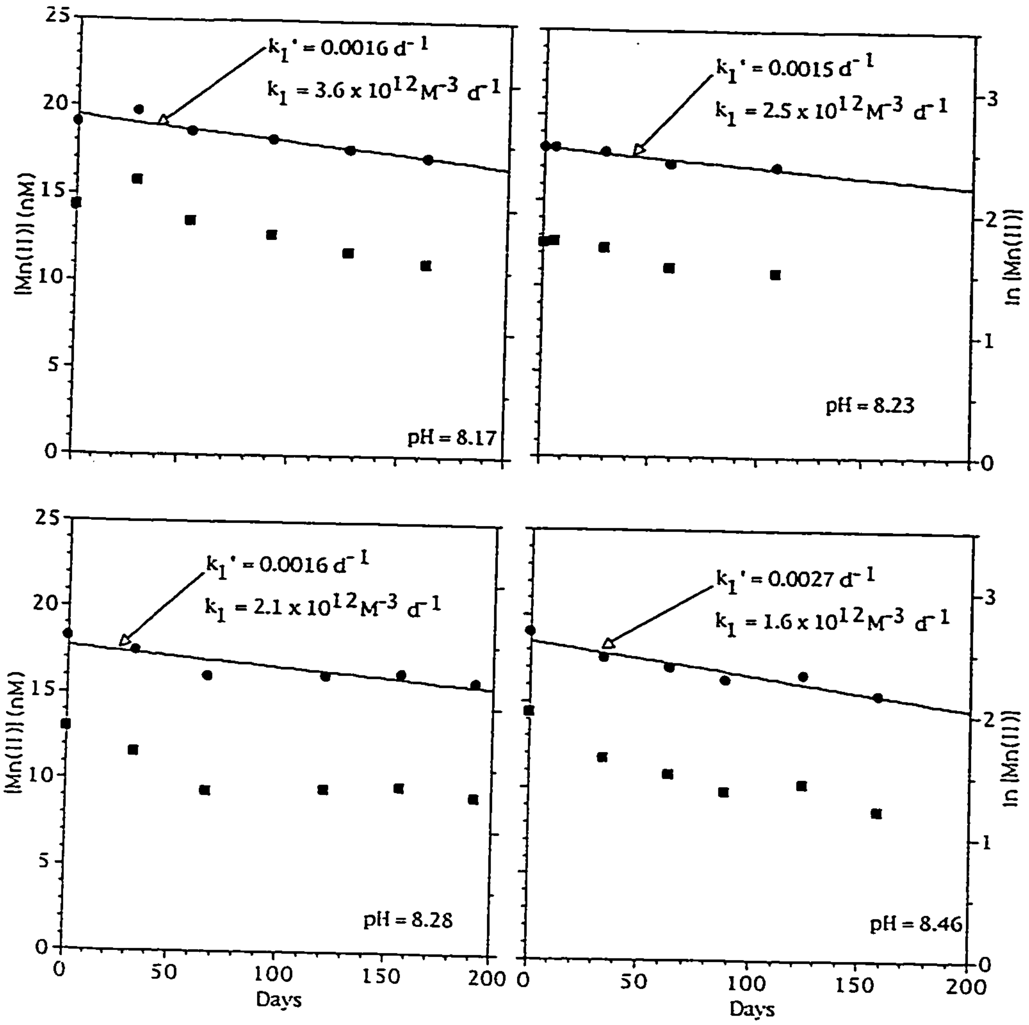
Figure 8. Mn(II) oxidation rate constant ($k_1/10^{12}$) in units $M^{-3}\ d^{-1}$ with 95% Confidence intervals vs. bacterial concentrations, measured at various times after filtration (0.2 μm), in 8 carboys of seawater from Monterey Bay and the Santa Barbara Channel. All carboys were stored in the dark at 25°C.

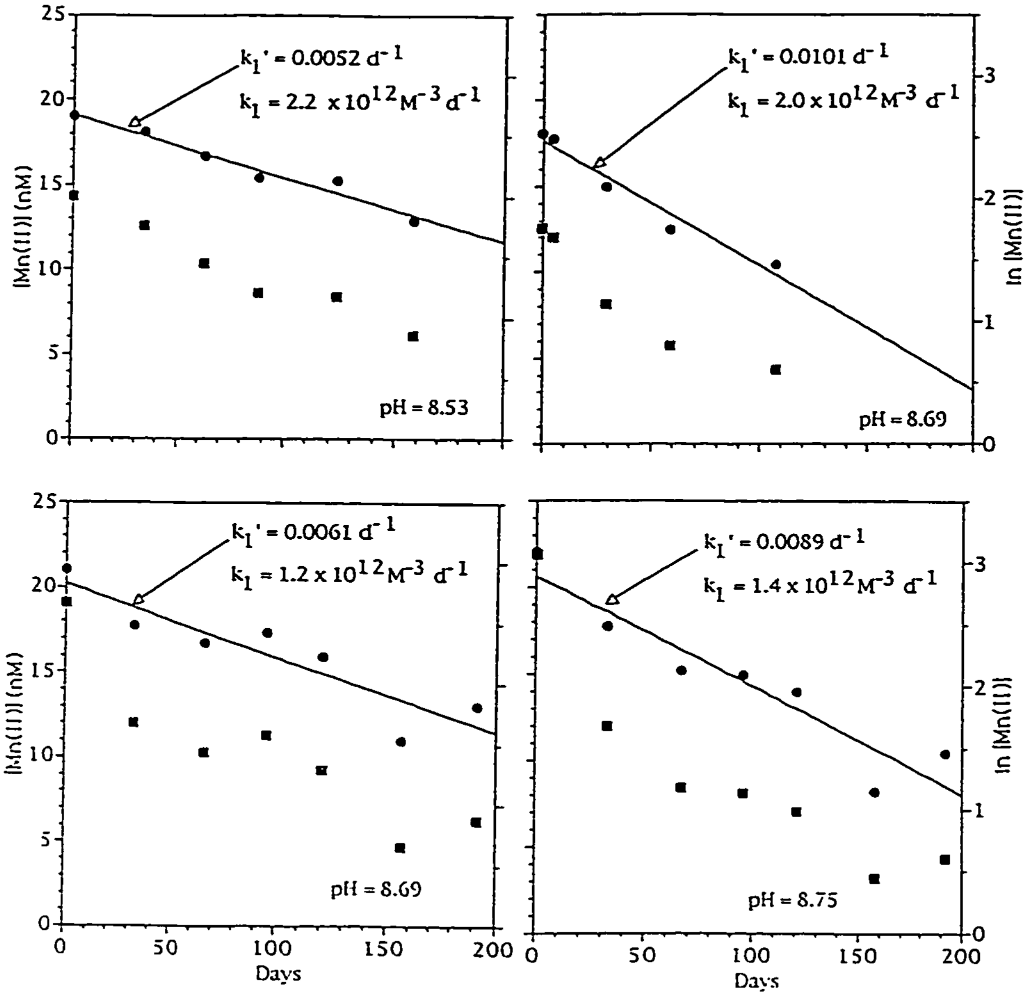
Figure 9. Pseudo first order rate constants (k_1') divided by hydrolysis coefficients (α_{Mn}) versus $1/[H^+]$. Data are combined from samples at 25°C from this work, Davies and Morgan (1989), and Morgan (1967). All pseudo first order rate constants have been converted to 1 atm. O_2 and are reported in units of per day. A least squares fit resulted in negative values for k_{10} and $k_{11}\beta_1$. Fixing these unrealistic values to zero and regressing k_1'/α_{Mn} versus $1/[H^+]^2$ results in a good fit ($R^2 = 0.96$) with a slope $k_{12}\beta_2 = 6.1 \pm 0.3 \times 10^{-19}\ d^{-1}$. A positive value for the rate constant k_{12} ($2.7 \pm 0.4 \times 10^4\ d^{-1}$) suggests the hydrolysis species $Mn(OH)_2$ is controlling Mn(II) oxidation.



