INTRODUCTION

Manganese (Mn) is one of the most abundant trace elements in atmospheric waters and has been measured in fog, snow, cloudwater, and rain (Siefert et al., 1998; Planchon et al., 2001; Church et al., 1990). Natural sources of Mn include seasalt spray, wild forest fires, volcanogenic particles and windblown dust (Nriagu, 1989). Windblown dust is by far the largest natural contributor of Mn to the atmosphere primarily because it is the twelfth most abundant element in the earth's crust, with a soil concentration of approximately 440 ppm (Emsley, 2001). In addition to natural sources, Mn has many anthropogenic sources including refuse incineration, iron and steel manufacturing, mining, gasoline combustion, and coal and oil combustion. Because of these anthropogenic sources, Mn concentrations in atmospheric waters are typically higher around areas of increased population and industry (Pacyna et al., 1986; Bhuie et al., 2005). Methylcyclopentadienyl manganese tricarbonyl (MMT) began being used in Canada in 1976 and the United States in 1995 as an octane improver and anti-knock agent in automobiles once lead was removed for environmental concerns in the mid- 1970's (Zayed et al., 2003; NRTEE), 1999). When this organic derivative of Mn is combusted, Mn phosphate, Mn sulfate, and a Mn phosphate/sulfate mixture are produced (Zayed et al., 1999; Ressler et al., 2000).

In order to understand its reactions in the troposphere, Mn speciation must be determined rather than simply total concentrations. Previous studies in which Mn concentrations were analyzed focused mainly on the total concentration in acidified unfiltered rainwater samples (Church et al., 1984; Lim and Jickells, 1990; Helmers et al., 1995; Halstead et al., 2000) as well as unacidified unfiltered rainwater (Church et al., 1990). Other studies have focused on the analysis of only filtered samples (Manoj et al., 2000; Takeda et al., 2000; Spokes et al., 2001; Al-Momani, 2003; Hou et al., 2005; Zheng et al., 2005) or with a small number of sample sets containing both filtered and unfiltered samples (Deutsch et al., 1997). Manganese concentrations in these studies typically range from 5 to 500 nM.

The first goal of this thesis is to determine concentration and speciation of Mn in Wilmington, NC rainwater. The species that are of interest in this study are Mn(II) and Mn(IV) because these are the oxidation states that are most likely to occur in rainwater at equilibrium. Figure 1 taken from Stumm and Morgan (1996) shows Mn(II) being the predominant oxidation state within the pH range of rain in the Wilmington area (pH of 4-6). Mn(IV) can also be found within this pH range but at very small concentrations. Manganese(III) is an unlikely oxidation state because it will simultaneously oxidize and reduce to Mn(II) and Mn(IV) (equation1).

$$\begin{array}{ll} 2\left[Mn^{3+} + e^{-} \rightarrow Mn^{2+}\right] & K^{2} = 10^{50} \\ Mn^{2+} \rightarrow Mn^{4+} + 2e^{-} & K = 10^{-40} \\ \hline 2Mn^{3+} \rightarrow Mn^{2+} + Mn^{4+} & K = 10^{50-40} = 10^{10} \end{array} \qquad (1)$$

The equilibrium constant for the simultaneous oxidation and reduction of Mn^{3+} is very large which implies that Mn^{3+} is not stable. Calculation of the Gibb's free energy produces a negative value, which indicates that this reaction is spontaneous (equation 2). Therefore, Mn^{3+} is an unlikely oxidation state in rainwater.

$$\begin{aligned} \Delta G^{\circ} &= -RT \ln K \\ \Delta G^{\circ} &= -RT \ln 10^{10} \\ \Delta G^{\circ} &= -RT(23.0) = -57.0 \;\; kJmol^{-1} \;\; at \;\; 25^{\circ}C \end{aligned} \qquad (2)$$

A study by Kim et al. (2000) in Delaware showed a seasonal trend with rainwater Mn concentrations at a maximum in the spring corresponding to soil disturbances related to regional agricultural practices. A kinetic model developed by Siefert et al. (1998) suggested Mn(II) would be the predominant oxidation state during daylight and nighttime conditions, with Mn(III) concentrations increasing during sunlight hours. A thorough understanding of Mn

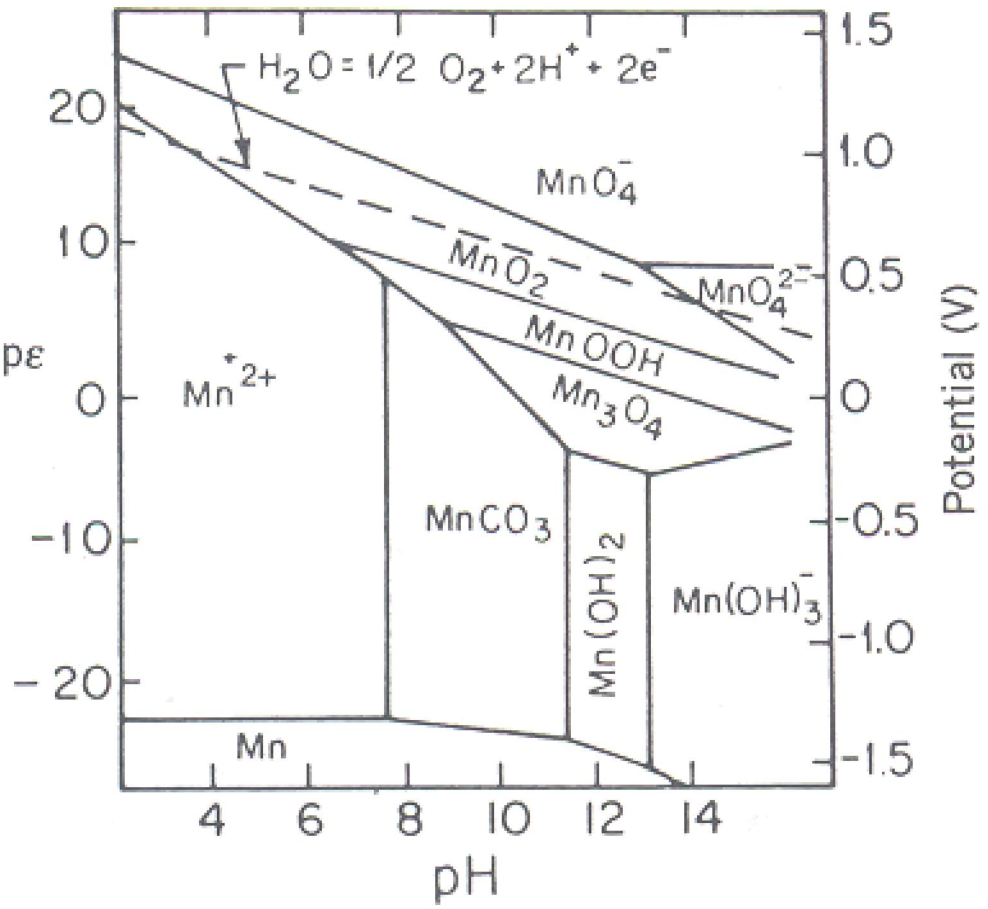


Figure 1. pε-pH diagram for the Mn-CO_2-H_2O systems (25°C). The solid phases considered are $Mn(OH)_2(s)$ (pyrochroite), $MnCO_3(s)$ (rhodochrosite), $Mn_3O_4(s)$ (hausmannite), γ-$MnOOH(s)$ (manganite), and γ-$MnO_2(s)$ nsutite). Total carbonate, $C_T = 1 \times 10^{-3}$ M and total Mn, $Mn_T = 1 \times 10^{-5}$M; taken from Stumm & Morgan, 1996 p. 462.

speciation must therefore include seasonal and diurnal variability. Consequently, a second goal of this thesis will be to address Mn speciation by examining seasonal and time of day variations. Previous studies have shown the impact of storm origin and storm type on the composition of rainwater. Significantly higher levels of Cu, Hg, and Fe have been observed in terrestrial rain (cold fronts and continental low-pressure systems) relative to coastal or marine rain (coastal storms, hurricanes, tropical storms, winter warm fronts, and El Nino rain) (Kieber et al., 2001; Kieber et al., 2004; Parler, 2005). Iron like Mn is a significant contributor to crustal trace metals and is generally regarded as one of the most efficient metal ion catalysts in atmospheric aqueous redox reactions along with Mn (Brandt & Elding, 1998; Zhang, 2000). Therefore another goal of this thesis will be to address the importance of storm origin and storm type as well as other rainwater components including pH, dissolved organic carbon (DOC), chloride, sulfate, nitrate, hydrogen peroxide and Fe on Mn speciation.

