THE EFFECTS OF OZONE DEPOSITION AND DISSOLVED ORGANIC MATTER ON MANGANESE SPECIATION IN THE SURFACE OCEAN

A Thesis

by

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ABSTRACT

Despite the known reactivity of ozone (O_3) in water and ozone's environmental importance in the atmosphere, there are relatively few studies published examining the chemistry of O_3 in seawater. This study focused on developing a flow injection analysis (FIA) chemiluminescence system to measure Mn(II) in order to investigate the effect of O_3 deposition to the sea surface on Mn speciation. Modifications to earlier FIA systems had to be made in order to accommodate the relatively high concentrations of Mn(II) (200 nmol/kg) in these experiments. Experiments were also conducted where seawater containing different concentrations of Mn(IV) particles and organic carbon were exposed to gas streams containing different levels of O_3. Ozone was not found to affect the concentration of Mn(II) in seawater.

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NOMENCLATURE

CH_4	Methane
CO_2	Carbon dioxide
CTFE	Chlorotrifluoroethylene
DI	Deionized water
DOM	Dissolved Organic Matter
Fe	Iron
FIA	Flow Injection Analysis
HCl	Hydrochloric acid
HCO_3^-	Bicarbonate
HDPE	High Density Polyethylene
H_2O_2	Hydrogen peroxide
$HO_2\cdot$	Hydroperoxy radical
I^-	Iodide
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
IDA	Iminodiacetate
Mn	Manganese
MnO_2	Manganese oxide
MQ	Milli-Q
NH_4OH	Ammonium hydroxide
Ni-NTA	Nickel-nitriloacetic acid
NO_x	$NO + NO_2$

O_2^-	Superoxide
O_3	Ozone
·OH	Hydroxyl radical
PEEK	Polyetheretherketone
PVC	Polyvinyl chloride
ROS	Reactive Oxygen Species
TETA	Triethylenetetramine
VOCs	Volatile Organic Compounds

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1. INTRODUCTION

1.1 Ozone

Ozone (O_3) is a key compound in the atmosphere, playing a number of different roles. In the stratosphere it blocks harmful ultraviolet radiation from reaching the Earth's surface. On the other hand, excess O_3 levels in the troposphere can be detrimental to human health (EPA, 2013). The photolysis of O_3 in the troposphere is a significant source of hydroxyl radicals (·OH), one of the most powerful oxidants in the atmosphere. Ozone also acts as a greenhouse gas, trapping heat in the atmosphere. Not only does O_3 play a number of different roles in the atmosphere, it is very reactive in water and commonly used to treat drinking water. Despite this knowledge, there are relatively few published studies examining the interaction of ozone with seawater in the marine environment.

In order to know where O_3 deposition could have a significant environmental impact, it is important to understand the sources of O_3. In the troposphere these include fluxes from the stratosphere and in situ production (Ganzeveld et al. 2009). Ozone formation in the troposphere is primarily dependent on the NO_x ($NO_x = NO + NO_2$) cycle (Figure 1). Natural sources of NO_x include lightning, forest fires, and bacterial production in soils. However, combustion of fossil fuels also produces NO_x (EPA 2013). This can result in elevated NO_x concentrations in urban areas like Houston, TX. Houston also has elevated peroxy radical concentrations due to a large number of petrochemical plants in the region. The combination of these two things and the strong

sunlight in Houston can result in high O_3 levels in the city. These high levels can have a number of different impacts.

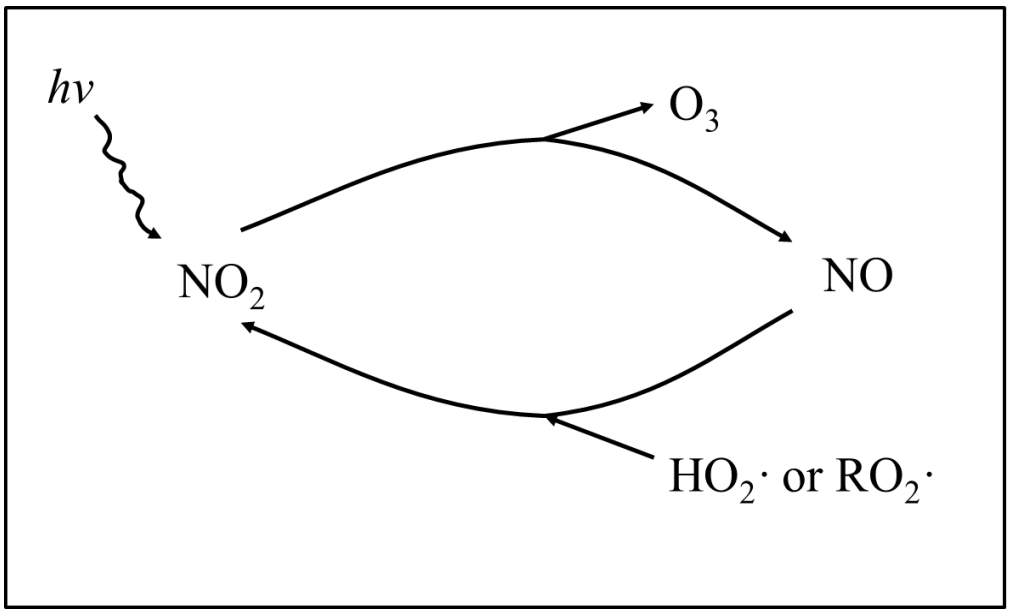

Figure 1. Schematic of the NO_x cycle.

For example, O_3 affects the oxidative capacity of the troposphere. The photolysis of O_3 results in the production of ·OH, one of the most reactive compounds in the atmosphere. This can affect many different processes, as ·OH oxidizes methane (CH_4) and volatile organic compounds (VOCs). That oxidation can lead to the production of peroxy radicals, perpetuating the NO_x cycle and O_3 production. In addition to its effect

on chemical reactions in the atmosphere, O_3 is a greenhouse gas and elevated O_3 levels contribute to climate warming. The increase in radiative forcing of O_3 since the industrial era is about 0.34 W/m^2, which is equal to about one fifth the change in radiative forcing attributed to carbon dioxide (CO_2) over that time period (Conley et al. 2013; Myhre and T. Nakajima 2013).

Beyond these chemical and physical effects, O_3 also impacts biology, including human health. Exposure to high O_3 levels over periods of hours has been directly connected to respiratory problems, such as decreased lung function and increased asthma incidence. It has also been correlated with changes in the cardiovascular system and increased mortality, though causality has not been definitively determined (EPA 2013).

With its high reactivity and wide range of effects, it is also important to understand the sinks of tropospheric O_3. Photolysis and chemical reaction with hydroperoxy radical ($HO_2\cdot$) are major loss processes for O_3 in the troposphere (Ehhalt 2001). As these processes are affected by light intensity and temperature, the rate of loss varies with latitude, time of year, and the concentration of $HO_2\cdot$ precursors like CH_4. Another significant sink for O_3 is reaction with surfaces, including bodies of water like lakes, rivers, and the ocean. Ozone deposition to the ocean can account for approximately 1/3 of O_3 deposition globally (Ganzeveld et al. 2009; Helmig et al. 2012). The loss rate due to dry deposition depends on a number of different factors.

From a purely physical perspective, O_3 deposition is controlled by wind speed, the solubility of O_3, and its molecular diffusivity (Chang et al. 2004). These are the most important factors for determining the rate of O_3 deposition to the sea surface. However,

these factors do not fully account for the deposition of O_3 to the ocean. Chang *et al*.(2004) added a chemical enhancement factor to their model for O_3 deposition in order to explain additional O_3 loss. The addition of a chemical enhancement factor is supported by experimental studies demonstrating an enhanced rate of O_3 deposition in the presence of chlorophyll, dissolved organic matter (DOM), and iodide (I^-) (Clifford et al. 2008; Martino et al. 2012).

The importance of chemical reactivity for O_3 deposition indicates the potential reactivity of O_3 in seawater. Few studies have been published investigating the reactions of O_3 and the products of its decomposition in seawater. One study focusing on this system tested the results of O_3 reaction with iodine species. It was found that the deposition of O_3 to seawater resulted in enhanced production of iodocarbons, including CH_2I_2, $CHClI_2$, and CHI_3 (Martino et al. 2009). The emissions of other iodine containing compounds, I_2 and HOI, have also been shown to be enhanced in the presence of O_3 (Carpenter et al. 2013). Other elements and compounds, such as iron (Fe), may also contribute to the level of I_2 produced relative to the O_3 concentration (Sakamoto et al. 2013). Sakamoto *et al.* (2013) propose that O_3 oxidizes Fe(II) in salt water and the resultant Fe(III) in turn scavenges hydroxide ions. This helps maintain the pH during the production of I_2. This process may not be relevant for marine environments, as the concentration of Fe(II) will be much less than the concentration of dissolved inorganic carbon (DIC). The DIC will probably have a much bigger effect on maintaining the pH than Fe(II) will. Nevertheless, the results from these experiments demonstrate the

potential effect O_3 can have on chemistry in the ocean, not only with respect to reaction with halogens, but also through reaction with other elements and compound classes.

This reactivity should be expected based on studies regarding the ozonation of drinking water. Ozonation is a commonly used process to treat drinking water, targeting a number of different pollutants (Camel and Bermond 1998). Ozone is a powerful oxidant and it can remove a number of species from water, including inorganics like metals. This has been shown to be true with both Fe and manganese (Mn), though the rate and extent of oxidation depends on the other species in solution, including organics and bicarbonate (HCO_3^-) (Reckhow et al. 1991). Ozone breaks down organic matter, removing harmful compounds and bad odors and tastes (Camel and Bermond 1998). It also disinfects the water, killing microbes. Part of this versatility stems from the fact that O_3 is not stable in water (Von Gunten 2003). It reacts with hydroxide ions, leading to the production of ·OH and superoxide (O_2^-), as well as other radical species. These molecules are also extremely reactive, helping to explain how the addition of O_3 to water can lead to so many different chemical reactions. However, this reactivity is strongly dependent on pH, organic matter composition, alkalinity, and the relative abundances of the reactants. (Von Gunten 2003). Seawater differs markedly from groundwater or other sources of freshwater in all four of those qualities. As such, while the drinking water literature gives an indication of the impacts O_3 could have on the chemistry of the surface ocean, seawater must be studied separately.

1.2 Manganese

One of the functions of ozonation is to remove inorganic pollutants, such as Fe and Mn, from drinking water. There has already been at least one study published suggesting that Fe will react with O_3 in seawater, affecting the chemistry of other compounds (Sakamoto et al. 2013). As Fe reacts with O_3 in seawater, it is likely that Mn will too, though Fe reacts with O_3 more quickly than Mn does (Reckhow et al. 1991). Manganese is an important element for a number of reasons, such as the fact that it is an essential micronutrient for organisms, including primary producers. It is an important element in Photosystem II and the cofactor in the enzyme superoxide dismutase, used to combat Reactive Oxygen Species (ROS) (Horsburgh et al. 2002). As such, the Mn requirements of an organism depend, in part, on the concentration of ROS inside cells. For example, the concentration of ROS can increase when diatoms are under Fe stress, causing Mn demand to increase under low Fe conditions (Peers and Price 2004).