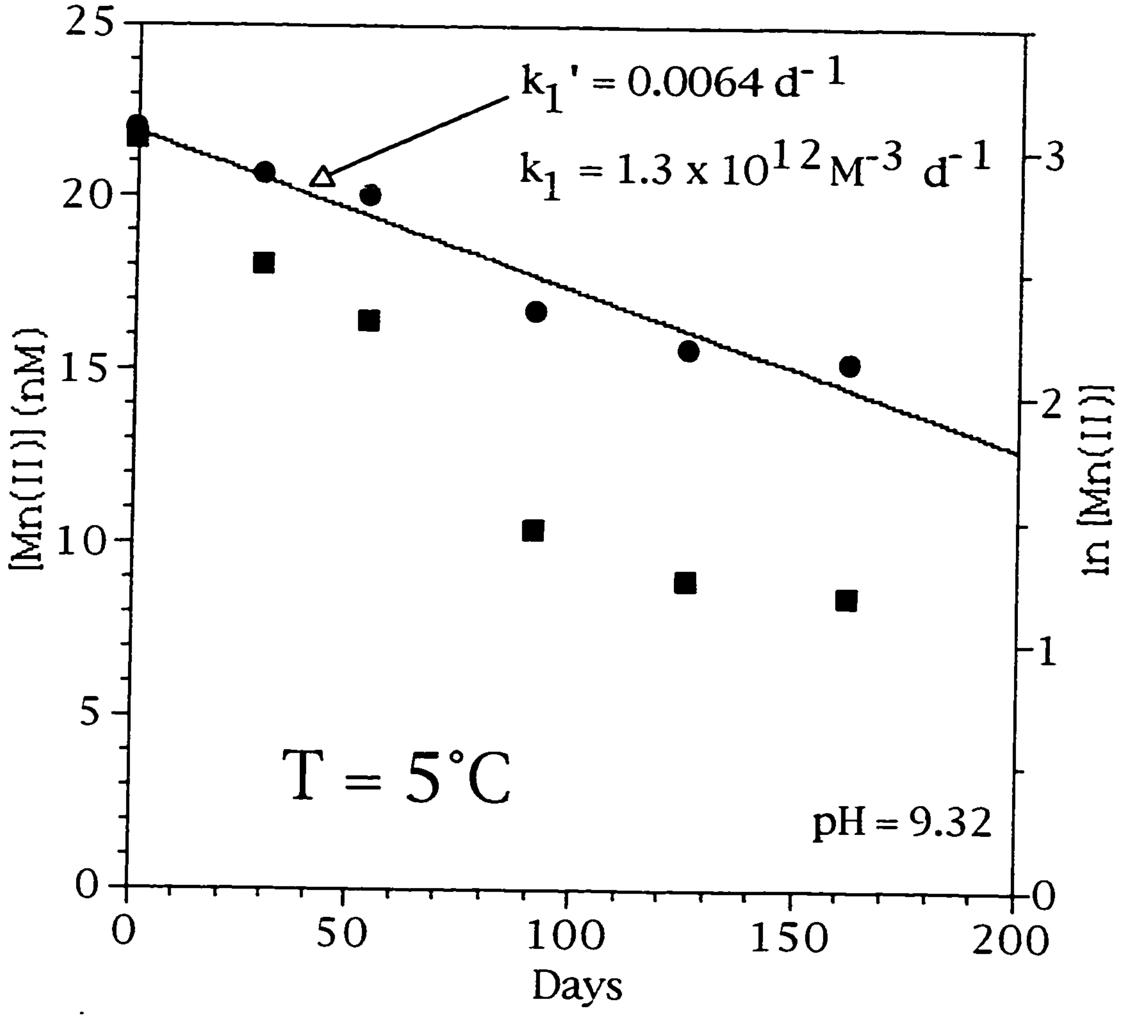
Oxygen (µM)
0
50
100
150
200
250
300
Manganese (nM)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
0
500
1000
1500
2000
Depth (m)
Mn
O$_2$
Primary Maximum
Secondary Maximum


25 L SW
+ ≈ 20 nM [Mn(II)]
25 L SW with ≈ 20 nM [Mn(II)]
+NH4OH
25 L buffered SW ≈ 20 nM [Mn(II)]
Filtered
11 liter carboys
Filtered
pH=8.17
pH=8.23
T = 25°C
pH=8.28
pH=8.69
Kept in the dark
pH=8.46
pH=8.75
pH=8.53
pH=8.69
T = 5°C
Kept in the dark
pH=9.32
Analysis of [Mn(II)] by FIA