METHODS

Cleaning Procedure

New high density polyethylene (HDPE) bottles for reagent preparation and sample storage were cleaned with a 4 week washing cycle involving sequential soaks in 2% Citranox (phosphate-free acid cleaner and detergent), 2 M HNO_3 (reagent grade), 3 M HCl (reagent grade) and pH 2 HCl (trace metal grade, Fisher) baths. The bottles spent a week in each stage of the washing process with an extensive wash with deionized water (DIW) between each stage. Graphite furnace sampling cups were cleaned in 10% HCl (reagent grade) for a minimum of 24 h and pH 2 HCl (trace metal grade, Fisher) for a minimum of 24 h. Perfluoroalkoxy (PFA) vials used for preconcentration steps were cleaned in concentrated HNO_3 (reagent grade) for a minimum of 24 h and pH 2 HCl (trace metal grade, Fisher) for a minimum of 24 h. Fluorinated ethylene propylene (FEP) vials used for photochemistry experiments were cleaned in 1M KOH for 24 h, concentrated HNO_3 (reagent grade) for a minimum of 24 h and pH 2 HCl (trace metal grade, Fisher) 2 for a minimum of 24 h. Polycarbonate filters (0.2 µm and 0.05 µm) were cleaned in 6 M HCl (trace metal grade, Fisher) for approximately 24 h. All cleaning procedures concluded with extensive rising of water (>18MΩ) from a Milli-Q Plus Ultra Pure water system (MQ) (Millipore, Bedford, MA).

All bottles, vials and pipettes were double zip-lock bagged to prevent contamination. Countertops were covered with a polyethylene overlay within a class 100 laminar flow-hood in which preparation of standards, reagents and samples including preconcentration steps took place. Polyethylene disposable gloves were used throughout.

Sample Collection

Rainwater was collected on the University of North Carolina Wilmington (UNCW) campus on an event basis from April 2, 2005 to March 24, 2006. The UNCW rainwater collection site is a large open area, approximately one hectare, within a turkey oak, long leaf pine, and wiregrass community, typical of inland coastal areas in southeastern North Carolina. This rainwater site (34º13.9'N, 77º52.7'W) is on the UNCW campus, approximately 8.5 km from the Atlantic Ocean. Due to the close proximity of the sampling location to the laboratory, analyses or storage procedures could be initiated within minutes of collection, which reduced the possibility of compositional changes between the time of collection and analysis. Real-time precipitation maps were used to initiate the sampling process.

Event rainwater samples were collected using four Aerochem-Metrics Automatic Wet-Dry Precipitation Collectors. One collector contained a 4 L muffled Pyrex glass beaker from which samples for dissolved organic carbon, hydrogen peroxide, pH and inorganic ions were collected. The other collectors for trace metal samples held an acid cleaned HDPE funnel leading through Teflon lined acid cleaned tubing to a 2.2 L Teflon bottle extensively cleaned using trace metal clean procedures and protocols (Bruland et al., 1979; Bruland, 1980; Tramontano et al., 1987; Williams, 1998).

Precipitation events were categorized using air-mass back-trajectories generated using version 4 of the Hybrid Single Particle Lagrangian Integrated Trajectory Model (HYSPLIT) developed at the National Oceanic Atmospheric Administration – Air Resources Laboratory (NOAA/ARL). Trajectories were generated using a stand-alone PC version of the model and calculated using pre-processed gridded horizontal and vertical wind fields generated at 6-h intervals from the National Center for Environmental Prediction's Global Data Assimilation System (GDAS) using the Medium Range Forecast model (MRF) to produce the forecast wind fields. Single back-trajectories were run for each measured precipitation event collected at UNCW starting at the recorded onset of precipitation. Trajectories were generated for a 120 h hind-cast starting at the 500 m level.

Mn Analysis

Reagents and Standards

Analytical grade reagents used for standard preparation were from Fisher Scientific and Perkin Elmer unless otherwise noted. A Mn primary standard was gravimetrically prepared by combining 100 µL Mn reference solution (18.2 ± 0.2 mM, AA standard), 125 µL Omnitrace HCl (O-HCl) (EMD) and diluting to 125 mL with MQ giving a final concentration of 14.7 mM. A secondary Mn standard was gravimetrically prepared by combining 1.00 mL Mn primary, 60 µL O-HCl and diluting to 125 mL with MQ, giving a final concentration of 6.45 µg L^{-1} or 117 nM. The Mn primary standard was prepared every six months and the Mn secondary standard was prepared every month. A matrix modifier was prepared by addition of 6 mL $Mg(NO_3)_2$ (67.4 mM, Atomic Absorption Modifier Solution) with 10 mL $Pd(NO_3)_2$ in 15% HNO_3 (43.4 mM, Atomic Absorption Modifier Solution) and bringing up to 100 g with MQ. A standard reference solution was prepared from a certified riverine reference material (National Research Council Canada, SLRS-4) with a certified concentration of 61.3 ± 3.3 nM. The certified reference was diluted by 50% with DIW yielding a final concentration of 30.7 ± 1.6 nM. The standard reference solution was prepared weekly.

Sample Preparation

Filtered and unfiltered rainwater samples were prepared for each rain event where sufficient volume allowed (> 2.5 mm rain). Total Mn (Mn_{total}) was determined in unfiltered samples, which were transferred directly into trace metal clean HDPE bottles from the 2.2 L Teflon rainwater collection bottles. Two different filtered samples were prepared from the 2.2 L Teflon rainwater collection bottles using a 47 mm diameter, 0.2 µm polycarbonate Millipore membrane filters and a 47 mm diameter, 0.05 µm polycarbonate Nuclepore membrane filter. Each sample was transferred into a trace metal clean HDPE bottle. Both filtered and unfiltered samples were acidified with 100 µL O-HCl per 30 mL of rainwater. Samples were refrigerated and allowed to sit for a minimum of 24 h to ensure complete digestion. Particulate Mn (Mn_{part}) is defined as the difference between the unfiltered and 0.2 µm filtered sample. Colloidal Mn (Mn_{coll}) is defined as the difference between the 0.2 µm filtered and 0.05 µm filtered samples. Both Mn_{part} and Mn_{coll} are assumed to be Mn(IV). Dissolved Mn is assumed to be Mn(II). If any of the calculated Mn concentrations were negative, “not detected” was used in tables whereas a value of zero was used for graphical purposes.

Samples that were analyzed with absorbances less than 0.015 (~ 12 nM) were subjected to non-boiling evaporation preconcentration (Görlach and Boutron, 1990). The samples were heated for ~9 h at ~85°C in a class 100 laminar flow-hood with a polyethylene overlay covering the countertop. The preconcentration technique involved evaporating a 20-25 mL rain sample to 4-5 mL giving a 5-9 fold increase in concentration.