As Mn is an essential micronutrient, its bioavailability in a region can impact that area's primary productivity. This is especially true in the Southern Ocean (Middag et al. 2011), but it could also be relevant in other areas. As such, it is important to understand the factors controlling the bioavailability of Mn in seawater. The oxidation state of Mn plays an important role in determining this. Mn(II) is the bioavailable, dissolved form, while Mn(IV) is the seawater insoluble, thermodynamically favored form in the presence of oxygen (Spokes and Liss 1995). Mn(III) can also be present, generally in Mn oxides. In the dissolved form it is very short-lived and only exists in extremely low (picomolar) concentrations in seawater (Wuttig et al. 2013b). For the purposes of this study,

dissolved Mn(III) will not be considered as its concentration is much lower than that of Mn(II), which is present in nanomolar concentrations. Additionally as many of the studies examining the chemistry of Mn oxides in seawater have focused on the Mn(IV) form in the oxides, that is what will be done here. The balance between Mn(II) and Mn(IV) is affected by their different sources and kinetics. Measured distributions of Mn(II) often exhibit a surface maximum (Landing and Bruland 1980). This maximum is partially explained through atmospheric deposition and dissolution from dust, but these processes are not enough to account for the observed concentration of Mn(II) in oxygenated surface waters (Mendez et al. 2010).

In addition to riverine inputs, photoreduction is invoked to explain elevated surface concentrations of Mn(II) (Sunda et al. 1983). The reduction of manganese oxides to dissolved Mn(II) occurs in the presence of organic matter such as humics and is strongly enhanced by the presence of light (Spokes and Liss 1995; Sunda and Huntsman 1994). Spokes and Liss (1995) showed that an increase in the concentration of humic acid in solution leads to an increase in the rate of photoreduction. This is presumably due to increased light absorbance and therefore energy available for the reaction. It is likely that the reduction of Mn oxides occurs via direct electron transfer between photo-excited organics and Mn oxides (Sunda and Huntsman 1994; Waite et al. 1988).

1.3 Ozone and Manganese

While photochemical reactions with DOM can lead to a reduction of Mn(IV) oxides, other natural processes oxidize dissolved Mn(II) to form Mn(IV) oxides. Studies

have shown that both bacterially-mediated and abiotic oxidation of Mn(II) in seawater occurs through O_2^- (Learman et al. 2011; Nico et al. 2002). The O_2^- can be produced enzymatically or photochemically (Learman et al. 2011; Wuttig et al. 2013a). It is proposed that O_2^- reacts with Mn(II), converting it to Mn(III), and that an additional step is required to form Mn(IV) oxides (Learman et al. 2013). The presence of hydrogen peroxide (H_2O_2) inhibits the production of manganese oxides by reducing the Mn(III) back to Mn(II) (Learman et al. 2013). As such, the formation of Mn(IV) via reaction of Mn(II) with O_2^- is partially dependent on the relative abundances of both O_2^- and H_2O_2. It can also be dependent on the relative abundances of other reduced species in solution. For example, both I^- and Mn(II) can be oxidized by O_2^-, but the I^- oxidation will only occur after all Mn(II) has been oxidized (Li et al. 2014). This has been explained by the Mn(II)/Mn(III/IV) system having a lower redox potential than the I^-/I_2 system. In this case, Mn(II) outcompetes iodide for O_2^-, but it is possible that other reduced species in seawater could be more reactive with O_2^- than Mn(II). Both O_2^- and H_2O_2 can be produced enzymatically and photochemically from organics, but there is another potential source of these species that has not been addressed in the literature. Deposition of O_3 to the sea surface could result in the production of ROS that could be important in Mn redox cycling.

The drinking water literature shows that adding O_3 to natural waters causes the oxidation of Mn(II) to both manganese dioxide (MnO_2) and permanganate (MnO_4^-) (Gregory and Carlson 2001). The formation of permanganate during ozonation seems to be negligible at pH 8.0 and will probably not be a significant formation product of O_3

deposition to seawater (Reckhow et al. 1991). The formation of MnO_2 in drinking water has been studied with respect to humic acids and bicarbonate, both of which could be important in seawater. Humics compete with Mn(II) for O_3, increasing the amount of O_3 needed to completely oxidize Mn(II). This suggests that increased humic acids in solution would decrease the possibility of an oxidation of Mn(II) in seawater. However, Paillard *et al.* (1987) have shown that the addition of HCO_3^- in concentrations close to those of seawater can increase the oxidation of Mn(II) by O_3 in the presence of humics. It is proposed that the HCO_3^- ions inhibit a radical chain reaction with ·OH. Breaking this radical chain reaction slows the decomposition of O_3, increasing the probability that the O_3 will react with Mn(II) (Paillard et al. 1989). The concentration of HCO_3^- only seems to affect the oxidation of Mn in the presence of organic matter (Reckhow et al. 1991).

In these studies, the concentration of HCO_3^- is close to that of seawater and the organic carbon concentrations are not very different from those in natural seawater environments, especially in coastal regions (Bauer et al. 2001). It is difficult to compare the structure of the organics in the experiments to those in a coastal environment though, rendering it difficult to compare the two situations directly. Additionally, the O_3 concentrations in these studies are over an order of magnitude greater than what would be found in the natural environment. It is also difficult to say what effect the extra ions in seawater could have on these processes as species like halogens also react with O_3 and ·OH (Von Gunten 2003).

This study aims to determine what impact, if any, O_3 can have on the formation or dissolution of Mn(IV) oxides in surface seawater. Since ozonation causes an oxidation of Mn(II) in drinking water that is enhanced by the presence of HCO_3^-, it seems likely that an oxidation would also happen in seawater. The role of ROS in the formation of Mn(IV) oxides in seawater also suggests that an oxidation would occur. However, the low concentrations of O_3 could result in no significant change in the oxidation state of Mn in seawater. It is also possible that O_3 could cause or enhance processes similar to those that lead to the photoreduction of Mn(IV) oxides in the presence of humics. The structure of the organic matter could have a significant impact on what processes occur. Given these observations, it is expected that O_3 deposition to seawater will have little effect on the oxidation state of Mn and that if there is any effect it is likely to be an oxidation of Mn(II) rather than a reduction of Mn(IV) particles.

2. METHODS

2.1 Technique Development

In order to investigate the effect of ozone deposition on Mn speciation in the surface ocean, an appropriate technique for measuring Mn is needed. As Mn(IV) is present in the particulate phase while Mn(II) is present in the dissolved phase, the two oxidation states can be separated via 0.2 micron filtration. That will leave Mn(II) dissolved in the filtrate and this can be measured. Changes in the Mn(II) concentration will reflect conversions between the dissolved and particulate forms of Mn over time.

It was initially decided to use the flow injection analysis technique of Doi *et al*. (2004) with a few modifications (Figure 2). In the Doi *et al.* (2004) technique, an acidified seawater sample is buffered off-line with ammonium chloride to pH 8.8. This sample is preconcentrated onto an iminodiacetate (IDA) column made in the laboratory and then rinsed with Milli-Q water. It is eluted using a pH 2.9 solution containing 0.1 M formic acid, 12 mM ammonium formate and 0.1 M H_2O_2. It then passes through a Kelex-100 column to remove Fe. The solution is then mixed downstream with 0.7 M ammonium hydroxide and a solution containing 0.06 mM luminol and 0.075 mM TETA. The luminol is oxidized by H_2O_2 and that reaction is catalyzed by Mn(II). The luminol oxidation produces light and the amount of light is proportional to the concentration of Mn(II) present. By detecting the light emission from this reaction, the amount of Mn(II) present in the preconcentrated sample can be determined.

The technique of Doi *et al*. (2004) has been modified by Middag *et al*. (2011). Middag *et al*. replaced the laboratory made IDA column with commercially available Toyopearl AF-Chelate 650M resin (also containing IDA functional groups). They also buffered in-line using 0.5 M ammonium borate to pH 8.5, as that pH is appropriate for trapping Mn(II) on the Toyopearl resin (Aguilar-Islas et al. 2006). The initial system for this study could not incorporate in-line buffering and so that was still done off-line. This system was limited by having only 4 channels on the peristaltic pump. Later a second pump was acquired that expanded the number of channels available.

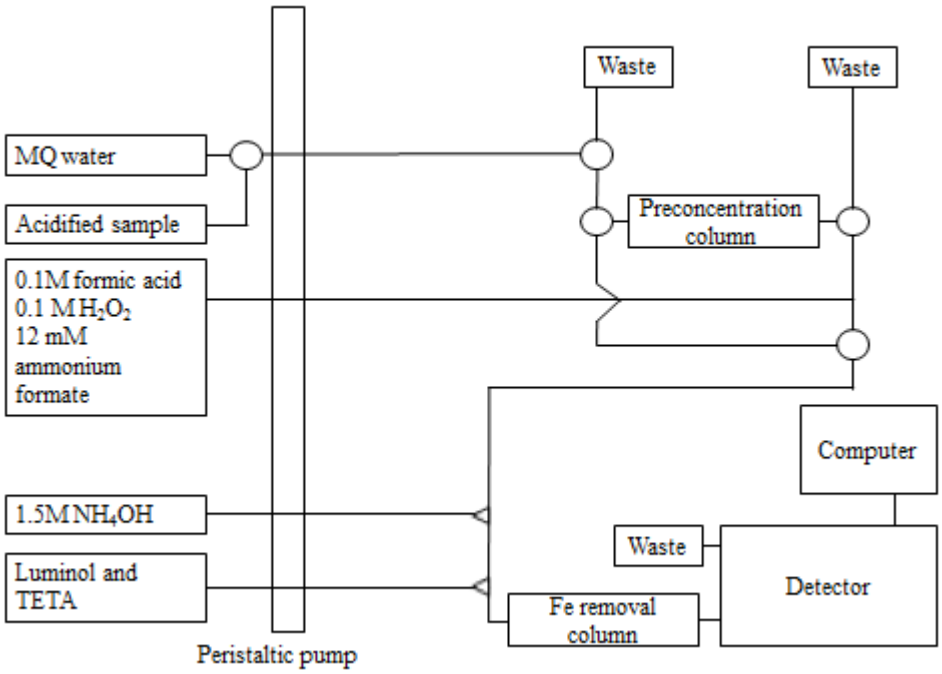

Figure 2. Instrument schematic for initial analytical system.