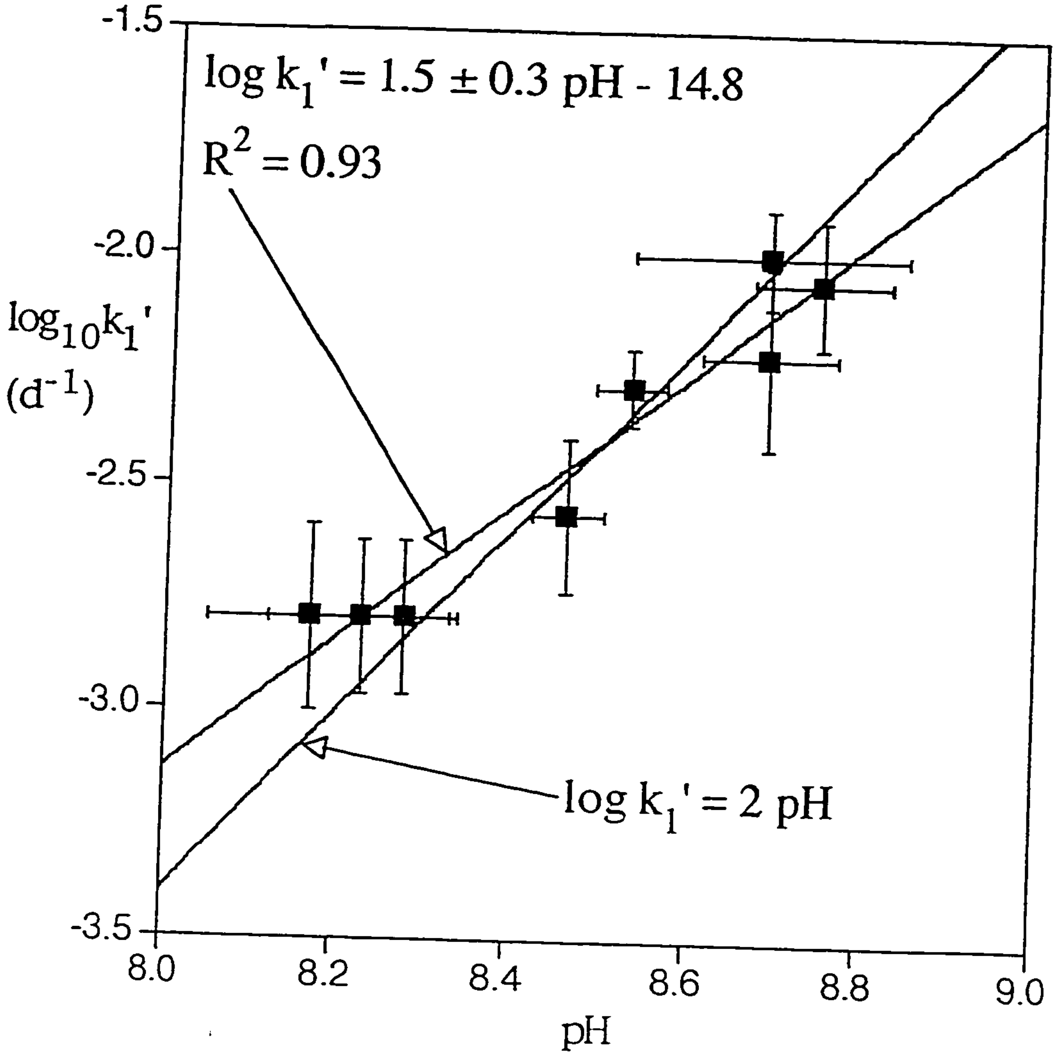

k1' = 0.0016 d-1
k1 = 3.6 x 10^12 M-3 d-1
pH = 8.17
k1' = 0.0015 d-1
k1 = 2.5 x 10^12 M-3 d-1
pH = 8.23
k1' = 0.0016 d-1
k1 = 2.1 x 10^12 M-3 d-1
pH = 8.28
k1' = 0.0027 d-1
k1 = 1.6 x 10^12 M-3 d-1
pH = 8.46
[Mn(II)] (nM)
ln [Mn(II)]
Days
0
5
10
15
20
25
0
1
2
3
0
50
100
150
200

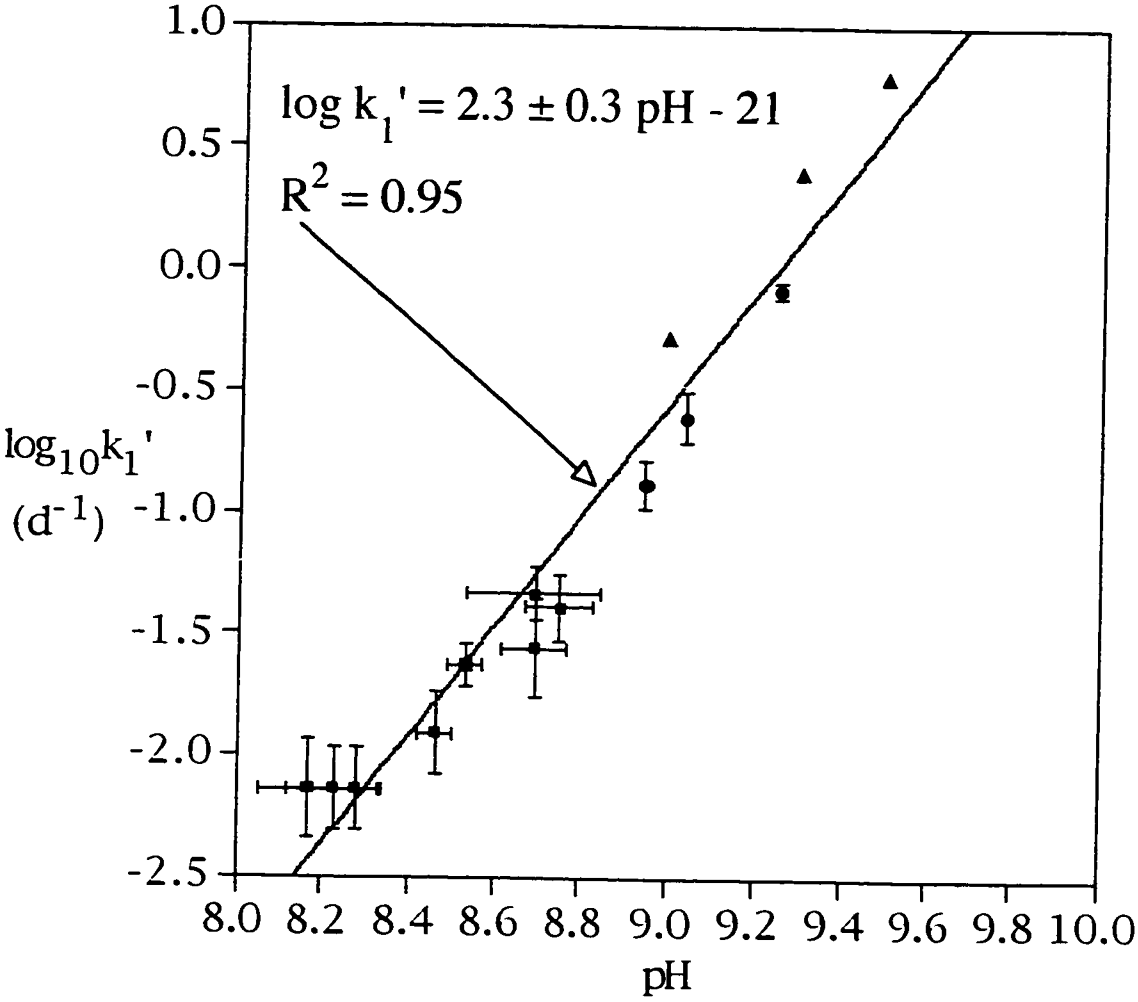


$k_1' = 0.0052\ d^{-1}$
$k_1 = 2.2 \times 10^{12} M^{-3} d^{-1}$
pH = 8.53
$k_1' = 0.0101\ d^{-1}$
$k_1 = 2.0 \times 10^{12} M^{-3} d^{-1}$
pH = 8.69
$k_1' = 0.0061\ d^{-1}$
$k_1 = 1.2 \times 10^{12} M^{-3} d^{-1}$
pH = 8.69
$k_1' = 0.0089\ d^{-1}$
$k_1 = 1.4 \times 10^{12} M^{-3} d^{-1}$
pH = 8.75
[Mn(II)] (nM)
ln [Mn(II)]
0
5
10
15
20
25
0
1
2
3
0
50
100
150
200
Days