Analysis

Manganese concentrations were analyzed by graphite furnace atomic absorption spectroscopy (GFAAS), using a Perkin Elmer 5100 PC atomic absorption spectrometer equipped with a 5100 ZL Zeeman furnace module and AS 70 autosampler. The temperature program used with the instrument is presented in Table 1A. Concentrations were determined using standard addition combined with GFAAS multiple injections. Two sampling cups were used for each sample with one analysis per cup. If concentrations differed by more than 15%, multiple analysis were performed and an average concentration was determined. Analysis of samples and blanks were carried out with 20 µL of sample, 5 µL of matrix modifier, and Milli-Q ultrapure water to give a final volume of 40 µL. The volume of diluent varied depending on the volume of Mn secondary standard added for the standard addition concentration.

To ensure the accuracy of the analysis, blanks and a certified standard reference were analyzed with each group of samples. A group consisted of (in order) a certified standard reference, sample blank, rain event A (0.05 µm, 0.2 µm, and unfiltered), sample blank, rain event B (0.05 µm, 0.2 µm, and unfiltered), sample blank, and a certified standard reference. Each sample used two sampling cups for each analysis except for the sample blank, which had one sampling cup. The certified standard reference was initially analyzed to verify that the concentration fell within the certified range before proceeding with analysis. Sample blanks consisted of 30 mL Milli-Q with 100 µL O-HCl; matrix modifier was added by the instrument.

Table 1. Atomic absorption spectroscopy temperature program for manganese and iron.

A. Graphite furnace temperature program for the analysis of manganese.

Step	Temperature (^oC)	Ramp(s)	Hold(s)
1	110	1	30
2	130	15	30
3	1300	10	20
4	1900 (stop flow)	0	5 (read)
5	2400	1	2

B. Graphite Furnace temperature program for the analysis of iron.

Step	Temperature (^oC)	Ramp(s)	Hold(s)
1	110	1	30
2	130	15	30
3	1400	10	20
4	2100 (stop flow)	0	5 (read)
5	2400	1	2

The average measured concentration of these blanks was 1.2 ± 0.7 nM. The certified standard reference, previously diluted by 50% as described earlier, had a concentration of 30.7 ± 1.6 nM. The average measured concentration of the standard reference was 31 ± 2 nM. The limit of detection of analysis, defined as 3 times the standard deviation of the blanks, was 2 nM for samples not requiring preconcentration. The reproducibility of the duplicate samples was averaged over 20 random samples to give a precision of 3% and was determined using equation 3. The supporting data are found in Table 2.

$$\Pr ecision = \frac{\frac{Conc1 - Conc2}{2}}{Avg.Conc} \times 100 \qquad (3)$$

Fe Analysis

Reagents and Standards

Analytical grade reagents used for standard preparation are from Fisher Scientific and Perkin Elmer unless otherwise noted. An iron primary standard was gravimetrically prepared by combining 165 µL Fe reference solution (17.9 ± 0.2 mM, AA standard), 100 µL O-HCl and diluting to 60 mL with MQ yielding a final concentration of 50.8 µM. A secondary Fe standard was gravimetrically prepared by combining 1.15 mL Fe primary standard, 100 µL O-HCl and diluting to 60 mL with MQ, yielding a final concentration of 53.2 µg L^{-1} or 953 nM. The Fe primary standard was prepared every six months and the Fe secondary standard was prepared every month. A matrix modifier was prepared from 30 mL $Mg(NO_3)_2$ (67.4 mM, atomic absorption modifier solution) brought up to 100 g with MQ. A standard reference solution was prepared from a riverine reference material (National Research Council Canada, SLRS-4) with a certified concentration of 2.00 ± 0.09 µM. The certified reference was diluted by 1:10 with MQ giving a concentration of 184 ± 9 nM. The standard reference solution was prepared weekly.

Table 2. Precision of duplicate analyses for manganese concentration.

Date	Conc 1 (nM)	Conc 2 (nM)	Avg. Conc (nM)	Precision %
6/6/2005	77	78	78	0.71
6/16/2005	4.2	4.5	4.4	3.0
6/23/2005	41	42	41	1.5
7/19/2005	34	33	33	1.8
8/17/2005	19	18	19	4.3
1/26/2006	16	17	17	4.5
1/27/2006	27	27	27	0.37
1/27/2006	21	20	21	3.6
1/30/2006	4.9	5.2	5.1	3.0
2/10/2006	4.8	4.4	4.6	4.4
2/10/2006	4.1	4.3	4.2	2.4
2/10/2006	0.83	0.79	0.81	2.5
2/14/2006	2.2	1.8	2.0	10
2/15/2006	2.2	2.4	2.3	4.4
2/16/2006	4.3	4.1	4.2	2.4
2/21/2006	52	54	53	1.1
2/21/2006	64	57	61	5.5
3/24/2006	5.2	4.9	5.1	3.0
3/27/2006	97	95	96	1.0
3/30/2006	7.1	7.7	7.4	4.1

Avg. Precision	3.2 %

Iron concentrations for each rain event were high enough that a preconcentration step was not required.

Analysis

The temperature program used with the 5100 ZL Zeeman furnace module for Fe is presented in Table 1B. Analysis was carried out with 20 µL of sample, 5 µL matrix modifier, and Mill-Q Plus ultra-pure water to give a final volume of 45 µL. Analysis for Fe was carried out in a similar fashion as Mn except one sampling cup was used for each sample with two replicate analyses per cup. If concentrations differed by more than 15%, multiple analysis were performed and an average concentration was determined. Sampling groups consisted of (in order) a certified standard reference, rain event A (0.05 µm, 0.2 µm, and unfiltered), rain event B (0.05 µm, 0.2 µm, and unfiltered), sample blank, and a certified standard reference. Sample blanks consisted of 30 mL MQ with 100 µL O-HCl; matrix modifier was added by the instrument. The average measured concentration of the blanks was 5 ± 3 nM. The average measured concentration of the standard reference was 196 ± 13 nM compared to the certified value of 184 ± 9 nM. The limit of detection for analysis, defined as 3 times the standard deviation of the blank, was 9 nM. Dissolved Fe (Fe_{diss}) is defined as the fraction of sample that passes through the 0.05 µm filter. Particulate Fe (Fe_{part}) is defined as the difference between the total unfiltered Fe (Fe_{total}) and 0.2 µm filtered sample. Colloidal Fe (Fe_{coll}) is defined as the difference between the 0.2 µm filtered and 0.05 µm filtered samples.

Photochemical Analyses

Rain events were divided into two aliquots for dark and light measurements in order to determine the effect of sunlight on Mn speciation. Samples were irradiated with a Spectral Energy Corp. solar simulator (LH 153 lamp housing, 1 kW Xe arc lamp, LPS 256 SM power supply) equipped with an AM1 filter to remove wavelengths not found in sunlight. The spectral quality and intensity of the solar simulator is very similar to that of midsummer, noon-time solar irradiance for 34°N latitude. Temperature was controlled by a water bath kept at 25 ± 3 ºC.

Unfiltered rain samples and MQ blanks in 30 mL FEP were filled to the top with no headspace prior to photolysis. One unfiltered rain sample and one blank were irradiated while one unfiltered rain sample and one blank were kept in the dark as controls. Samples were irradiated or kept in the dark for 6 h. The samples that were irradiated for 6 h were rotated every 1 h to ensure even distribution of light among all samples. After irradiation, all samples were 0.2 µm filtered and acidified with 100 µL of O-HCl.