There were a few problems with this technique that made it unusable for the ozone experiments. Obtaining Kelex-100 was found to be difficult, so another resin had to be used. A Nickel-nitrolacetic acid (Ni-NTA) resin was used in its place. The Ni-NTA resin traps Fe(III) [the form expected to interfere most with a luminol chemiluminescence reaction (Doi et al. 2004)] at a pH of 2.9 but it does not trap Mn. However, the Ni-NTA column was not stable over time when constantly exposed to this carrier stream. Over time the back pressure in the system increased tremendously, causing the peristaltic pump tubing to disconnect and the system to be unusable. This problem was not alleviated by reversing the column direction daily or storing refrigerated in MQ water overnight. The Ni-NTA column was removed and an assumption was made that the Mn concentrations would be significantly higher than those of Fe, so the Fe should not contribute significantly to the signal during the experiments. It was also assumed that Mn would not be organically bound but that Fe would be, preventing Fe from adsorbing to the preconcentration column. The samples were no longer acidified, as acidification releases Fe from its organic ligands.

It was also determined that the pH of 2.9 was not strong enough to remove all of the Mn from the Toyopearl column at the concentrations used for this study. Middag *et al.* (2011) used the FIA system to measure Mn concentrations in the Southern Ocean, which are significantly lower than the concentrations of Mn in the seawater collected for the ozone experiments. Testing carrier solutions with concentrations of formic acid greater than 0.1 M did not significantly impact the amount of Mn removed from the Toyopearl column. Hydrochloric acid has been successfully used to remove Mn(II) from

Toyopearl (Aguilar-Islas et al. 2006) and it has also been successfully used in the carrier stream for an FIA system using the oxidation of luminol by Fe (Klunder et al. 2011). It was decided to use 0.9 M HCl as that had been demonstrated to remove a 40 nM Mn sample that had been preconcentrated for 1 minute when exposed to the 0.9M HCl for 3 minutes. At the time of system development, it was assumed that the concentration of Mn(II) in the seawater would be lower than that 40 nM amount. Also, the preconcentration and elution times could be changed as needed to fully elute a sample. Replacing the formic acid with HCl required separating the H_2O_2 from the acid, necessitating another channel for the peristaltic pump. The H_2O_2 was not stable in the HCl solution and this resulted in a very poor baseline signal.

Changing the concentration of acid present also required changing the concentration of the ammonium hydroxide solution in order to reach the optimal pH for the luminol chemiluminescence reaction. The optimal pH for the chemiluminescence reaction is reported to be 10.2 (Doi et al., 2004), though the reaction pH was measured to be 9.2. Using concentrations of the ammonium hydroxide solution greater than 1.5 M did not seem to improve the signal response even though they brought the reaction pH close to 10.2. However, these tests were run before final adjustments to the system were made and should be repeated.

With these adjustments, the chemistry of the luminol reaction was set. However, other changes had to be made with respect to the samples and rinsing procedures. Doi *et al.* (2004) rinsed the preconcentration column using MQ water. However, the pH of MQ is lower than 8.3-8.7, the optimal pH for preconcentration of Mn onto a Toyopearl resin.

This could result in loss of Mn from the Toyopearl resin during rinsing. Aguilar-Islas *et al.* (2006) used a weak buffer (0.05 M ammonium borate) to rinse their column, reducing the chance of Mn desorption during the rinse process. In this system, the MQ was replaced with a 0.05 M ammonium borate rinse.

At this point, the unacidified samples were buffered in-line using the 0.05 M ammonium borate rinse. Attempts were also made to directly interface the two glass experimental chambers with the FIA system. It was shown that filtering the seawater samples was necessary, as Mn(IV) particles could get trapped on the Toyopearl column and degrade the column. Filtering in-line, which would have allowed the samples to be taken directly from the chamber, analyzed without any handling and significantly reduce the chances of contamination, created too much pressure in the system for the peristaltic pump. However, this was only done with Teflon filters. The hydrophobicity of Teflon filters is very high, making it very difficult to filter through 0.2 micron Teflon manually. For this reason, cellulose acetate filters were used for the experiments. Filtering in-line with cellulose acetate filters was not tested. As the pressure in the system with the Teflon filters was so high, the idea of directly interfacing the experimental chambers with the FIA system was abandoned.

It was then discovered that Fe adsorbs really well to glass and that Fe loss to the walls could be affecting the results of experimental tests in the glass chambers. This required adding a mechanism to remove Fe from the samples. The samples had to be acidified to pH 1.7 to free organically bound Fe and reduce the likelihood of wall adsorption in the glass sample vials. These samples then had to be passed through a Ni-

NTA column to remove Fe but retain Mn in the samples. This was attempted manually to reduce the degradation of the Ni-NTA column observed when the column was in line, but proved to be too difficult. The Ni-NTA column was added to the system in a location so that the samples would pass through the column before being buffered to pH 8.3-8.7. No degradation of the Ni-NTA column was observed in this location, so it is possible that the exposure to formic acid caused the degradation, not the pH. In order to buffer the acidified samples appropriately, the 0.05 M ammonium borate buffer was replaced with a 0.5 M ammonium borate buffer with a pH of 9.5. The 0.5 M ammonium borate buffer was also shown to contain Mn(II), so a Toyopearl clean-up column was added to remove as much additional Mn(II) as possible at pH 9.5.

Adding the Ni-NTA column required other adjustments to be made. The Ni-NTA column could not be rinsed with the 0.05 M ammonium borate solution because this could potentially cause Fe to desorb from the Ni-NTA column and affect the analysis. Additionally, the 0.05 M ammonium borate solution would have been buffered in-line with 0.5 M ammonium borate, causing the pH of the Toyopearl rinse solution to be greater than 8.7, which could result in loss of Mn from the Toyopearl preconcentration column. For these reasons, it was decided to use MQ acidified to pH 1.7 as the rinse solution. It would pass through the Ni-NTA column without changing its pH and therefore the amount of Fe retained. Then it would be buffered to the same pH range as the acidified seawater samples. The pHs were tested and shown to be in the correct range. The final version of this system was used for all experiments described except the seawater control test.

2.2 Final System

2.2.1 Cleaning procedure

All materials (e.g. beakers, vials, tubing etc) labeled as “trace metal clean” were cleaned with the same procedure (Middag et al. 2009). They were rinsed with deionized (DI) water and then kept in a solution of Alconox soap and DI water at 60 °C for 24 hours. Then they were rinsed with DI water until all visible soap was removed, followed by two rinses with MQ water. They were then placed in approximately 6 M trace metal grade HCl at 60 °C for 24 hours. The final step was rinsing 5 times with MQ water. All cleaned materials were stored in a wood and Plexiglas box to prevent any metal contamination prior to use.

2.2.2 Apparatus

The apparatus used for the detection of Mn(II) is an FIA chemiluminescence system (Figure 3). All tubing was 1/16” Teflon (Valco) and connected using non-metal fittings (chlorotrifluoroethylene [CTFE] or polyetheretherketone [PEEK]) (Valco). The sample clean-up and preconcentration columns were 1 cm long bounded by polyethylene frits with 20 μm pore size (Global FIA). The sample clean-up column was packed with a Ni-NTA Superflow resin (Qiagen, Inc.). The preconcentration column was packed with a Toyopearl AF-Chelate resin (Tosoh Biosciences) with an IDA functional group. The 0.5 M ammonium borate clean-up column was a 5 cm long piece of 1/8” Teflon tubing filled with Toyopearl AF-Chelate resin held with polyethylene frits. A peristaltic pump with polyvinyl chloride (PVC) tubing (Cole-Parmer) controlled all solution flow rates.

PVC tubing had to be used, as silicone was found to introduce air bubbles into the system. Five 12 volt 3 way valves with Teflon wetted parts (Cole-Parmer) were used to control the direction of flow. All flow rates were approximately 1 mL/min. For the luminol-containing and 0.5 M ammonium borate solutions, 0.87 mm i.d. peristaltic pump tubing was used. For the other solutions 1.02 mm i.d. peristaltic pump tubing was used. The chemiluminescence signal was detected using a Gilson 121 fluorometer with the excitation window blocked. The system was controlled via a custom-built LabVIEW program.

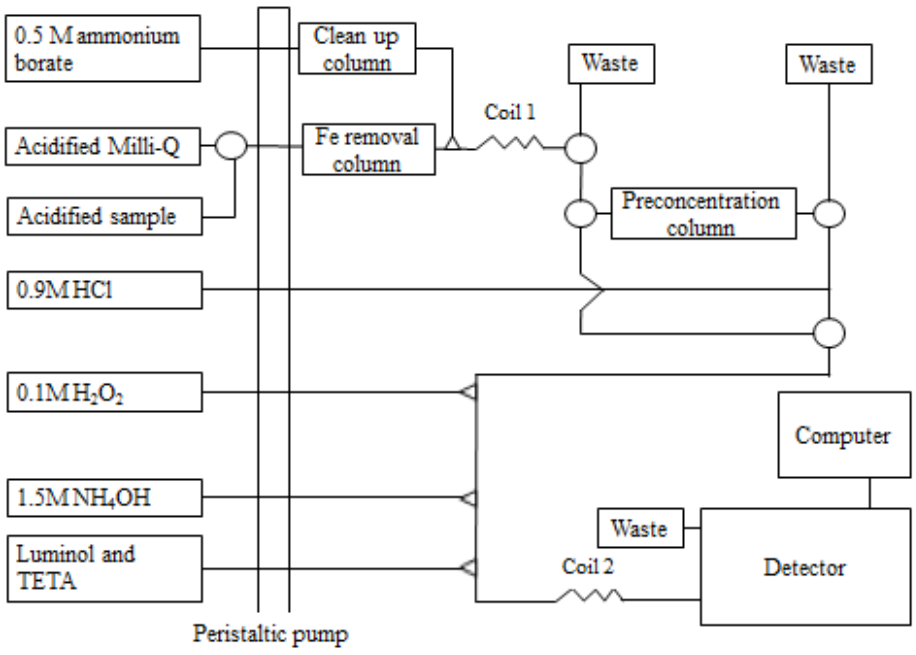

Figure 3. Schematic of final Mn detection system. (○) solenoids; (∆)mixing tees; (⩘) reaction coil.