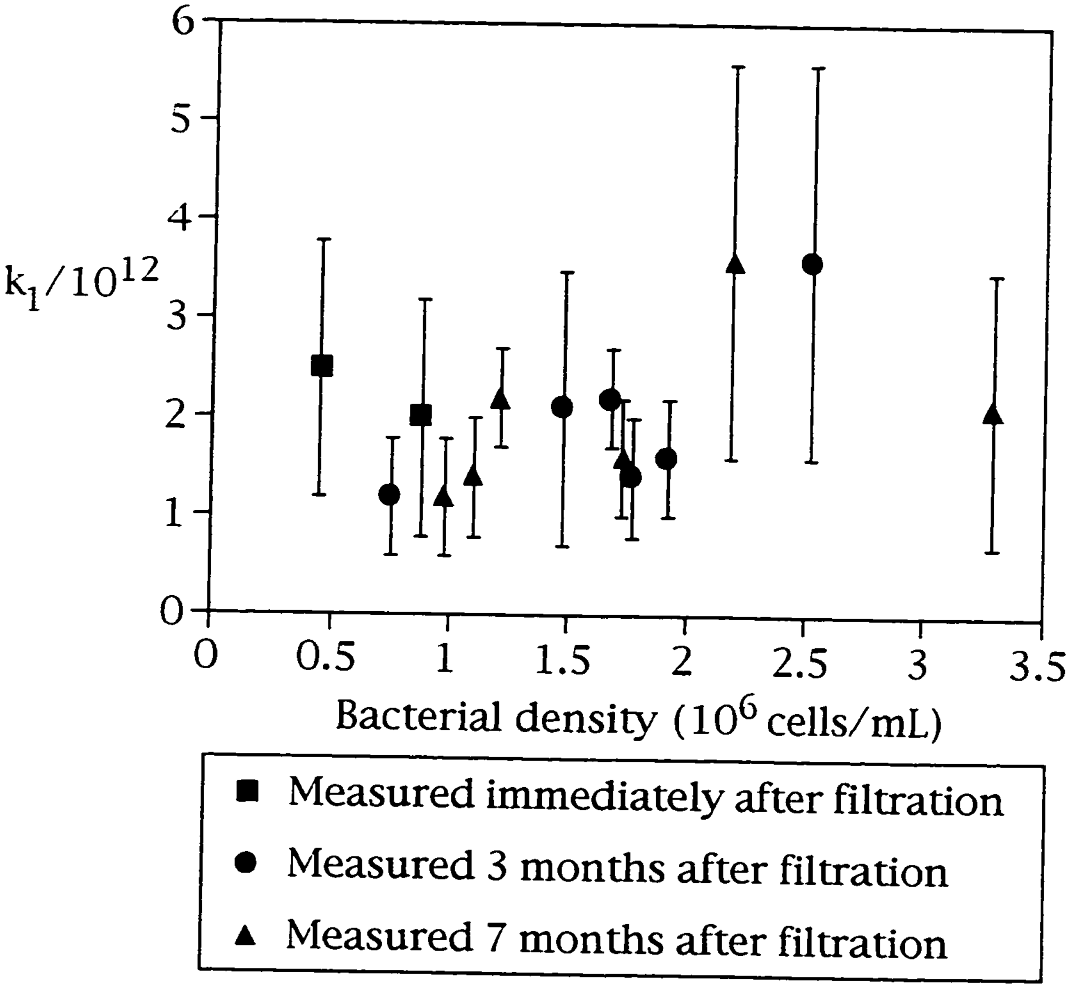


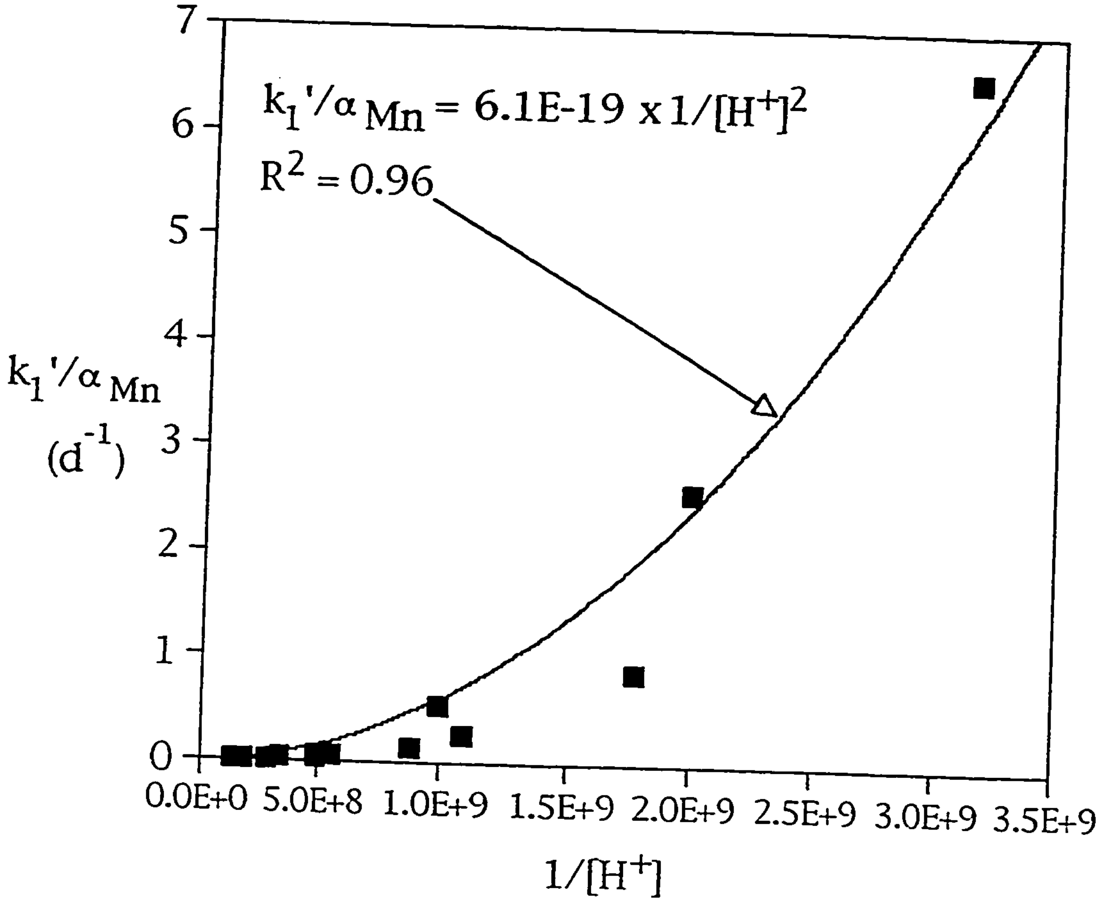
25
20
15
10
5
0
[Mn(II)] (nM)
0
50
100
150
200
Days
3
2
1
0
ln [Mn(II)]
k$_1$' = 0.0064 d^{-1}
k$_1$ = 1.3 x 10^{12} M^{-3} d^{-1}
T = 5°C
pH = 9.32


$\log k_1' = 1.5 \pm 0.3\ \mathrm{pH} - 14.8$
$R^2 = 0.93$
$\log k_1' = 2\ \mathrm{pH}$
$\log_{10} k_1'$ (d^{-1})
-1.5
-2.0
-2.5
-3.0
-3.5
8.0
8.2
8.4
8.6
8.8
9.0
pH



log k1' = 2.3 ± 0.3 pH - 21
R2 = 0.95
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
log10k1'
(d-1)
8.0
8.2
8.4
8.6
8.8
9.0
9.2
9.4
9.6
9.8
10.0
pH


$k_1/10^{12}$
0
1
2
3
4
5
6
0
0.5
1
1.5
2
2.5
3
3.5
Bacterial density (10^6 cells/mL)
■ Measured immediately after filtration
● Measured 3 months after filtration
▲ Measured 7 months after filtration



$k_1'/\alpha_{Mn} = 6.1E\text{-}19 \times 1/[H^+]^2$
$R^2 = 0.96$
k_1'/α_{Mn} (d^{-1})
0
1
2
3
4
5
6
7
0.0E+0
5.0E+8
1.0E+9
1.5E+9
2.0E+9
2.5E+9
3.0E+9
3.5E+9
$1/[H^+]$

Table Caption

Table 1. Samples of increasing pH with rates of Mn(II) oxidation (k_1') and resulting rate constants (k_1). Samples 1-8 are at temperature 25°C and sample 9 is at 5°C. Samples 2 and 6 are filtered (0.2 μm) 50m Santa Barbara Channel Seawater (SBCS), the remaining samples are filtered (0.2 μm) Monterey Bay Surface Seawater (MBSS). All samples are in equilibrium with the atmosphere ($pO_2 = 0.22$ atm.).