Seawater Mixing Analysis

Atmospheric deposition of Mn to the ocean was investigated in order to determine any changes in speciation due to the mixing of rainwater and seawater. A seawater sample was collected approximately 30 m from the shoreline at Wrightsville Beach, NC (salinity = 35). Synthetic rainwater (SRW) was prepared by adding 5.0 mL of 5 mM H_2SO_4 diluted to 1 L with MQ giving a final pH of 4.3. A Mn primary standard was prepared gravimetrically by adding 100 µL Mn reference solution (18.2 ± 0.2 mM, AA standard) diluted to 100 mL with SRW. A secondary Mn solution used as a control was gravimetrically prepared by adding 440 µL Mn primary standard diluted to 100 µL with SRW to a final concentration of approximately 80 nM. A 1:1 ratio of authentic rain (E633) and seawater as well as a 1:1 ratio of Mn secondary solution and seawater samples was prepared. These samples were placed in the dark and allowed to age for 4 h at ambient temperature. Samples were then filtered (0.2 µm) and acidified with 100 µL of O-HCl per 30 mL sample. Initial samples of E633, seawater, and Mn secondary solution were also 0.2 µm filtered and acidified with 100 µL O-HCl per 30 mL sample.

Statistical Data Analysis

All data was statistically analyzed using Sigma Stat (v. 2.03, SPSS Inc.). Experimental data obtained was analyzed using one or two way analysis of variance (ANOVA) as appropriate. Data were initially analyzed for normality and equal variance. For data sets that failed the normality test but passed the equal variance test, a parametric ANOVA and Tukey pairwise multiple comparison was utilized. For data sets that failed both normality and equal variance test, non-parametric ANOVA on ranks was implemented. Post-hoc tests included the Kruskal-Wallis test and Dunn's method for pairwise multiple comparison.

RESULTS AND DISCUSSION

Concentration and Speciation

Rainwater was collected in Wilmington, North Carolina from 56 storms between April 2, 2005 and March 24, 2006. Volume weighted averages for Mn_{total}, Mn(II), and Mn(IV) were 11 ± 3 nM, 11 ± 3 nM, and 1.2 ± 0.4 nM respectively (Table 3). No significant difference was determined between Mn concentrations found in 0.05 µm and 0.2 µm filtered fractions ($p = 0.768$, Mann-Whitney rank sums), indicating that the colloidal fraction was undetectable. Mn(II) was defined as the fraction that passed the 0.2 µm filter, and Mn(IV) was defined as the difference between the concentration in the unfiltered sample and Mn(II) assuming that particulate Mn occurs primarily as $MnO_2(s)$. The data in Table 3 represent the most comprehensive set of speciation data for Mn in rainwater.

The range of total Mn (Mn_{total}) concentrations in Wilmington rainwater (Table 4) fell within the range observed for rain collected in Germany (Deutsch et al., 1997) but was notably higher than that found in oceanic rain collected aboard ships at sea (Church et al., 1990; Lim & Jickells, 1990; Helmers & Schrems, 1995). Substantially lower concentrations of Mn were

Table 3. Volume weighted average concentrations (nM) and volume weighted standard deviations of Mn total, Mn(II), Mn(IV) and Mn(IV)/Mn(II) ratio in rainwater collected at Wilmington, NC between April 2, 2005 and March 24, 2006. n = number of samples and Amt = rain amount in mm. Standard deviation of Mn(IV)/Mn(II) ratio calculated using absolute uncertainty.

	n	Amt	pH	Mn_{total}	Mn(II)	Mn(IV)	Mn(IV)/Mn(II)
All Data	56	1474	4.69	11 ± 3	11 ± 3	1.2 ± 0.4	0.12 ± 0.05
Summer	23	643	4.81	8.8 ± 1.2	8.1 ± 1.1	1.4 ± 0.5	0.18 ± 0.06
Winter	13	199	4.40	26 ± 12	28 ± 14	1.7 ± 0.6	0.059 ± 0.036
Terrestrial	18	305	4.67	23 ± 7	22 ± 8	2.1 ± 0.5	0.10 ± 0.04
Marine	15	694	4.89	4.4 ± 1.2	4.9 ± 1.3	0.34 ± 0.21	0.07 ± 0.05

Table 4. Manganese concentrations measured in rainwater and other atmospheric waters.

Environment	Location	n	Mn_{total} (nM)	$Mn_{filtered}$ (nM)	Reference
Rainwater	Wilmington, NC	56	0.61-184	0.81-195 [a*]	This Study
		28	-	1.4-159 [b]	This Study
	Lewes, DE	NR	6.6-47.9 [c]	-	Church et al. (1984)
	Bermuda	NR	1.1-9.2 [c]	-	Church et al. (1984)
	North Atlantic Ocean	9	7.3-74	-	Church et al. (1990)
	North Atlantic Ocean	11	<1-96	-	Lim & Jickells (1990)
	Atlantic Ocean	13	2.0-62.4	-	Helmers & Schrems (1995)
	Paradise, New Zealand	36	0.18-4.44	-	Halstead et al. (2000)
	Higashi-Hiroshima, Japan	152	-	2.9-535 [a]	Takeda et al. (2000)
	Darmstadt, Germany	7	7-206	7-200 [d]	Deutsch et al. (1997)
	Rajasthan, India	35	-	18-16400 [e,h]	Manoj et al. (2000)
	Tsukuba, Japan	51	-	5-1020 [c,d,g]	Hou et al. (2005)
	Hong Kong	7	-	4.9-230 [f]	Zheng et al. (2005)
	Stillpond, MD	NR	2-67[i]	-	Kim et al. (2000)
	Lewes, DE	NR	1-24[i]	-	Kim et al. (2000)
Cloud and Fog	San Pedro Hill, CA	5	54-240	-	Siefert et al. (1998)
	Bakersfield, CA	5	1-34	-	Siefert et al. (1998)
	Whiteface Mtn., NY	45	3-544	-	Siefert et al. (1998)
Snow	Darmstadt, Germany	2	64-98	58-91 [d]	Deutsch et al. (1997)
	Coats Land, Antarctica	59	0.005-0.46	-	Planchon et al. (2001)

NR=not reported; [a] 0.2 µm filter, *one outlier removed, 224 nM. [b] 0.05 µm filter, one outlier removed, 209 nM. [c] Average monthly totals. [d] 0.45 µm filter. [e] 20-25 µm filter. [f] 2.7 µm filter. [g] bulk precipitation, wet plus dry deposition. [h] contains some dry deposition. [i] Monthly intergrated wet deposition found in Paradise, New Zealand, a coastal location on the South Island (Halstead et al., 2000). Concentrations of total Mn found in coastal locations on Bermuda and Lewes, Delaware (Church et al., 1984) were slightly lower than those found in Wilmington, North Carolina. Total Mn concentrations in Wilmington rain were much lower than cloudwater and fogwater concentrations found in more anthropogenicaly impacted sites in California and New York (Siefert et al., 1998). Manganese concentrations found in snow in Antarctica were much lower than those found in rainwater (Table 4), indicating the pristine nature of the Antarctic snow. Very high concentrations of total Mn were observed in rain that also included dry deposition (Manoj et al., 2000). The data presented in Table 4 suggest there is a strong terrestrial and/or anthropogenic input of Mn to the atmosphere resulting in higher concentrations near population centers and lower concentrations in rural or remote marine rain.

Filtered Mn concentrations found in Wilmington were considerably lower than all other sites listed in Table 4. Aside from Higashi-Hiroshima, Japan (Takeda et al., 2000), all filtered samples were through a much larger pore size thereby possibly accounting for higher Mn concentrations. Data presented by Hou et al. (2005) were markedly higher in Mn concentration because their sampling site collected bulk precipitation collected monthly; rain collected beneath the forest canopy (throughfall) was on average five times greater in Mn concentration than their bulk rain samples.