2.2.3 Solutions

All solutions were made using MQ water in trace metal clean glass volumetric flasks before being stored in 500 mL trace metal clean high density polyethylene (HDPE) brown bottles (VWR). The 0.5 M ammonium borate solution was prepared by adding 17 mL of trace metal grade ammonium hydroxide (NH_4OH) (Sigma-Aldrich) to 15.45 g of trace metal grade boric acid (Alfa Aesar) and diluting to 500 mL with MQ. It was then adjusted to pH 9.5 using boric acid. The 1.5 M NH_4OH solution was made with 50 mL of the same stock of NH_4OH diluted with MQ to 500 mL. The pH 1.7 MQ solution was made by adding small amounts (hundreds of microliters) of 11.2 M HCl to 500 mL of MQ until the pH reached the desire value. The 0.9 M HCl was made by diluting 40 mL of 11.2 M HCl to 500 mL with MQ water. The 0.1 M H_2O_2 was made using 5.4 mL of trace metal grade H_2O_2 (Sigma Aldrich) diluted to 500 mL. The H_2O_2 solution was made fresh daily. The 0.067 millimolar (mM) luminol and 0.05 mM triethylenetetramine (TETA) solution was made by adding 300 µL of stock luminol and 5 µL of TETA (Sigma Aldrich) and diluting to 500 mLs with MQ. The stock luminol solution contained 270 mg luminol (Sigma Aldrich), 500 mg potassium carbonate (Sigma Aldrich), and MQ water in a 15 g solution.

Manganese(IV) oxide particles were made inorganically following the work of Spokes and Liss (1995). Potassium hydroxide (Sigma Aldrich), trace metal grade Mn(II) chloride tetrahydrate (Sigma Aldrich), and potassium permanganate (Sigma Aldrich) were combined in molar ratios of 4:3:2 in Milli-Q water to generate fine Mn(IV) oxide particles. For these experiments, 0.01 g potassium permanganate, 10 µL potassium

hydroxide, 0.02 g Mn(II) chloride tetrahydrate, and 20 g MQ were combined to yield a stock solution with a concentration of 0.04 mol/kg suspended Mn(IV) oxide particles.

A stock solution of organic compounds was made in order to add fresh organics to some of the experiments. The stock solution was made by combining 0.05 g D-tryptophan (Sigma Aldrich), 0.08 g D-galactose (Sigma Aldrich), 0.0508 g vanillin (Eastman Organic Chemicals), and 20 g MQ water in a solution with a total concentration of 5.4 mg-C/g. These organic compounds were chosen to ensure that a wide range of functional groups (including amines, carboxylic acids, ethers, hydroxyl groups, and aromatics) would be present in solution and maximize reactivity. Using humics may have been better to maximize reactivity, but by using model compounds, the exact chemical structure of the organics was known. This would allow for the determination of important functional groups and potential chemical mechanisms in further experiments if a reaction occurred in the presence of the model compounds.

A 1.82 μM stock Mn(II) solution for making calibration standards was made from a Mn(II) standard for ion chromatography (Sigma Aldrich) and stored in MQ water acidified to pH 2.7 with nitric acid (Fisher Scientific). To make the stock solution, 50 μL of the Mn(II) standard for ion chromatography were added to 500 mL of MQ and acidified with 100 μL nitric acid. Daily standard additions were made by adding microliter amounts of the stock Mn(II) solution to seawater and acidifying to pH 1.7. The standards were made at least one day before performing a calibration.

2.2.4 Procedure

The pH 1.7 MQ is pumped through the Fe removal (Ni-NTA) column before being buffered to a pH range of 8.3-8.7 with the addition of 0.5 M ammonium borate (pH = 9.5) in a 15 cm reaction coil (Figure 3, Coil 1). The ammonium borate is first pumped through a clean-up column to remove unwanted Mn. Buffered MQ then rinses the preconcentration column containing Toyopearl AF-Chelate resin for 250 seconds, preconditioning the pH of the column. Then the sample is pumped instead of the pH 1.7 MQ, flushing the line for 250 seconds before loading the sample directly onto the preconcentration column for 45 seconds. The Fe removal column serves to remove any Fe(III) from the samples while the Toyopearl column traps Mn quantitatively between pH 8.3 and 8.7 (Aguilar-Islas et al. 2006). Following sample load, the preconcentration column is again rinsed with buffered MQ for 250 seconds to remove excess seawater ions from the column. The sample is then eluted from the preconcentration column with 0.9 M HCl for 250 seconds. Subsequently, 0.1 M H_2O_2, is added to the sample stream using a mixing tee, followed by addition of 1.5 M NH_4OH with a mixing tee and, finally, a solution of 0.067 mM luminol and 0.05 mM TETA in a 35 cm reaction coil (Figure 3, Coil 2) to ensure complete reaction and maximum luminescence signal. This solution then passes through the detector and is recorded using a Mini-Lab 1008 (Measurement Computing) data acquisition device and a custom-designed LabVIEW program.

2.2.5 Daily maintenance

Two MQ samples, two acidified MQ samples, and two acidified junk seawater samples were analyzed each day to precondition the columns before analyzing any samples. There were indications that this process was insufficient to fully prepare the columns, as the first few samples analyzed after this process often had much greater peak areas than subsequent samples. If this was observed, those samples were removed from any analysis.

After all analyses had been performed for one day, the direction of the Fe removal and clean up columns was reversed. The system was rinsed with 0.9 M HCl for 12 minutes, followed by rinsing with MQ water for 12 minutes. Each valve configuration used during an analytical run was maintained for 2 minutes while the cleaning solutions flowed through the system. The MQ water was left in the system overnight.

2.2.6 Calibrations and error

The system was calibrated daily using a series of standard additions to the same seawater stock as the experimental solution. For the ozone experiments, four standards were run, with additions of 0, 49, 100, and 149 nmol/kg. Each was analyzed twice and the standards were spread throughout the analysis of the samples for a given experiment. The response peak for each sample was analyzed using peak area. While Middag *et al.* (2011) used peak height to quantify the peak signal, comparisons of peak height to peak area showed analyses with peak area to have greater reproducibility than those using

peak height for this system. A sample peak generally showed a flat baseline, a narrow peak followed by a much larger one and a gradual tapering of the signal until a return to baseline (Figure 4). A second peak was often seen after the sample peak, likely due to a change in pressure in the system when the Toyopearl column was no longer in line with the carrier stream. The initial narrow peak was included in all calculations of peak area and the baseline was determined from just before the appearance of the initial peak. It is thought that the initial narrow peak is a function of the tubing between the solenoid and the preconcentration column. During the rinsing of the column, the solution would pass through the solenoid before passing through the preconcentration column. When the Mn(II) is eluted, the 0.9 M HCl passes through the preconcentration column and then the solenoid. There is a piece of tubing between the column and the solenoid that contains some of the rinse solution. It is possible that this rinse solution contains some Mn(II) and becomes slightly mixed with the HCl before the preconcentrated Mn(II) from the sample desorbs from the column, as the pH change is not instantaneous. The Mn(II) present in the rinse solution could be creating the narrow peak before the actual sample peak elutes. The narrow peak was included in calculations of peak area because there were times when the narrow peak and the sample peak would not be clearly distinguished from one another.

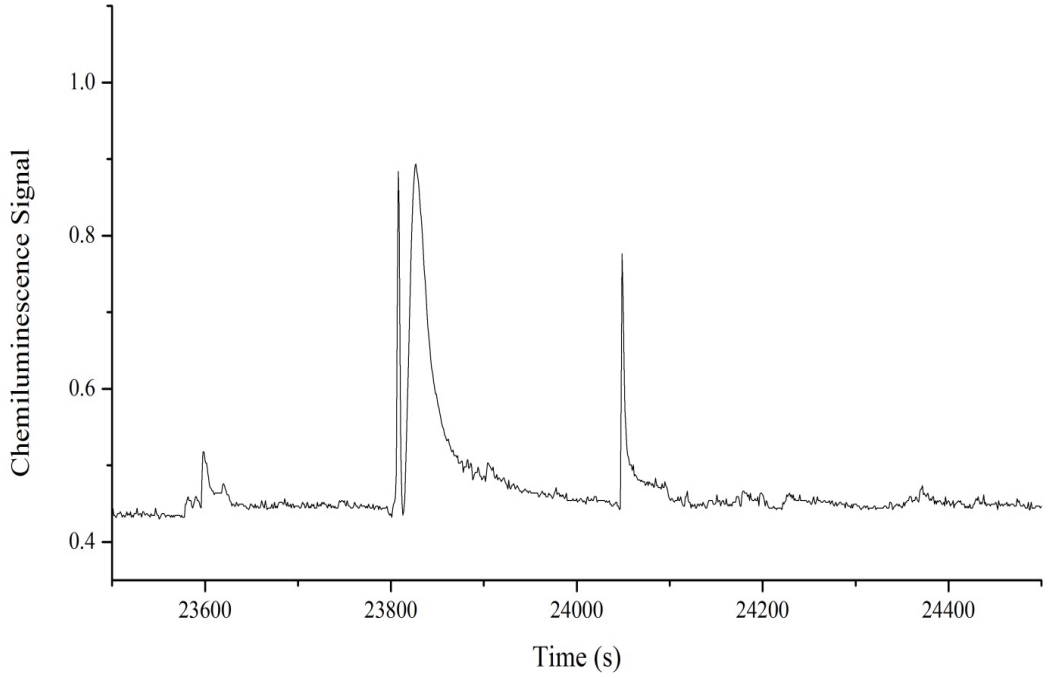

Figure 4. Example peak.

The reproducibility for this system was poor and replicate analyses of the same sample often differed by more than 10%. This resulted in poor and highly variable daily calibrations, though the slopes of the calibrations did not consistently increase or decrease over time. This suggests that the variation is not due to degradation of any system components over time. The preconcentration and Fe removal columns were also replaced during the experiments and this change did not seem to affect the calibrations or the reproducibility of the samples. To reduce the error from the highly variable daily calibrations, all of the standards analyzed throughout the experiments were combined in one calibration (Figure 5, Table 3). If the difference between replicate analyses of the

same standard was less than 10% both values for the standard were included in the calibration. This calibration was applied to all experiments except the seawater test, as the seawater test was analyzed using a different version of the analytical system. This calibration contains 30% error in the slope and 134% error in the y-intercept.