Sample #	pH ± 95% CI	k1' ± 95% CI (d^-1)	k1/10^12 ± 95% CI (M^-3 d^-1)
1	8.17 ± 0.12	0.0016 ± 0.0007	3.6 ± 2.0
2	8.23 ± 0.11	0.0016 ± 0.0006	2.5 ± 1.3
3	8.28 ± 0.05	0.0016 ± 0.0010	2.1 ± 1.4
4	8.46 ± 0.04	0.0027 ± 0.0010	1.6 ± 0.6
5	8.53 ± 0.04	0.0052 ± 0.0010	2.2 ± 0.5
6	8.69 ± 0.16	0.0101 ± 0.0025	2.0 ± 1.2
7	8.69 ± 0.08	0.0061 ± 0.0026	1.2 ± 0.6
8	8.75 ± 0.08	0.0089 ± 0.0028	1.4 ± 0.6
9	9.32 ± 0.03	0.0064 ± 0.0015	1.3 ± 0.3

CHAPTER 3

IMPLICATIONS FOR MANGANESE(II) OCEANOGRAPHY AND CONCLUSIONS

MANGANESE(II) KINETIC MODEL

A kinetic model (Johnson *et al.*, 1996) uses inorganic Mn(II) oxidation rates as a scavenging parameter to predict open ocean Mn(II) concentrations below the photic zone (100 m). In this model Mn(II) is regenerated in proportion to particulate organic carbon (POC) remineralization and is removed by oxidation and subsequent scavenging onto particles. The rate of inorganic Mn(II) oxidation in seawater was determined in laboratory experiments (Chapter 2) and is shown below to be proportional to scavenging. Mn(II) concentrations for each depth are considered to represent a balance between sources (POC remineralization) and sinks (scavenging). In this model, Mn(II) concentrations are set at the point where removal by oxidation balances production from release of Mn(II) during carbon remineralization. Low pH and oxygen values in the oxygen minimum result in a reduction of the pseudo first order rate constant for Mn(II) oxidation ($k_1' = k_1 [O_2] \{OH^-\}^2$). Higher Mn(II) concentrations will accumulate in the oxygen minimum until a steady state is reached, where scavenging rates ($k_1'[Mn(II)]$) are equivalent to Mn(II) input from particulate organic carbon (POC) remineralization.

MANGANESE(II) PRODUCTION

In this model, Mn(II) production at depth is driven by the rate of remineralization of particulate organic matter (POM) (Landing and Bruland, 1980). Carbon remineralization is calculated as the derivative of the vertical POC flux with respect to depth (dF_C/dZ). The POC flux with depth was found by Martin *et al.* (1987) to fit the equation:

$$F_c = F_{100}\,(Z/100)^{-b} \qquad (1)$$

In Eqn. 1, F_{100} is the flux of carbon (mol C m^{-2} y^{-1}) at 100 m depth, Z is depth (m), and b was empirically determined by Martin *et al.* (1987) as 0.858.

Mn(II) is remineralized (Fig. 1) during the oxidation of POM below the photic zone. Mn(II) produced from remineralization of POM is estimated by the carbon flux with depth and a Redfield-like proportionality of Mn to carbon. If the Mn/C ratio of POM is Q (μmol Mn mol C^{-1}), the resulting rate of Mn(II) production (P_{Mn}, nM y^{-1}) from POM remineralization is:

$$P_{Mn} = Q(dF_c/dZ) = (b/100^{-b})\,QF_{100}\,Z^{-(1+b)} = 45\,QF_{100}\,Z^{-1.858} \qquad (2)$$

The rate of Mn(II) production at each depth (P_{Mn}) is dependent on the ratio of Mn to carbon in POM (Q = 44 μmol Mn mol C^{-1}, see below) and the extent of POC exportation from the euphotic zone (F_{100}).

MANGANESE(II) REMOVAL

Maintaining steady state Mn(II) profiles in this one-dimensional model requires a Mn(II) removal term to prevent continual increases in ocean Mn(II) concentrations. A scavenging index (Whitfield and Turner, 1987) characterizes the behavior of trace metals in seawater. This index is a ratio of the affinity of ions for solution (the inorganic side reaction coefficient) to their attraction onto particle surfaces (the first hydrolysis constant). Mn(II) and Cd(II) have similar scavenging index values which suggests that vertical profiles for these metals should be alike. Profiles of Mn(II) concentrations, however, are completely different from the nutrient-like profiles observed for Cd(II) (Bruland and Franks, 1983). Nyfeller *et al.*, (1984) found Mn(II) scavenging in laboratory studies involves an oxidation step to Mn(III) or Mn(IV). Mn chemistry is different from that of Cd, because of its ability to change redox states. In this thesis (Chapter 2), Mn(II) was found to slowly oxidize in seawater. In the Mn(II) distribution model by Johnson *et al.* (1996), Mn oxides are considered to be scavenged onto particles which sink through the water column and eventually contribute to the sediments. Mn(II) removal by scavenging in this model is therefore assumed to be controlled by the rate of Mn(II) oxidation.

The Mn(II) oxidation rate law was determined by Morgan (1967) to be dependent on oxygen concentration and hydroxide activity:

$$-d[\mathrm{Mn(II)}]/dt = k_1' [\mathrm{Mn(II)}] + k_2' [\mathrm{Mn(II)}] [\mathrm{MnO_x}] \qquad (3)$$

$$\text{where} \qquad k_1' = k_1 [O_2] \{OH^-\}^2 \text{ with } k_1 = 4 \times 10^{12}\ M^{-3}\ d^{-1}$$

$$\text{and} \qquad k_2' = k_2 [O_2] \{OH^-\}^2 \text{ with } k_2 = 10^{18}\ M^{-4}\ d^{-1}$$

This first term (k_1' [Mn(II)]) in Eqn. 3 describes homogeneous oxidation and the second term (k_2' [Mn(II)] [$\mathrm{MnO_x}$]) describes a heterogeneous autocatalytic mechanism due to Mn oxide surfaces. The heterogeneous Mn oxidation term is important in coastal regions with high particulate Mn concentrations but is insignificant in the deep open ocean where there are low concentrations of these Mn oxides. Particulate manganese concentrations were determined to be less than 0.4 nM in the open North Pacific Ocean (Landing and Bruland, 1980; Martin *et al.*, 1985). If this particulate manganese is assumed to be in the form of manganese oxides, the upper limit on the third order heterogeneous manganese oxidation rate constant (Eqn. 3) is $k_2 \times [MnO_x] < 2 \times 10^9\ M^{-3}\ d^{-1}$. This is three orders of magnitude less than the homogeneous third order rate constant (Eqn. 3). Mn oxidation kinetics in open ocean seawater are therefore modeled by the homogeneous rate equation:

$$R_{Mn} = -d[Mn(II)]/dt = k_1' [Mn(II)] = k_1 [Mn(II)] [O_2] \{OH^-\}^2 \qquad (4)$$

Mn(II) removal (R_{Mn}) by scavenging is limited by the homogeneous Mn(II) oxidation rate (Eqn. 4) and therefore dependent on *in situ* oxygen and pH.