Almost all the Mn in Wilmington rainwater occurred in the dissolved phase similar to what has been reported previously for Cu in rainwater at this location (Table 5). In contrast to the other metals, Mn is soluble primarily in the reduced state (Mn(II)), therefore the % reduced and % dissolved (0.2 µm filtered) are equivalent. The oxidation/reduction ratio is quite different from the other metals listed in Table 5 with Mn occurring to a much greater extent in the reduced

Table 5. Percentages of Mn(II), Cu(I), Cr(III), Fe(II) of total metal concentration and % dissolved relative to total Mn, Cu, Cr, and Fe in Wilmington, NC rain. The oxidized:reduced ratio for dissolved Mn, Cu, Cr, and Fe in rainwater is also presented.

	% Reduced Form of Total	% Dissolved of Total	Oxidized:Reduced Ratio	Reference
Mn	97	97	0.12	This Study
Cu	26	87	2.3	Kieber et al. (2004)
Cr	24	52	1.2	Kieber et al. (2002)
Fe	16	26	0.7	Kieber et al. (2001)

form. This suggests that the thermodynamic and kinetic processes controlling the oxidation of Mn(II) in rainwater may be different than those of the other metals studied.

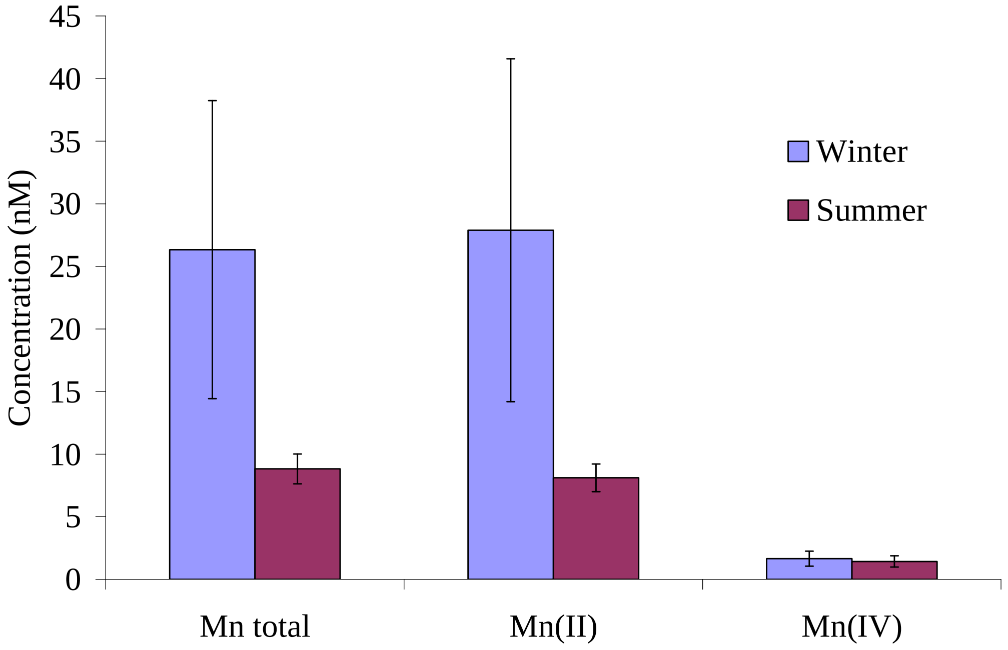
Seasonality

All rain events were subdivided into summer, winter, spring and fall categories to evaluate the impact of season on Mn speciation. Seasons were defined as follows: summer June 1-September 30, fall October 1- November 30, winter December 1-February 28 and spring March 1-May 31. The volume weighted average Mn_{total} concentration in winter was 26 ± 12 nM compared to 8.8 ± 1.2 nM in summer whereas Mn(II) concentrations were 28 ± 14 nM for winter and 8.1 ± 1.1 nM in the summer (Figure 2). The winter concentrations of Mn_{total} and Mn(II) were highly variable, with RSD ~ 50% compared with a RSD of 14% in the summer rain. High variability results from higher wind in the winter of 3.3 cm sec^{-1} verses 2.8 cm sec^{-1} in the summer (when hurricane winds are omitted). In contrast to Mn(II) and Mn_{total}, Mn(IV) showed no observable difference between seasons (Table 6).

Comparison of the spring months to both summer and winter seasons showed no observable difference for Mn(II), Mn_{total}, and Mn(IV) (Figure 2b). During the fall season however, all Mn species were considerably lower. This can be attributed to only seven rain samples that were collected of which three were tropical storm samples (Tammy). When the tropical storm data are removed, Mn concentrations increase to 0.81 ± 0.23 nM for Mn(IV), 3.6 ± 0.7 nM for Mn(II) and 4.4 ± 0.5 nM for Mn_{total} but still remain considerably less than what is seen for other seasons. This suggests that tropical rain events dilute Mn concentrations.

The ratio of Mn(IV)/Mn(II) also displayed a distinct seasonal variability with a much larger ratio in summer relative to winter rain; however the ratio was always much less than 1 (Figure 3). The impact of seasonality on the ratio of Mn(IV)/Mn(II) concentrations in

A. Winter and Summer



B. Winter, Spring, Summer and Fall

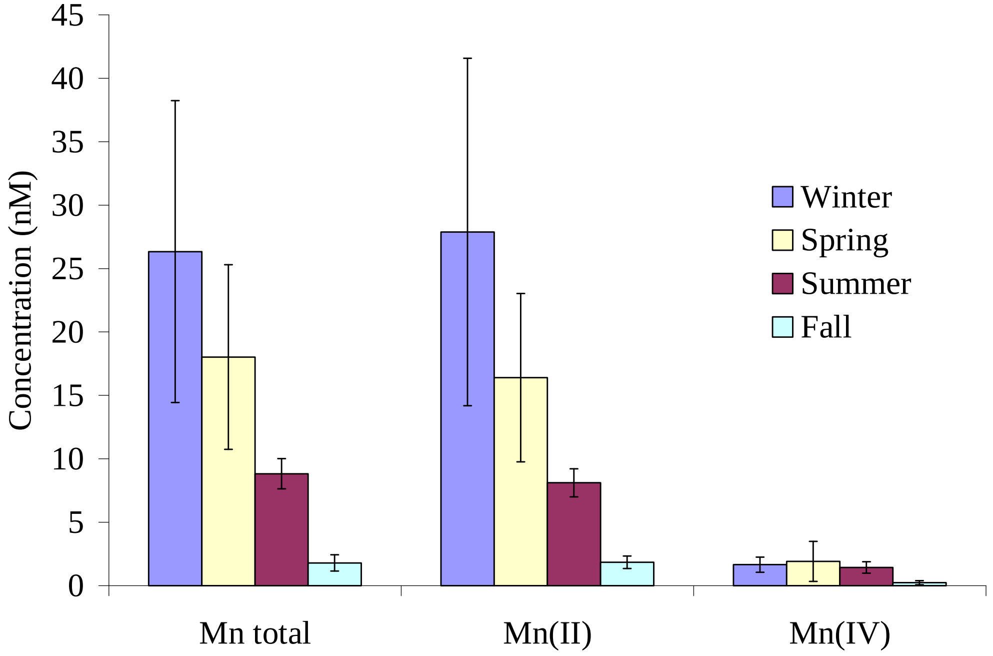


Figure 2. Volume weighted average concentrations (nM) of Mn_{total}, Mn(II) and Mn(IV) for winter, spring, summer and fall rain collected in Wilmington, NC rainwater between April 2, 2005 and March 24, 2006. Error bars represent ± one standard deviation.

Table 6. Volume weighted average concentrations and standard deviations (±) (nM) for Mn_{total}, Mn(II), Mn(IV), Mn(IV)/Mn(II), Fe_{total}, Fe_{diss}, Fe_{part} and Fe_{part}/Fe_{diss} ratio occurring in Winter, Spring, Summer and Fall rainwater collected between April 2, 2005 and March 24, 2006. Standard deviation of Mn(IV)/Mn(II) ratio calculated using absolute uncertainty. n = number of samples.