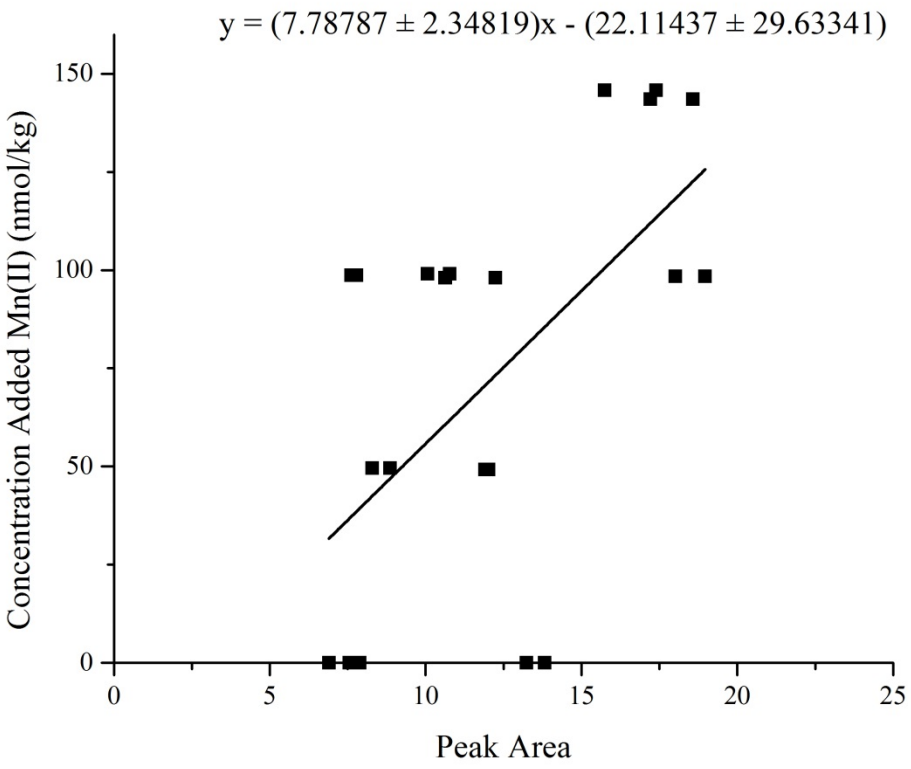

Figure 5. Calibration used for all experiments.

An extended calibration shows a much different correlation (Figure 6). The error for the slope in this calibration is 18% and the error for the y-intercept of the extended calibration is 17%. This clearly has lower error than the combined calibrations, especially in the y-intercept. The actual values for the slopes and y-intercepts are very different, suggesting that the signal response over the range of 0 to 350 nmol/kg added Mn(II) is non-linear. The y-intercept of -20 for the shorter calibration, meaning that the seawater contained 20 nmol/kg Mn(II), is closer to the concentration expected for open ocean Gulf of Mexico water. A concentration of 600 nmol/kg Mn(II), as determined using the extended calibration, seems high. However, the depth of collection of the Gulf of Mexico water is unknown, making it difficult to predict the exact range of Mn(II) concentrations expected. There was no evidence suggesting that Mn was retained on the preconcentration column between analyses at the high concentrations of Mn(II), though this should be investigated further.

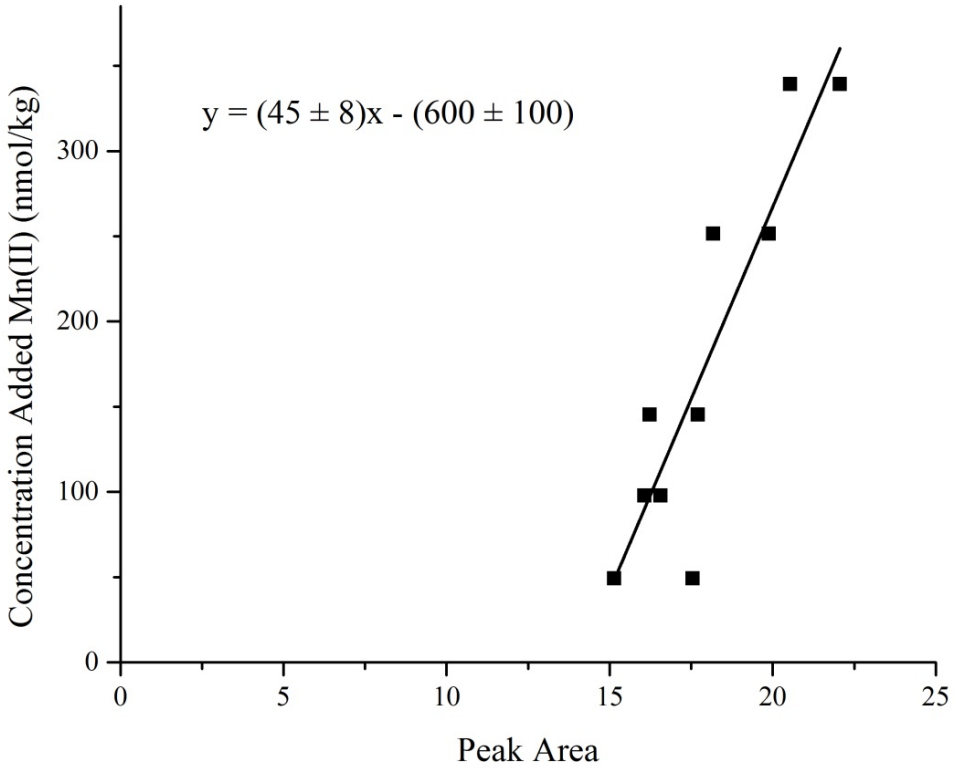

Figure 6. A calibration using standards with a higher concentration of added Mn(II).

Unfortunately, the reproducibility of the system is too poor to determine whether the signal response is non-linear over a large range of Mn(II) concentrations. The reproducibility of this system must be improved in order for it to be applied to additional experiments. One factor that could affect the reproducibility of the system is the timing of the sample preconcentration and the rinses. Different load times, which affect the amount of sample preconcentrated, should be tested. Another factor affecting the reproducibility of the analyses could have been the peristaltic pump. In reality, this

system uses two peristaltic pumps. The 0.5 M ammonium borate buffer and the luminol solution are located on a very old pump that degrades the peristaltic pump tubing very quickly. The lifetime of this tubing is less than 24 hours of use. When this tubing degrades, the signal baseline becomes variable with many random spikes. This is going to affect any peak measurements. Degraded peristaltic pump tubing could also affect the amount of solution dispensed, in turn affecting the peak signal, especially if the amount of luminol dispensed was reduced.

None of these calibrations include a blank. Passing seawater through a Toyopearl column to remove background Mn was attempted, but it did not decrease the Mn signal. Obtaining a system blank was also attempted by analyzing acidified (pH 1.7) MQ water as a sample. This should account for any Mn present in the analytical solutions. However, the peak from the acidified MQ water was often larger than the peaks from the seawater samples. This is probably due to the preconcentration column having been incompletely cleaned before analyzing the acidified MQ water samples, as they were analyzed early in an analytical run. Otherwise, this implies that the MQ water contains more Mn than the seawater, which would be a significant problem.

Many of the careful characterization tests that were done with the earliest iterations of the analytical system were not performed for the last iteration. They need to be done in order to better understand the system, choose appropriate calibration standards, and optimize the peak signal. The pHs used for preconcentration were taken from the literature for other FIA systems but should be tested for this system. Also, the

ability of the Ni-NTA column to truly retain Fe and not become saturated during an analytical run needs to be evaluated.

2.3 Ozone Experiments

To test the effect of O_3 deposition on Mn speciation in seawater, an apparatus containing two test chambers was constructed (Figure 7). Air that has been cleaned of all compounds except nitrogen and oxygen (zero air) flows through an Aqua Medic Ozone 25 generator to add O_3. This stream is then diluted with zero air to create the desired O_3 concentration before splitting in two streams. Each stream then passes through a flow controller to set the flow rate at 1 L/min. Extra gas exits through the bypass. The gas then enters a jacketed glass chamber with 1 L internal volume. The chambers contain two ports at the top allowing for gas entrance and exit. Each chamber also contains a port to allow for seawater sampling and is temperature controlled to 25 °C for these experiments. After the gas stream exits the chamber, the O_3 concentration is measured using a Thermoelectron 49C analyzer (Thermo Scientific).

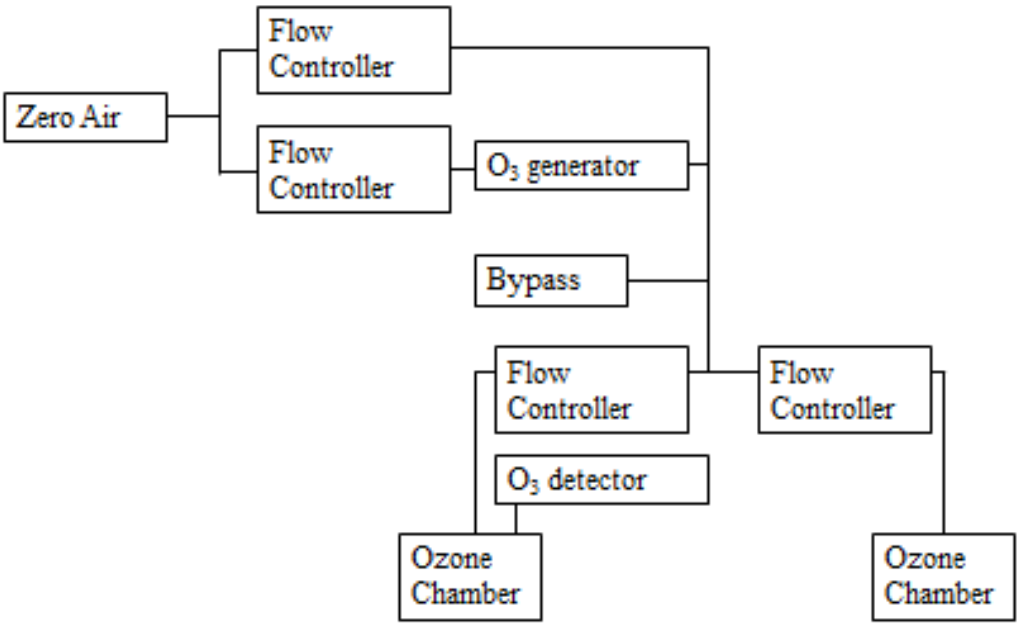

Figure 7. Schematic of experimental chamber set up.