SOLUTION OF KINETIC MODEL

The vertical inputs and removal of Mn(II) due to mixing is quantified in the kinetic model by the following equation for vertical eddy diffusion:

$$D_{Mn} = K_z \frac{d^2Mn}{dz^2} \qquad (5)$$

The steady state model requires the Mn(II) production, removal and mixing terms to sum to zero:

$$0 = P_{Mn} - R_{Mn} + D_{Mn} \qquad (6)$$
$$0 = 45\,QF_{100}\,Z^{-1.858} - k_1 [Mn(II)] [O_2] \{OH^-\}^2 + K_z \frac{d^2Mn}{dz^2}$$

Mn(II) profiles are obtained by numerically solving the differential Eqn. 6 for Mn(II) at discrete depths using values for Q, F_{100}, k_1, $[O_2]$, $\{OH^-\}$, and K_z that have been directly measured. Boundary conditions are set to 1 nM Mn(II) above 100 m and 0.1 nM Mn(II) below 2000 m. These values are in the normal range of observations for open ocean Mn(II) concentrations.

MODEL RESULTS AND DISCUSSION

The model results described by Johnson *et al.* (1996) used values of Q=44 μmol Mn mol C^{-1} (Martin and Knauer, 1983; Martin *et al.*, 1985), $k_1 = 4 \times 10^{12}\ M^{-3}\ d^{-1}$ (Morgan, 1967), $K_z = 0.25\ cm^2\ s^{-1}$ (Ledwell *et al.*, 1986) and *in situ* oceanographic data for F_{100},O_2, and pH at stations in the Pacific and Atlantic Oceans to predict Mn(II) concentrations (Fig. 2). Model results and actual data from Vertex 4 Station 5 (Martin *et al.*, 1985) are shown in higher resolution (Fig. 3). The model does an excellent job reproducing surface Mn(II) maxima, subsurface Mn(II) minima, and secondary (Mn(II) maxima associated with oxygen minima for all stations.

Low pH and oxygen concentrations in the oxygen minimum result in reductions of the pseudo first order scavenging rate constant (Eqn. 4). The low pseudo first order Mn(II) oxidation rate constants (0.005 y^{-1} at pH = 7.68 and $[O_2] = 15\ \mu M$) result in slow Mn(II) oxidation rates and allows for the buildup of the subsurface Mn(II) maximum. The long time required in these regions for Mn oxidation, and therefore scavenging, is supported by observations of long (25-50 year) Mn(II) oceanic residence times (Weiss, 1977).

An independent check on the model and the Mn oxidation rate constant is achieved by comparing the calculated particulate Mn flux to the measured particulate Mn flux at Vertex 4 Station 5 (Fig. 4). Morgan's (1967) Mn oxidation rate constant ($k_1 = 4 \times 10^{12}$ M^{-3} d^{-1}) results in an overestimation of the particulate Mn flux by approximately a factor of three. The homogeneous inorganic Mn(II) oxidation rate constant determined in Chapter 2 ($k \approx 2 \times 10^{12}$ M^{-3} d^{-1}) is approximately one half of that reported by Morgan (1967). If this rate constant is used instead of Morgan's (1967), the particulate Mn flux value is also reduced by a factor of two (Fig. 4). The particulate Mn flux using this lower value more accurately matches the observed Mn flux data. If the Mn to C ratio (Q) and the eddy diffusion coefficient (K_z) are simultaneously reduced by a factor of two, Mn(II) profiles are left unchanged (Fig. 4). A reduction of these parameters by a factor of two is well within the range of reliable reported values for Q (e.g. Landing and Bruland, 1980) and K_z (Ledwell *et al.*, 1993). The good agreement with Mn(II) concentrations and better fit to the particulate Mn flux determined with the Mn(II) oxidation rate constant measured here($k \approx 2 \times 10^{12}$ M^{-3} d^{-1}) is strong evidence in favor of these results.

CONCLUSIONS

A kinetic model by Johnson *et al.* (1996) accurately predicts Mn(II) concentrations in the open ocean below the photic zone. The model balances Mn(II) production, Mn(II) scavenging, and mixing terms which sum to zero at steady state. In this model, Mn(II) production at depth is proportional to the rate of POC oxidation (Landing and Bruland, 1980). Mn(II) removal is based on scavenging that is dependent on the homogeneous Mn oxidation rate equation given by Morgan (1967). Agreement with an independent test of particulate

Mn flux suggests that a lower inorganic homogeneous Mn(II) oxidation rate constant determined in Chapter 2 ($k \approx 2 \times 10^{12}\ M^{-3}\ d^{-1}$) may be more appropriate than the value determined by Morgan (1967, $k = 4 \times 10^{12}\ M^{-3}\ d^{-1}$). Low deep sea Mn(II) and particle concentrations result in a slow inorganic homogeneous Mn oxidation reaction mechanism (Chapter 2). This reaction rate is significantly decreased in regions of low pH and oxygen concentration. Slow Mn oxidation kinetics and, consequently, reduced scavenging rates can account for the persistence of the Mn(II) maximum associated with the oxygen minimum. Neither the dissolution of Mn oxides nor the lateral transport of shelf-derived Mn(II) is required to explain the observed distribution of Mn(II) in seawater.

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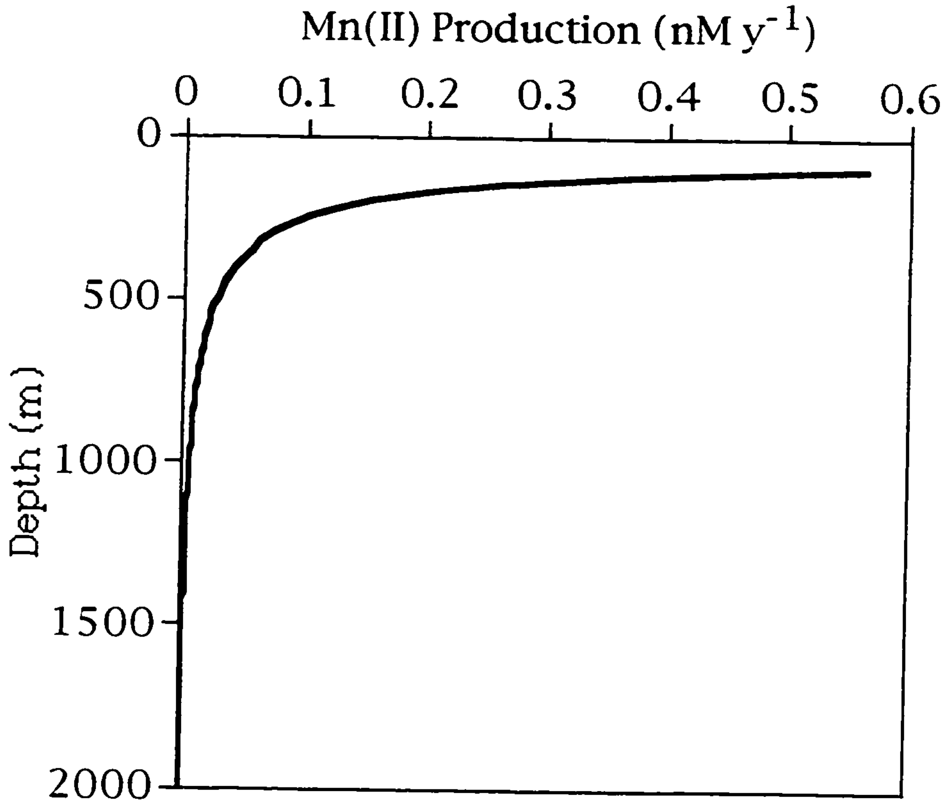
Figure Captions