A. Mn_{total}, Mn(II), Mn(IV) and Mn(IV)/Mn(II)

	Mn_{total}	±	Mn(II)	±	Mn(IV)	±	Mn(IV)/Mn(II)	±	n
Winter	26	12	28	14	1.7	0.6	0.059	0.036	13
Spring	18	7.3	16	6.6	1.9	1.6	0.12	0.11	13
Summer	8.8	1.2	8.1	1.1	1.4	0.5	0.18	0.06	23
Fall	1.8	0.6	1.8	0.5	0.24	0.16	0.13	0.09	7

B. Fe_{total}, Fe_{diss}, Fe_{part} and Fe_{part}/Fe_{diss}

	Fe_{total}	±	Fe_{diss}	±	Fe_{part}	±	Fe_{part}/Fe_{diss}	±	n
Winter	107	29	79	25	33	12	0.31	0.14	13
Spring	135	61	51	19	83	45	0.62	0.44	13
Summer	142	23	61	6.4	82	24	0.57	0.19	23
Fall	12	4.5	15	1.7	4.5	2.4	0.36	0.24	7

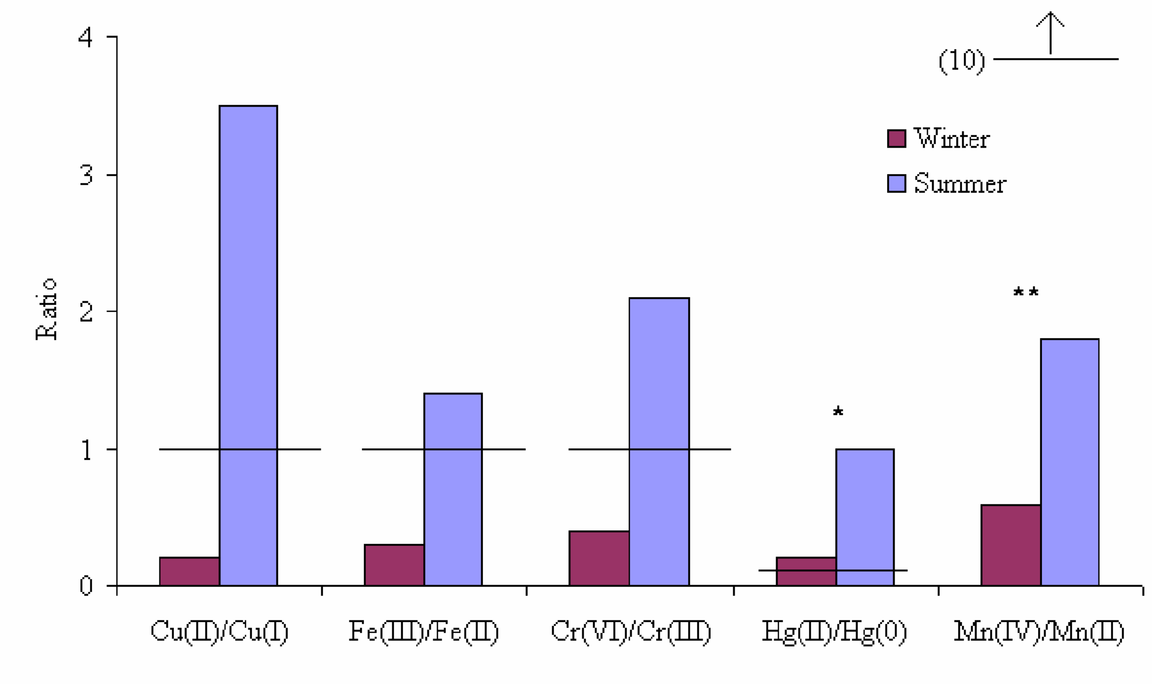


Figure 3. Volume weighted ratios of Cu(II)/Cu(I), Fe(III)/Fe(II), Cr(VI)/Cr(III), Hg(II)/Hg(0) and Mn(IV)/Mn(II) in Wilmington, NC rainwater. *Mercury ratios are presented at one tenth the actual ratio. **Manganese ratios are presented at ten times the actual ratio. Horizontal line indicates a 1:1 ratio for each metal. Data compiled from Parler, 2005 (Hg), Kieber et al., 2004 (Cu), Kieber et al., 2003 (Cr) and Kieber et al., 2001 (Fe).

rainwater is similar to results observed for other redox active trace metals in precipitation including Hg (Parler, 2005), Cu (Kieber et al., 2004) Cr (Kieber et al., 2003) and Fe (Kieber et al., 2001) at this location (Figure 3). For all metals the ratio of oxidized to reduced metal concentration is higher in the summer relative to the winter although the amplitude of this difference varies for each metal (Figure 3). This higher ratio in summer precipitation suggests a more oxidizing environment present in the atmosphere during the warmer season at this location.

The reason behind the higher Mn(IV)/Mn(II) ratio during the summer may be related to the speciation of Fe in these rain samples. There was a strong positive correlation between Mn(IV) and Fe_{part} (n = 56, r = 0.35, p = 0.007) in these rain samples, probably reflecting the association of these metals in terrestrial dust particles. A seasonal influence was also observed for Fe_{part} with higher concentrations in summer versus winter (Figure 4). It is likely that that particulate Fe and Mn are associated in dust as in equation 4.

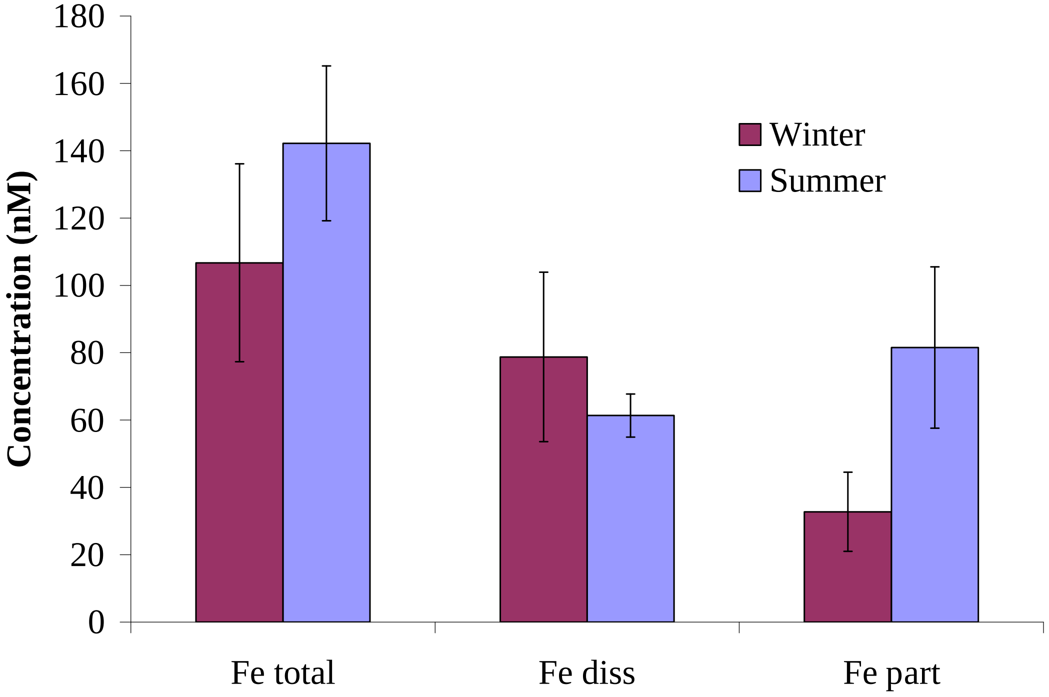
$$FeOOH_{(s)} / MnO_{2(s)} \rightarrow Mn(II)_{(aq)} + Fe(II)_{(aq)} \qquad (4)$$

where particulate Fe is represented by $FeOOH_{(s)}$ and Mn(IV) as $MnO_{2(s)}$. Copper may also behave in a similar way as Mn with $FeOOH_{(s)}$ (Kieber et al., 2004). The larger particulate Fe concentrations containing Mn(IV) in summer in combination with lower Mn(II) concentrations correspond to a higher ratio of Mn(IV)/Mn(II) during the summer. As the particulate Fe decreases during the winter months, much more dissolved Mn(II) is present resulting in a lower ratio of Mn(IV) to Mn(II) in winter rain.