Seawater for these experiments was collected from the central Gulf of Mexico and 0.2 micron filtered. The water was stored in the dark at 4 ºC for over 1 year before beginning the experiments. All experiments were conducted in the dark. Each chamber was rinsed 3 times with 0.9 M hydrochloric acid (HCl) (trace metal grade, Fisher Scientific) followed by 3 rinses with Milli-Q (MQ) (Barnstead Nanopure Thermo Scientific) water. The chambers were then flushed with zero air overnight before beginning an experiment. For each experiment a 1 kg batch of seawater containing any added materials was made in a high density polyethylene (HDPE) Nalgene container approximately 1 hour before adding it to the experimental chambers. The Nalgene

container was rinsed 3 times with seawater before filling but was not trace metal cleaned. During early attempts to trace metal clean the Nalgene containers the containers melted. When Mn(IV) particles were added, the target concentration of Mn(IV) in the experimental solution was approximately 200 nmol/kg. When organics were added, the target concentration of total organics in solution was approximately 5 mg-C/kg. Each chamber was rinsed with unaltered filtered seawater 3 times before adding the experimental solution. Approximately 500 g of experimental solution were added to each chamber, and each chamber was allowed to equilibrate to temperature approximately 20-30 minutes before beginning sampling. The samples were drawn with a plastic syringe (Becton Dickinson) and filtered through a 0.2 micron filter immediately after sampling using a cellulose acetate syringe filter (Thermo Scientific) to remove any Mn(IV) oxides and separate dissolved Mn(II) from particulate Mn(IV). Each sample was filtered into a light-shielded trace metal clean 10 mL glass vial. Initially, it was intended to use HDPE vials, but the HDPE vials were occasionally degraded by the strong acid in the trace metal cleaning procedure. The degraded vials leached Fe or Mn into the samples, drastically increasing the size of sample peaks. The syringe was rinsed with 30 mL of sample before dispensing into the vial. The vial was not rinsed with sample in order to minimize the volume of sample drawn from the chambers. The sample was then acidified to pH 1.7 using 30 μL of 11.2 M HCl and stored at least overnight before analysis. All samples for each experiment were analyzed on the same day. Each sample was analyzed twice. Control tests did not reveal any significant loss of Mn(II) to reaction

with the chamber walls, suggesting that Mn adsorption to glass would not affect the experiments or samples stored in glass vials

2.4 System Changes

This system needs to have better reproducibility in order to be used for future ozone experiments. There are many adjustments to the system that can help improve this. These include testing the timing of the system, testing different pHs for Mn(II) preconcentration and the luminol reaction, and verifying the behavior of the Fe removal column. If these problems can be addressed, this system may be useful for laboratory experiments testing the chemistry of Mn in seawater. The technique has the ability to address slightly higher concentrations of Mn(II) than normally observed in open ocean surface seawater. This can be useful for doing experiments like the ozone tests, particularly if they are not done in a trace metal clean environment or are simulating coastal areas with relatively high Mn(II) concentrations.

This technique could also potentially be adapted to measure Fe relatively easily. This could be done by replacing the Toyopearl AF-Chelate resin in the preconcentration column with a Ni-NTA resin and removing the inline buffering capacity and Fe removal column. The Ni-NTA column will selectively retain Fe(III) at a pH of 1.7, allowing for speciation studies between Fe(II) and Fe(III). The FIA technique is fast and much more cost effective than alternatives like inductively coupled plasma mass spectrometry (ICP-MS). For conducting experiments like these, it can be very important to get results

quickly and analyze samples as needed in order to determine the next appropriate test. The FIA system gives the scientist this flexibility.

3. RESULTS AND DISCUSSION

Eight experiments were designed to test the impacts of O_3 deposition, DOM, and Mn(IV) particles on the concentration of Mn(II) in seawater (Table 1). For experiments with added O_3, the concentration of O_3 was not constant and varied between the two chambers, with one generally having a higher O_3 concentration than the other. This could be due to incomplete mixing during dilution of the O_3 stream. For each test the initial samples were taken before adding O_3 to the system. Then steady O_3 concentrations were established as close to ambient as possible, though the O_3 generator was too powerful to generate ambient levels well. The concentration of O_3 was found to rise throughout an experimental run. This could be due to a decrease in the number of available reactants for O_3 over the course of an experimental run, allowing for a buildup in O_3 concentration. However, it could also be that the output of the O_3 generator increased over time. The magnitude of the change in O_3 varied depending on the experiment.

Table 1. List of all experimental runs. Tests are named by the components present. SW = open Gulf of Mexico seawater, Mn(IV) = Mn(IV) particles, OC = a mixture of tryptophan, galactose, and vanillin, O_3 = ozone

Test Name	Concentration Mn(IV)[a] **(nmol/kg)**	Concentration organic mixture **(mg-C/kg)**	Ozone concentration **(ppb)**
SW	-	-	-
SW + O_3	-	-	195 to 230
SW + Mn(IV)	212	-	-
SW + Mn(IV) + O_3	212	-	240 to 460
SW + OC	-	5.9	-
SW + OC + Mn(IV)	212	6.1	-
SW + OC + O_3	-	5.7	185 to 410
SW + OC + O_3 + Mn(IV)	212	6.1	110 to 175

[a]Based on a mass of 0.2 g for 20 μL of suspended Mn(IV) particles.

The Mn(II) concentration varied over time under different concentrations of Mn(IV) particles, organic compounds and O_3 (Figure 8). The two glass chambers were assumed to experience the same trends. Even though the chambers were exposed to slightly different levels of O_3, no differences in the concentration of Mn(II) in the two chambers could be attributed to different O_3 concentrations. Combining the data from the two chambers together allowed for greater temporal resolution (Table 4). If the two analyses for a given sample had greater than 10% relative error, those data were removed.

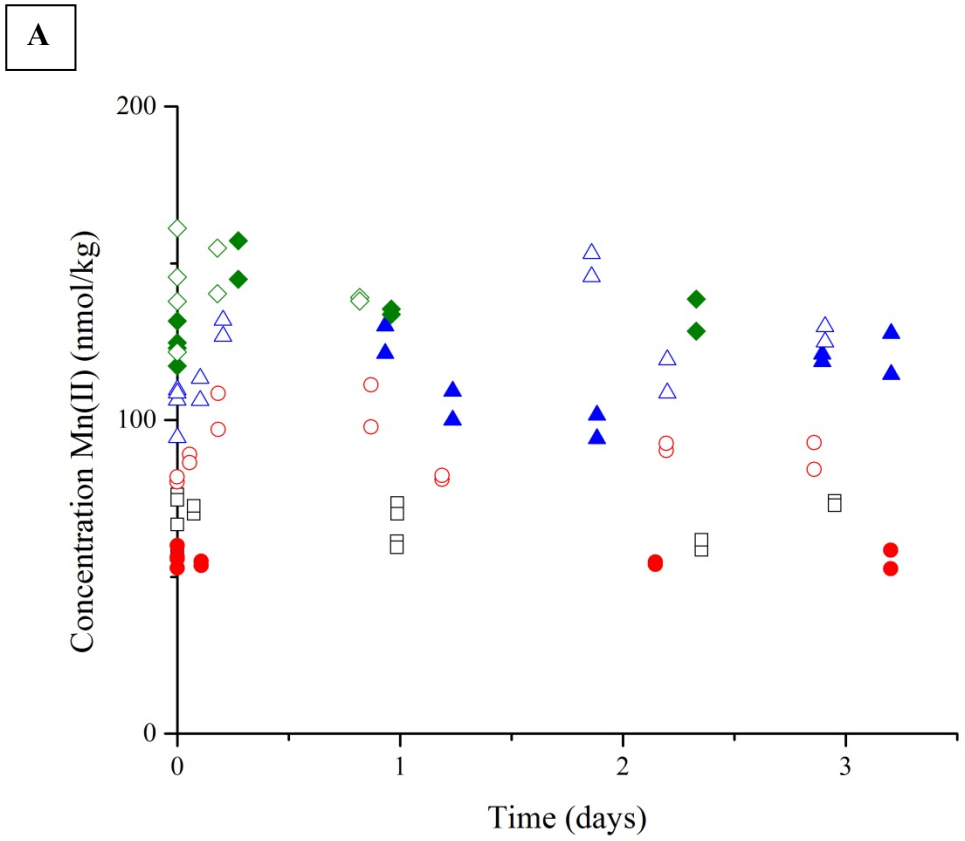

Figure 8. Plots of time vs. concentration of Mn(II) for the different experimental runs. Plot A shows the data points and Plot B shows the averages for each time point with associated error. Each data point has 30% error in the concentration of Mn(II) due to the calibration. The SW test is not shown because it was analyzed using a different analytical system. (□) SW + O_3; (●) SW + Mn(IV); (○) SW + Mn(IV) + O_3; (▲) SW + OC; (Δ) SW +OC + O_3; (◆) SW + OC + Mn(IV); (◊) SW + OC + Mn(IV) + O_3

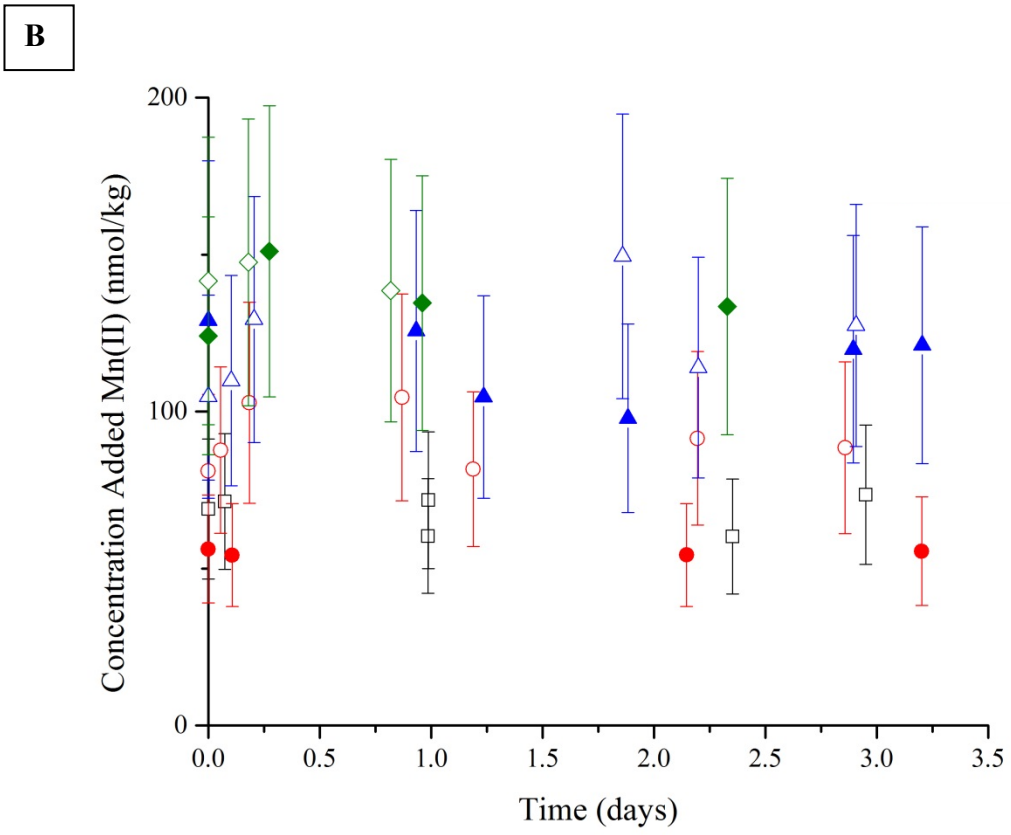

Figure 8. Continued.