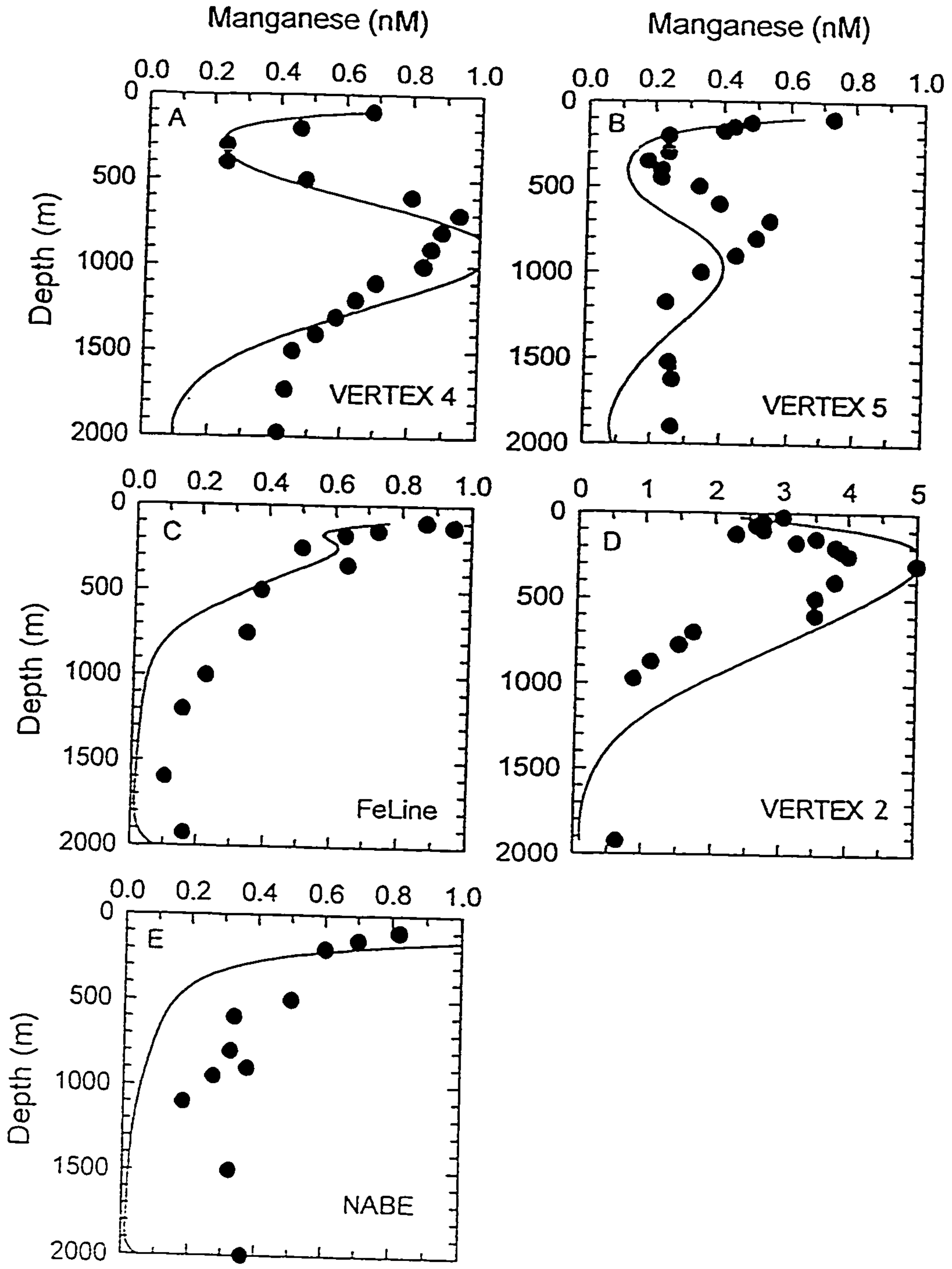
Figure 1. Mn(II) production (nM y^{-1}) (—) calculated from remineralization of Mn(II) associated with carbon for Vertex Cruise IV Station V in the Central North Pacific (Martin *et al.*, 1985). Carbon flux with depth is estimated from the equation $F_c = F_{100}(Z/100)^{-b}$ (Martin *et al.*, 1987).

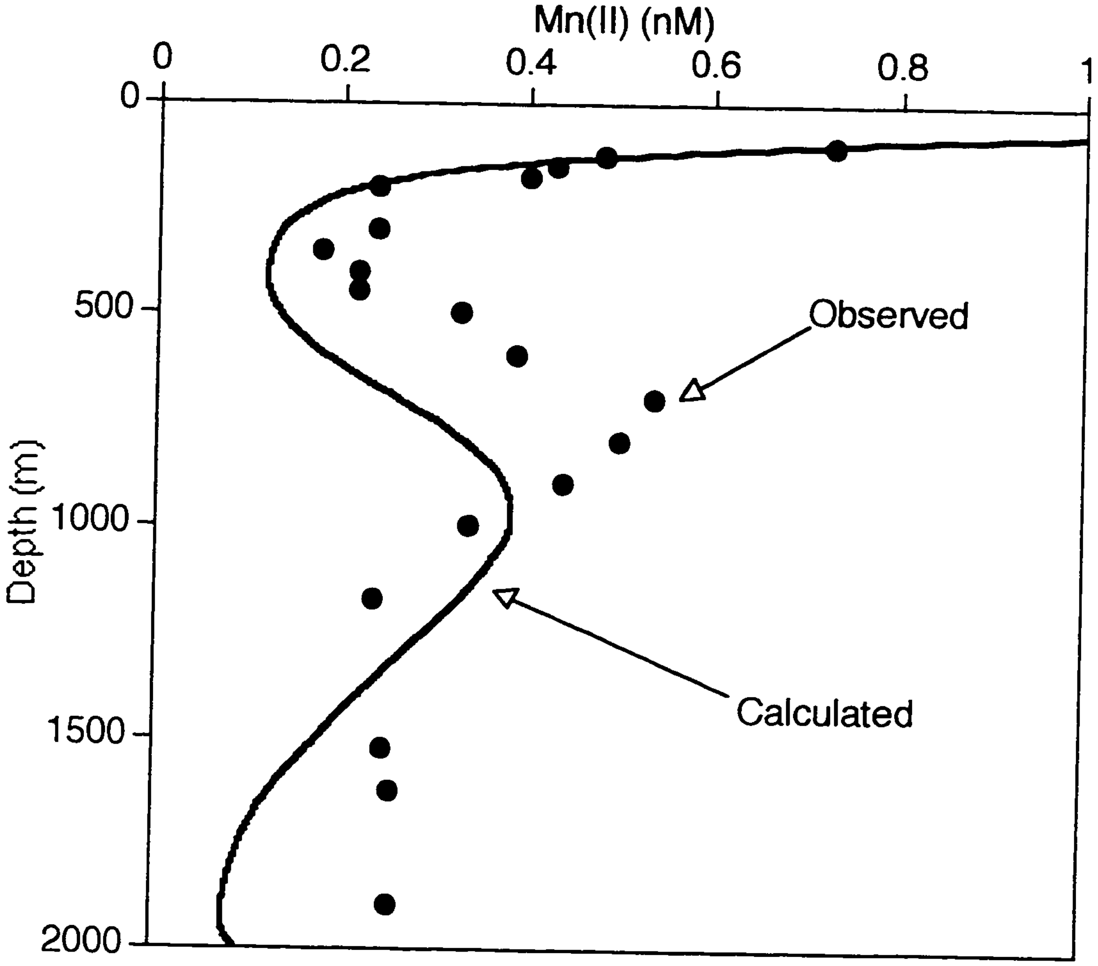
Figure 2. Observed Mn(II) concentrations (●) at Stations in the Atlantic and Pacific Oceans (Martin *et al.*, 1985) and calculated (—) from a kinetic model using *in situ* F_{100}, oxygen, and pH values (from Johnson *et al.*, 1996).