Storm Origin

Rain events were subdivided by back trajectory into five separate categories (Figure 5) compiled by NOAA HYSPLIT. The trajectories consisted of two end members terrestrial (trajectory 2) and marine (trajectory 5), with the remaining classified as mixed (trajectories 1, 3

A. Winter and Summer



B. Winter, Spring, Summer and Fall

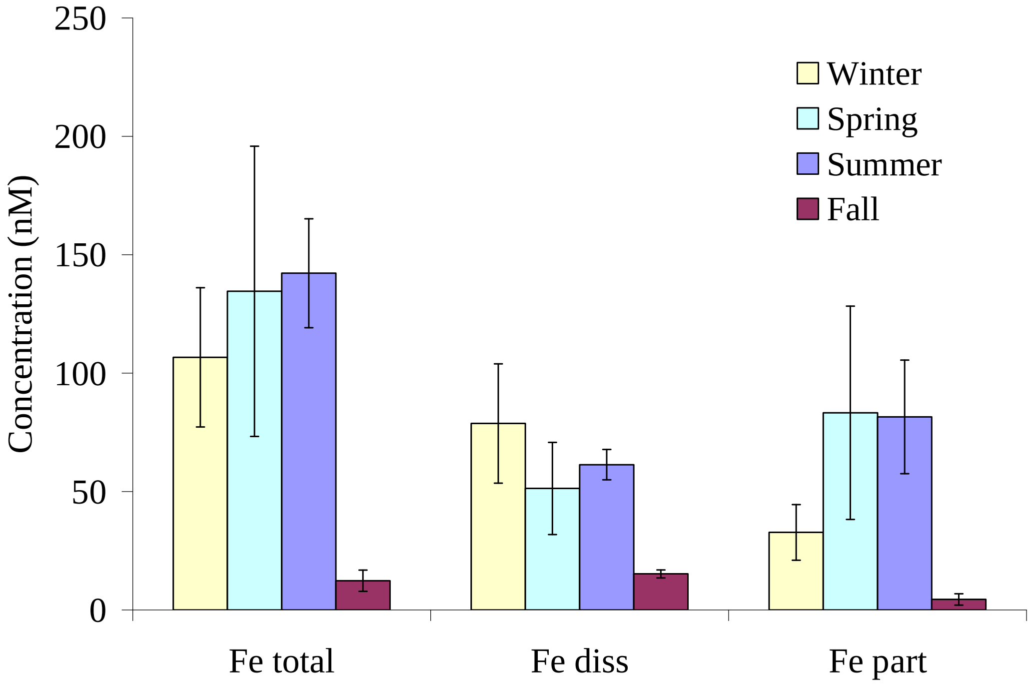


Figure 4. Volume weighted average concentration and standard deviation (nM) of Fe_{total}, Fe_{diss} and Fe_{part} for winter, spring, summer and fall rain collected in Wilmington, NC between April 2, 2005 and March 24, 2006. Error bars represent ± one standard deviation.

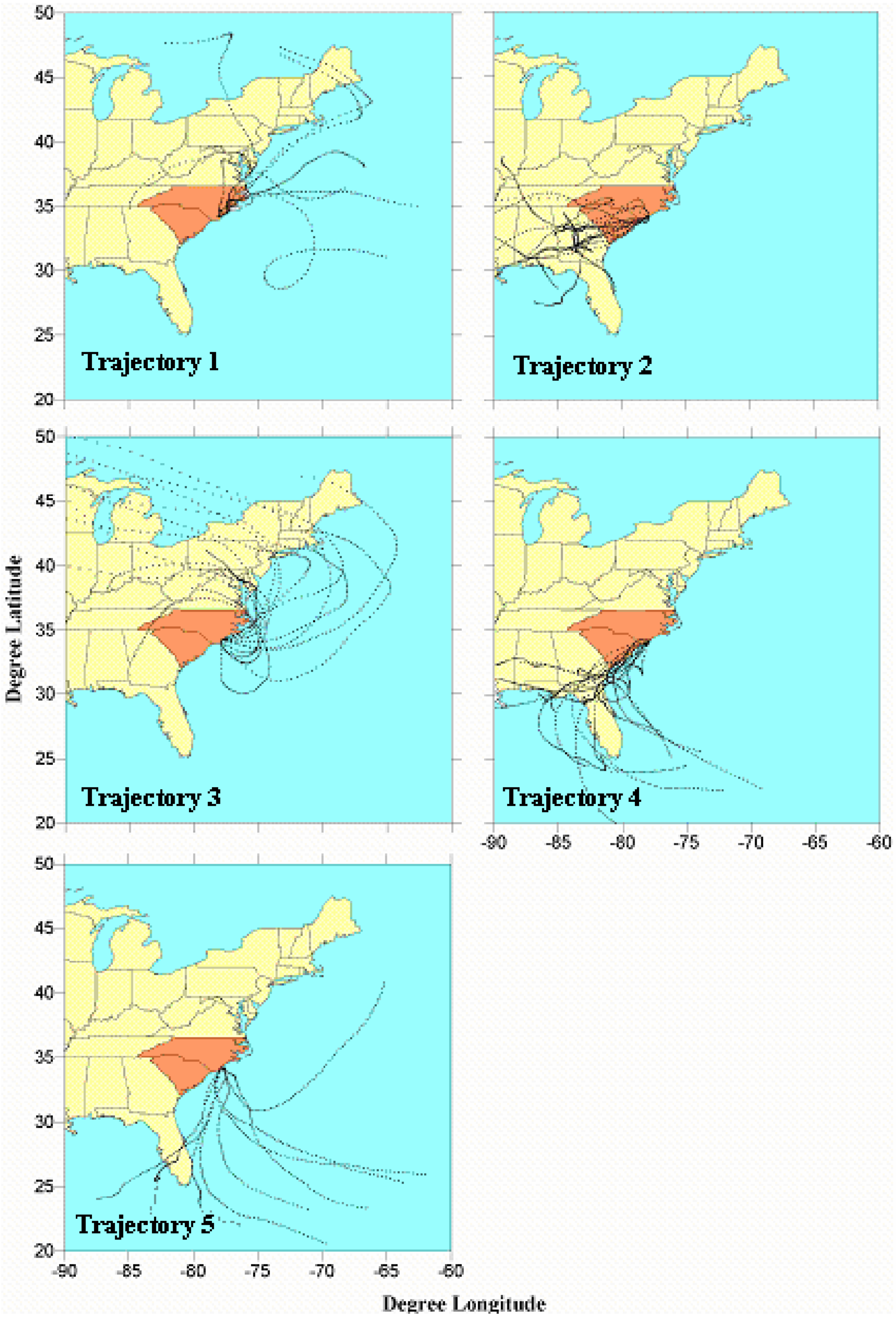
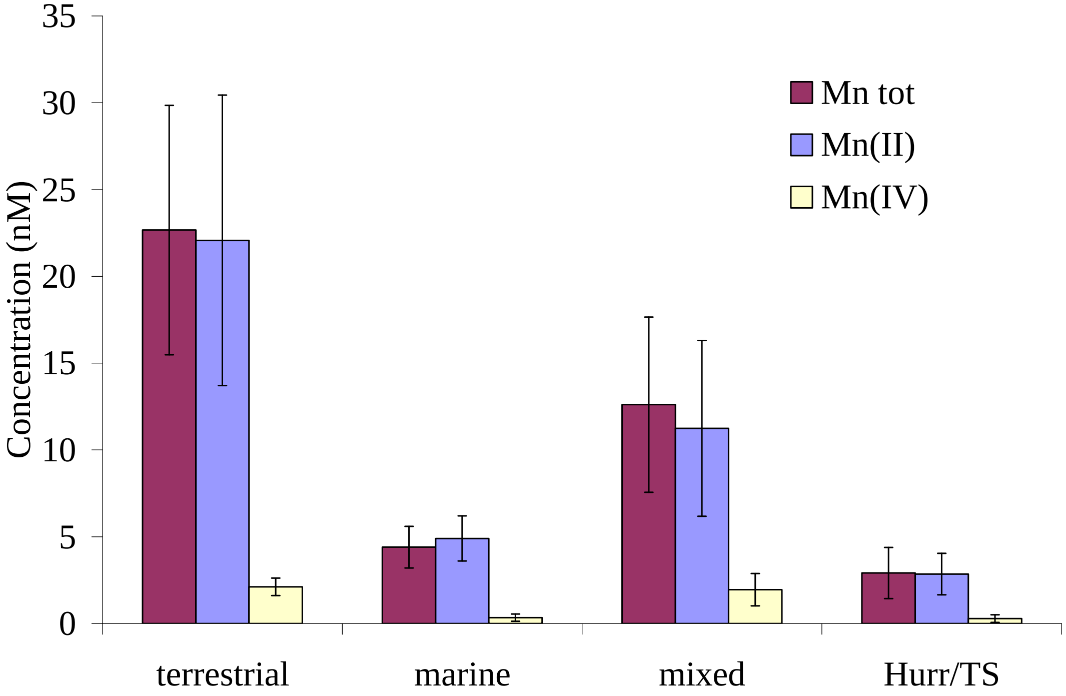