The addition of Mn(IV) particles to the experiments does not appear to change the concentration of Mn(II) present. For these comparisons, the SW + O_3 test is used to represent the concentration of Mn(II) present in the seawater as the SW test was analyzed using a different calibration than all other tests. Since the O_3 was not added until after the first time point, there should be no difference between the SW and SW + O_3 tests at time zero. It appears that the addition of organics can result in adding Mn(II)

to these experiments (Table 2, Figure 8), but this cannot be claimed with any certainty. The average initial concentration of Mn(II) for the tests without added organics (excluding SW) is 70 ± 40 nmol/kg and the initial concentration of Mn(II) for the tests with added organics is 120 ± 80 nmol/kg. These values are not statistically significantly different. However, at the later time points in the experiments, the Mn(II) concentrations for some of the experiments containing added organics are statistically significantly greater than the Mn(II) concentrations for the experiments without added organics. The organics used were not trace metal clean and so it is not implausible that they could result in the addition of Mn(II) to the experiments.

Table 2. Average initial concentration of Mn(II) in both chambers. For the tests with O_3, the initial samples were taken before the addition of O_3.

Test	Initial concentration Mn(II) (nmol/kg)
SW	90 ± 10
SW + O_3	70 ± 20
SW + Mn(IV)	60 ± 20
SW + Mn(IV) + O_3	80 ± 20[a]
SW + OC	130 ± 60[b]
SW + OC + O_3	110 ± 30
SW + OC + Mn(IV)	120 ± 40
SW + OC + O_3 + Mn(IV)	140 ± 50

[a] Together the chambers had greater than 15% error in the two analyses for the same sample. One had less than 15% error while the other had greater than 15% error so only the one with smaller error was used.
[b] Neither of the chambers had less than 15% error in the two analyses for the same sample, but both chambers were still used to generate a starting concentration.

The tests show no clear changes in Mn(II) concentration over time. The only potentially statistically significant difference occurred with the added Mn(IV) tests with no added organics. This can be seen more clearly by focusing on the first 8 hours of the experiments (Figure 9).

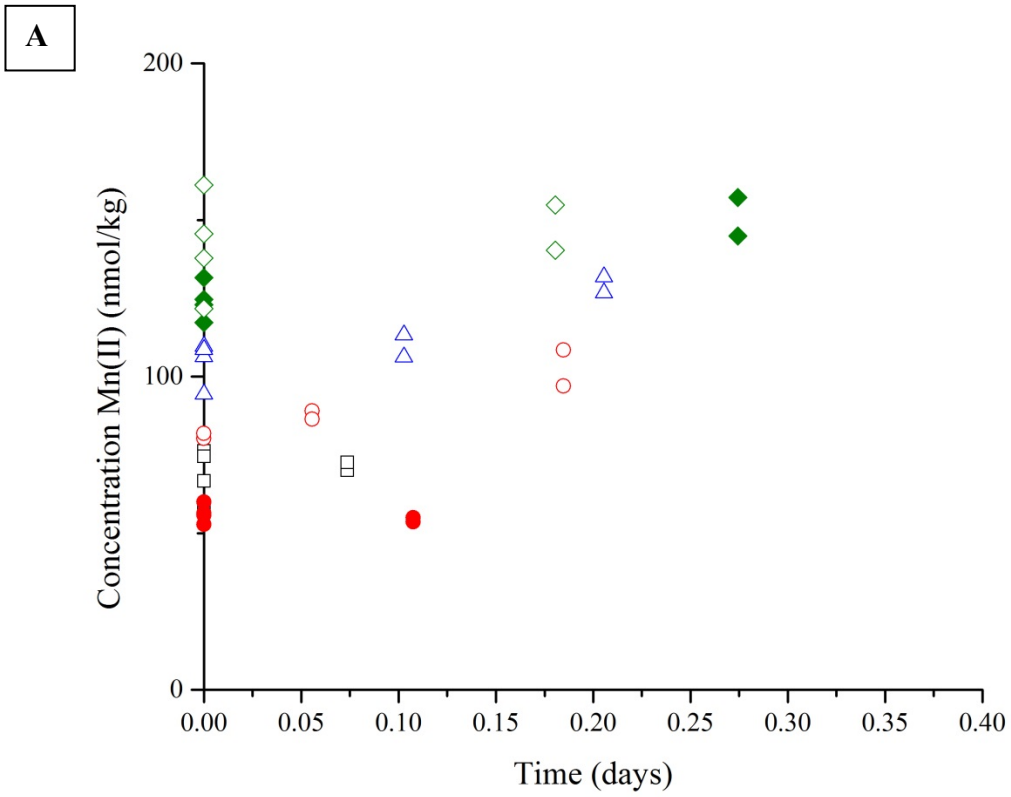

Figure 9. An expansion of time vs. concentration of Mn(II) for the first 8 hours of each experiment. Plot A shows the data points and Plot B shows the averages for each time point with associated error. Each data point has 30% error in the concentration of Mn(II) due to the calibration. The SW test is not shown because it was analyzed using a different analytical system. (□) SW + O_3; (●) SW + Mn(IV); (○) SW + Mn(IV) + O_3; (▲) SW + OC; (△) SW +OC + O_3; (♦) SW + OC + Mn(IV); (◊) SW + OC + Mn(IV) + O_3

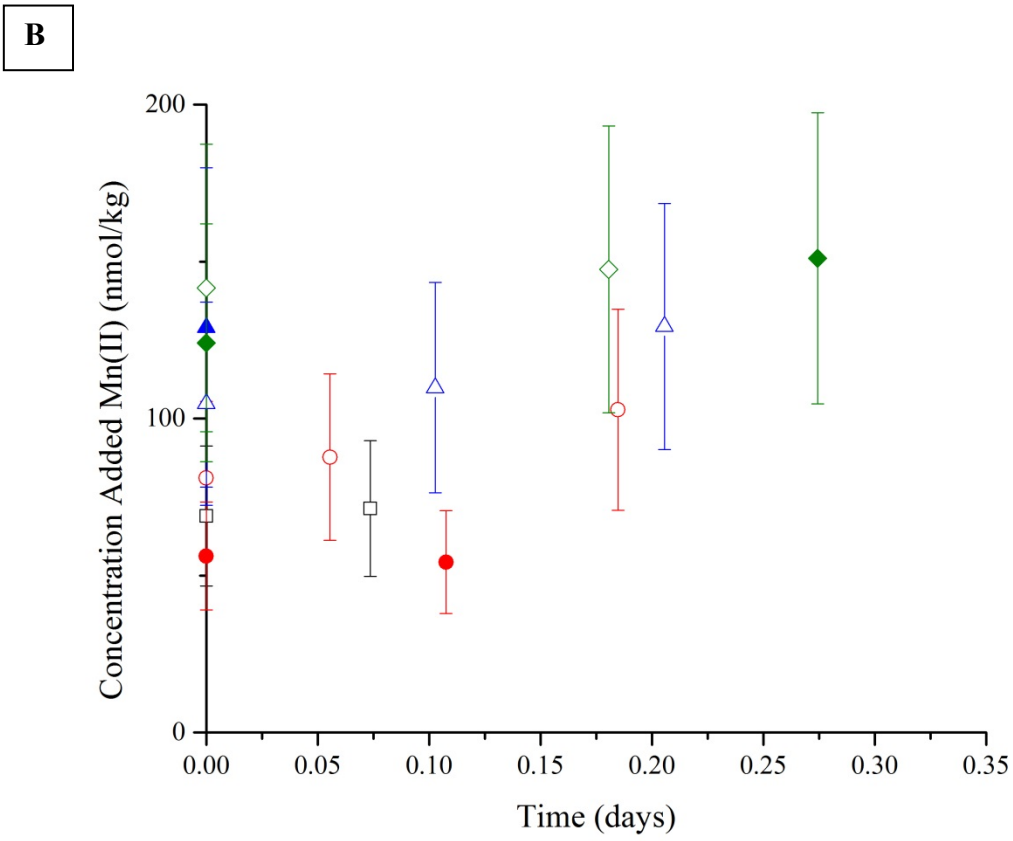

Figure 9. Continued.

Between 0.1 and 0.2 days (2.4 to 4.8 hours), it appears possible that the SW + Mn(IV) and SW + Mn(IV) + O_3 tests could have statistically significantly different concentrations of Mn(II). If these tests are different, then it would appear that the concentration of Mn(II) increases in the presence of O_3. As O_3 would not directly reduce Mn(IV) particles, O_3 would likely be oxidizing some other compound in the seawater and that other compound would reduce the Mn(IV) particles. The seawater was collected from the open ocean Gulf of Mexico and likely contains relatively unreactive organics. It

is possible that O_3 could react with those and that they in turn could reduce the Mn(IV) particles.

From all the other tests, it does not appear that O_3 affects the concentration of Mn(II) in seawater. First consider the likelihood of a direct oxidation of Mn(II) by O_3 in seawater. For this to happen in drinking water treatment O_3 needs to be present in very high concentrations to produce Mn(IV) oxide particles at the pH of seawater(Von Gunten 2003). The low concentration of both Mn(II) and O_3 and the much higher concentrations of other compounds in seawater, particularly halogens and organics, could make the chances of Mn(II) and O_3 directly interacting very small.

The likelihood of O_3 oxidizing organic compounds and those organics reducing Mn(IV) particles seems much greater than O_3 reacting directly with Mn(II), simply because the concentration of organics is so high. In these tests, the number of moles of carbon of added organics was 4 orders of magnitude greater than the number of moles of Mn(II) present. However, even if a reductive process were occurring, it is possible that the changes in Mn(II) concentration would be smaller than the analytical variability. The largest changes in Mn(II) concentration observed for the photoreduction studies were on the order of 20% (Sunda and Huntsman 1994). With an analytical variability greater than 30% even those changes would be too small to be observed using the FIA system.

4. CONCLUSIONS

This work has served as an important first step in determining the impact of O_3 on metal speciation in the environment. The initial work has been done to develop a fast, cost effective technique to measure Mn(II) in seawater over a relatively wide range of concentrations. Further work needs to be done on the system to reduce the analytical variability so that it can be used to investigate the chemistry of Mn in seawater through laboratory experiments. This can be done by doing a more rigorous characterization of the FIA system, verifying optimal pHs and sample preconcentration times. The linearity of standard addition calibrations over different ranges of concentrations of Mn(II) should also be determined.

Additionally, this work has provided initial results that can be used to direct future experiments investigating the relationships between O_3, Mn, and organic matter in the ocean. No significant changes in Mn(II) concentration were measured, indicating that any changes in Mn(II) will deviate less than 30% from the initial concentration of Mn(II) in the seawater. This information will be useful for determining appropriate calibration standards for experiments using this analytical system and the appropriate concentration of Mn(IV) particles to add. Using different added components needs to be done to more fully characterize this system. Adding fresh Mn(II) in addition to the background levels present in seawater could change the reactivity of the Mn(II), affecting the chemistry of the system. It will also be necessary to test more types of organic compounds, like humics, as the organic mixture likely has a strong effect on the overall system. Testing

different organics can enhance the probability of a meaningful reaction occurring and can potentially be a way to identify which functional groups are most important for this reaction.