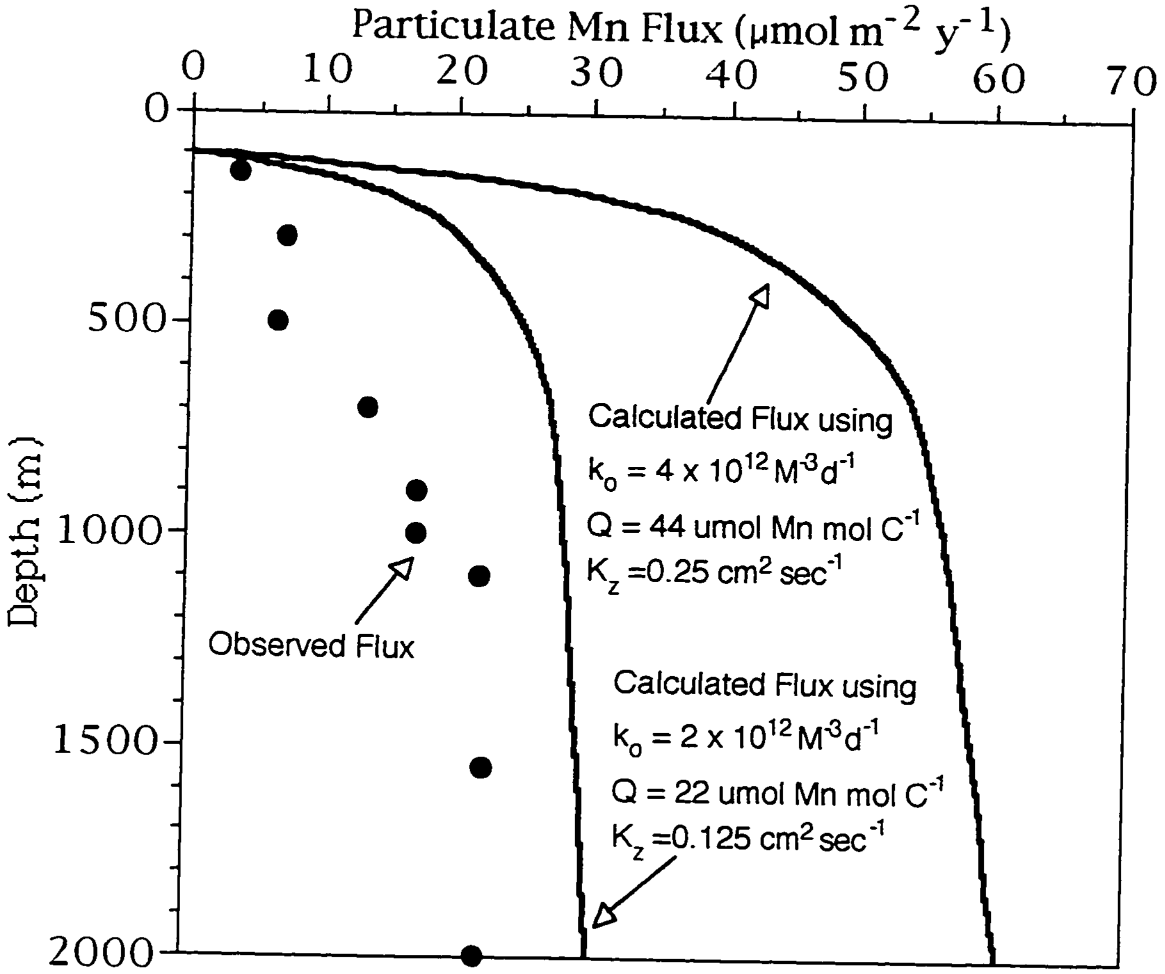
Figure 3. Observed Mn(II) concentrations (●) at Vertex 4 Station 5 in the Central North Pacific (Martin *et al.*, 1985) and calculated (—) from a kinetic model (Johnson *et al.*, 1996) using *in situ* F_{100}, oxygen, and pH values.

Figure 4. Flux of weak acetic acid leachable Mn observed at Vertex 4 Station 5 (Martin *et al.*, 1985) and calculated from a kinetic model (Johnson *et al.*, 1996). The Mn oxidation rate constant (k_o), ratio of Mn to C in POM (Q), and vertical eddy diffusion coefficient (k_z) are adjustable parameters with two resulting flux calculations shown for comparison. The Mn flux calculated using the value determined in chapter 2 for the homogeneous inorganic Mn(II) oxidation rate constant ($k_1 = 2 \times 10^{12}\ M^{-3}\ d^{-1}$), more accurately describes the observed Mn flux (●), than does a calculation using Morgan's (1967) value for the homogeneous inorganic Mn(II) oxidation rate constant ($k_1 = 4 \times 10^{12}\ M^{-3}\ d^{-1}$).


Mn(II) Production (nM y^{-1})
0
0.1
0.2
0.3
0.4
0.5
0.6
0
500
1000
1500
2000
Depth (m)


Manganese (nM)
Manganese (nM)
0.0 0.2 0.4 0.6 0.8 1.0
0.0 0.2 0.4 0.6 0.8 1.0
Depth (m)
0
500
1000
1500
2000
A
VERTEX 4
B
VERTEX 5
C
FeLine
0 1 2 3 4 5
D
VERTEX 2
E
NABE


Mn(II) (nM)
0
0.2
0.4
0.6
0.8
1
Depth (m)
0
500
1000
1500
2000
Observed
Calculated


Particulate Mn Flux (μmol m^{-2} y^{-1})
0
10
20
30
40
50
60
70
Depth (m)
0
500
1000
1500
2000
Calculated Flux using
k$_o$ = 4 x 10^{12} M^{-3}d^{-1}
Q = 44 umol Mn mol C^{-1}
K$_z$ =0.25 cm^2 sec^{-1}
Observed Flux
Calculated Flux using
k$_o$ = 2 x 10^{12} M^{-3}d^{-1}
Q = 22 umol Mn mol C^{-1}
K$_z$ =0.125 cm^2 sec^{-1}