These changes, when combined with refinements to the concentrations of Mn used with the FIA system, will allow for better experiments for determining the effect of O_3 on Mn speciation in seawater. This study has provided the groundwork for future investigations by beginning to develop an analytical technique for measuring dissolved Mn, starting to identify the appropriate range of concentrations for that technique during these tests, and determining an appropriate time interval for these experiments. It has also identified one of many unnoticed connections between the disciplines of chemical oceanography, atmospheric chemistry, and drinking water treatment. By learning more about other disciplines we are able to identify more areas of research and begin understanding interfaces. This study serves as an example of the kinds of questions we can ask and the insights we can gain by working at the intersection of disciplines.

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APPENDIX

Table 3. Data for all calibration standards. Each pair of 0 nmol/kg standards was analyzed on a different day. Relative error is expressed as a percentage.

Concentration of Added Mn(II) in Standard (**nmol/kg**)	Peak Area	Average Peak Area	Relative Error
0	7.8879	7.8903	0.04
0	7.8927		
0	6.9026	7.2275	6.36
0	7.5524		
0	13.6930	12.7775	10.13
0	11.8620		
0	13.8221	13.5282	3.07
0	13.2342		
0	16.4797	15.2184	11.73
0	13.9550		
48.57	18.7775	16.9871	14.91
48.57	15.1967		
48.64	14.9969	13.3852	17.03
48.64	11.7734		
48.90	16.7827	14.9399	17.44
48.90	13.0971		
48.99	13.3539	15.4176	18.93
48.99	17.4812		
49.19	11.9081	11.9659	0.68
49.19	12.0237		
49.36	8.1249	7.5878	10.01
49.36	7.0507		
49.62	8.2847	8.5753	4.7917
49.62	8.8658		
97.44	6.8006	8.8002	32.13
97.44	10.7998		
98.08	10.6265	11.4341	9.99
98.08	12.2416		
98.19	14.0801	17.6880	28.85
98.19	21.2959		
98.40	18.0128	18.4890	3.64
98.40	18.9652		
98.42	13.8028	16.4320	22.63
98.42	19.0611		

Table 3. Continued.

Concentration of Added Mn(II) in Standard (**nmol/kg**)	Peak Area	Average Peak Area	Relative Error
98.69	7.7872	7.6987	1.63
98.69	7.6101		
99.03	10.0676	10.4202	4.78
99.03	10.7727		
143.51	18.5740	17.8933	5.38
143.51	17.2126		
144.85	14.5743	15.7151	10.27
144.85	16.8578		
145.49	15.3079	13.8891	14.45
145.49	12.4703		
145.82	15.7429	16.5701	7.06
145.82	17.3972		
146.03	11.4379	10.2648	16.16
146.03	9.0917		
146.09	14.3610	12.4013	22.35
146.09	10.4416		
146.83	8.7577	9.8081	15.15
146.83	10.8585		

Table 4. Data for all experimental tests. Tests are named by the components present. SW = open Gulf of Mexico seawater, Mn(IV) = Mn(IV) particles, OC = a mixture of tryptophan, galactose, and vanillin, O_3 = ozone

Experiment	Time (**days**)	Concentration Mn(II) (**nmol/kg**)	Average Concentration Mn(II) (**nmol/kg**)	Replicate Error[a]	Total Error[b]
SW[c]	0	102.90	91.50	14.31	23.39
	0	77.19			
	0	94.39			
	0.10	105.80	101.55	5.91	27.38
	0.10	97.31			
	4.85	116.81	115.34	1.80	18.50
	4.85	113.87			
	5.07	92.62	91.99	0.97	19.43
	5.07	91.36			
	6.191	117.74	116.37	1.66	18.50
	6.191	114.99			
	6.192	113.23	107.68	7.29	18.59
	6.192	102.12			
$SW + O_3$	0	66.74	68.96	11.85	32.40
	0	58.38			
	0	76.21			
	0	74.51			
	0.07	70.15	71.37	2.42	30.25
	0.07	72.59			
	0.986	61.33	60.36	2.26	30.25
	0.986	59.40			
	0.988	73.46	71.80	3.28	30.33
	0.988	70.13			
	2.353	58.63	60.22	3.75	30.38
	2.353	61.82			
	2.354	72.81	65.44	15.93	34.10
	2.354	58.07			
	2.95	74.21	73.50	1.37	30.18
	2.95	72.78			

[a]Relative error between replicate samples expressed as a percentage
[b]Error for the average including error from the calibration expressed as a percentage
[c]The SW test was analyzed using a different analytical technique and calibration than the other tests.

Table 4. Continued.

Experiment	Time (**days**)	Concentration Mn(II) (**nmol/kg**)	Average Concentration Mn(II) (**nmol/kg**)	Replicate Error[a]	Total Error[b]
SW + Mn(IV)	0	59.95	56.22	5.22	30.60
	0	56.34			
	0	55.80			
	0	52.79			
	0.11	54.93	54.26	1.75	30.20
	0.11	53.59			
	0.31	55.68	61.00	12.33	32.58
	0.31	66.32			
	0.97	65.18	59.12	14.51	33.46
	0.97	53.05			
	2.15	53.98	54.34	0.93	30.17
	2.15	54.69			
	2.20	48.17	58.99	25.95	39.78
	2.20	69.82			
	3.15	48.40	60.71	28.67	41.61
	3.15	73.02			
	3.20	58.54	55.55	7.61	31.10
	3.20	52.56			

[a]Relative error between replicate samples expressed as a percentage
[b]Error for the average including error from the calibration expressed as a percentage

Table 4. Continued.

Experiment	Time (**days**)	Concentration Mn(II) (**nmol/kg**)	Average Concentration Mn(II) (**nmol/kg**)	Replicate Error[a]	Total Error[b]
SW + Mn(IV) + O_3	0	80.24	81.05	1.41	30.19
	0	81.86			
	0.06	89.04	87.71	2.14	30.23
	0.06	86.39			
	0.18	108.56	102.79	7.93	31.18
	0.18	97.03			
	0.87	111.22	104.52	9.07	31.49
	0.87	97.82			
	1.19	81.03	81.69	1.13	30.17
	1.19	82.34			
	1.88	105.94	92.95	19.76	36.05
	1.88	79.96			
	2.20	90.35	91.48	1.74	30.20
	2.20	92.60			
	2.86	92.77	88.49	6.83	30.92
	2.86	84.22			
	3.19	65.38	75.38	18.75	35.51
	3.19	85.37			

[a]Relative error between replicate samples expressed as a percentage
[b]Error for the average including error from the calibration expressed as a percentage

Table 4. Continued.

Experiment	Time (**days**)	Concentration Mn(II) (**nmol/kg**)	Average Concentration Mn(II) (**nmol/kg**)	Replicate Error[a]	Total Error[b]
SW + OC	0	124.28	129.03	25.41	39.43
	0	95.17			
	0	173.94			
	0	122.72			
	0.20	92.36	105.89	18.07	35.15
	0.20	199.42			
	0.93	130.07	125.70	4.92	30.55
	0.93	121.33			
	1.24	109.23	104.64	6.21	30.78
	1.24	100.04			
	1.88	94.09	97.88	5.47	30.64
	1.88	101.67			
	2.25	117.26	127.45	11.30	32.20
	2.25	137.64			
	2.90	121.05	119.88	1.38	30.18
	2.90	188.71			
	3.20	114.64	121.14	7.59	31.09
	3.20	127.65			

[a]Relative error between replicate samples expressed as a percentage
[b]Error for the average including error from the calibration expressed as a percentage

Table 4. Continued.

Experiment	Time (**days**)	Concentration Mn(II) (**nmol/kg**)	Average Concentration Mn(II) (**nmol/kg**)	Replicate Error[a]	Total Error[b]
SW + OC + O_3	0	106.35	104.79	6.71	30.89
	0	94.46			
	0	109.66			
	0	108.69			
	0.10	113.38	109.84	4.55	30.49
	0.10	106.30			
	0.21	126.75	129.34	2.84	30.285
	0.21	131.94			
	0.95	163.78	152.58	10.38	31.89
	0.95	141.38			
	1.19	118.15	109.83	10.72	32.00
	1.19	101.50			
	1.86	145.75	149.46	3.51	30.36
	1.86	153.17			
	2.20	108.73	114.00	6.54	30.85
	2.20	119.26			
	2.91	124.96	127.40	2.70	30.27
	2.91	129.83			
	3.23	146.22	134.54	12.28	32.56
	3.23	122.86			

[a]Relative error between replicate samples expressed as a percentage
[b]Error for the average including error from the calibration expressed as a percentage

Table 4. Continued.

Experiment	Time (**days**)	Concentration Mn(II) (**nmol/kg**)	Average Concentration Mn(II) (**nmol/kg**)	Replicate Error[a]	Total Error[b]
SW + OC + Mn(IV)	0	131.57	124.11	4.73	30.52
	0	122.97			
	0	117.30			
	0	124.61			
	0.11	149.58	134.00	16.43	34.34
	0.11	118.44			
	0.27	144.86	151.03	5.78	30.70
	0.27	157.20			
	0.96	133.67	134.57	0.94	30.17
	0.96	135.46			
	1.28	216.21	173.27	35.04	46.23
	1.28	130.34			
	1.99	152.40	136.36	16.64	34.44
	1.99	120.31			
	2.33	128.40	133.48	5.38	30.63
	2.33	138.55			
	2.95	113.73	133.60	21.03	36.76
	2.95	153.47			
	3.29	125.03	115.38	11.82	32.39
	3.29	105.73			

[a]Relative error between replicate samples expressed as a percentage
[b]Error for the average including error from the calibration expressed as a percentage

Table 4 . Continued.

Experiment	Time (**days**)	Concentration Mn(II) (**nmol/kg**)	Average Concentration Mn(II) (**nmol/kg**)	Replicate Error[a]	Total Error[b]
SW + OC + Mn(IV) + O_3	0	137.86	141.60	11.60	32.31
	0	121.72			
	0	145.61			
	0	161.20			
	0.07	183.82	162.52	18.53	35.39
	0.07	141.23			
	0.18	154.81	147.56	6.95	30.94
	0.18	140.30			
	0.82	139.09	138.52	0.58	30.16
	0.82	137.95			
	1.17	146.26	134.01	12.93	32.81
	1.17	121.76			
	1.83	140.00	186.31	35.15	46.31
	1.83	232.61			
	2.15	137.76	127.98	10.80	32.62
	2.15	118.21			
	2.84	159.43	146.54	12.44	32.62
	2.84	133.65			
	3.16	99.27	124.54	28.70	41.63
	3.16	149.82			

[a]Relative error between replicate samples expressed as a percentage
[b]Error for the average including error from the calibration expressed as a percentage