Figure 5. Plots of air mass back-trajectories calculated from the HYSPLIT model grouped by trajectory classification.

and 4) (Long, 2003). Of the 56 rain events analyzed, 23 were mixed, 15 were marine and 18 were of terrestrial origin. Two rain samples from Hurricane Ophelia and three rain samples from Tropical Storm Tammy were also collected. Rain from terrestrial storms was higher in Mn_{total} (ANOVA, p = 0.020) and Mn(II) (ANOVA, p = 0.087) compared with marine storms with higher volume weighted average concentrations in terrestrial relative to marine storms (Figure 6 and Table 7). This large difference in concentration suggests a strong terrestrial and/or anthropogenic input of Mn to the atmosphere at this location. When the hurricane and tropical storm data were omitted, no significant difference in Mn_{total} (ANOVA, p = 0.132) or Mn(II) (ANOVA, p = 0.338) was observed. In contrast to Mn_{total} and Mn(II), no significant difference was observed for Mn(IV) (ANOVA, p = 0.504) or the Mn(IV)/Mn(II) ratio (t test, p = 0.286) among terrestrial and marine storm origins when hurricane and tropical storm data were included (Figure 6 and 7). No correlation was seen for Mn(IV) (ANOVA, p = 0.500) or the Mn(IV)/Mn(II) ratio (t test, p = 0.240) when hurricane and tropical storm data were omitted.

The impact of storm origin on Mn concentrations in rainwater was similar to results observed for Hg (Parler, 2005), Cu (Kieber et al., 2004) and Fe (Kieber et al., 2001) at this rain site location. Storms with terrestrial origin have higher concentrations of dissolved Hg, Cu (II), Cu(I), Fe(III) and Fe(II) relative to marine storms, similar to what is observed for Mn, suggesting significant terrestrial inputs of these metals into the atmosphere. Contrary to previous Fe studies at this location, this study showed no significant difference for Fe_{total} (ANOVA, p = 0.171), Fe_{diss} (ANOVA, p = 0.276), Fe_{part} (ANOVA, p = 0.265) or Fe_{part}/Fe_{diss} ratio (ANOVA, p = 0.223) for terrestrial versus marine storm origins (Figure 6 and 7). In contrast to Mn, Hg and Cu, Cr concentrations were not significantly different for dissolved and total Cr between terrestrial and marine influenced storms (Kieber et al., 2003). Different sources for Cr that are not associated

A. Mn_{total}, Mn(II) and Mn(IV)



B. Fe_{total}, Fe_{diss} and Fe_{part}

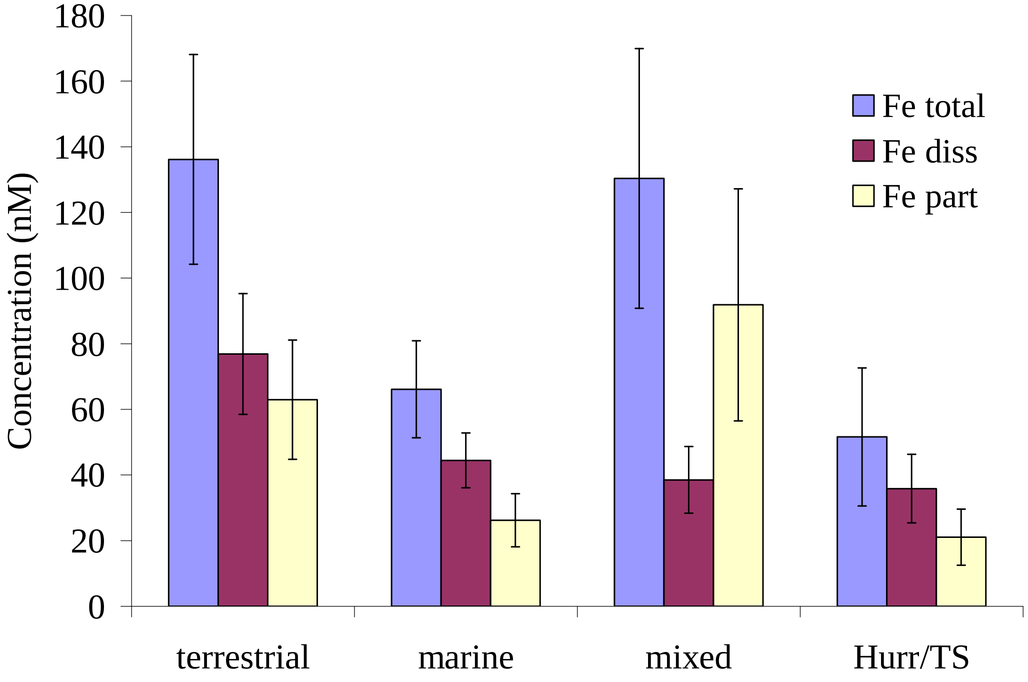


Figure 6. Volume weighted average concentrations and standard deviation (nM) of Mn_{total}, Mn(II), Mn(IV), Fe_{total}, Fe_{diss} and Fe_{part} for terrestrial (trajectory 2), marine (with hurricane and tropical storms) (trajectory 5), mixed and hurricane and tropical storm rain events.

Table 7. Volume weighted average concentrations (nM) and standard deviation (±) of Mn_{total}, Mn(II), Mn(IV), Mn(IV)/Mn(II), Fe_{total}, Fe_{diss}, Fe_{part} and Fe_{part}/Fe_{diss} for terrestrial, marine (contains hurricane and tropical storm data), mixed, hurricane and tropical storm and marine minus hurricane and tropical storm rain events. n = number of samples. Standard deviation of Mn(IV)/Mn(II) ratio calculated using absolute uncertainty.

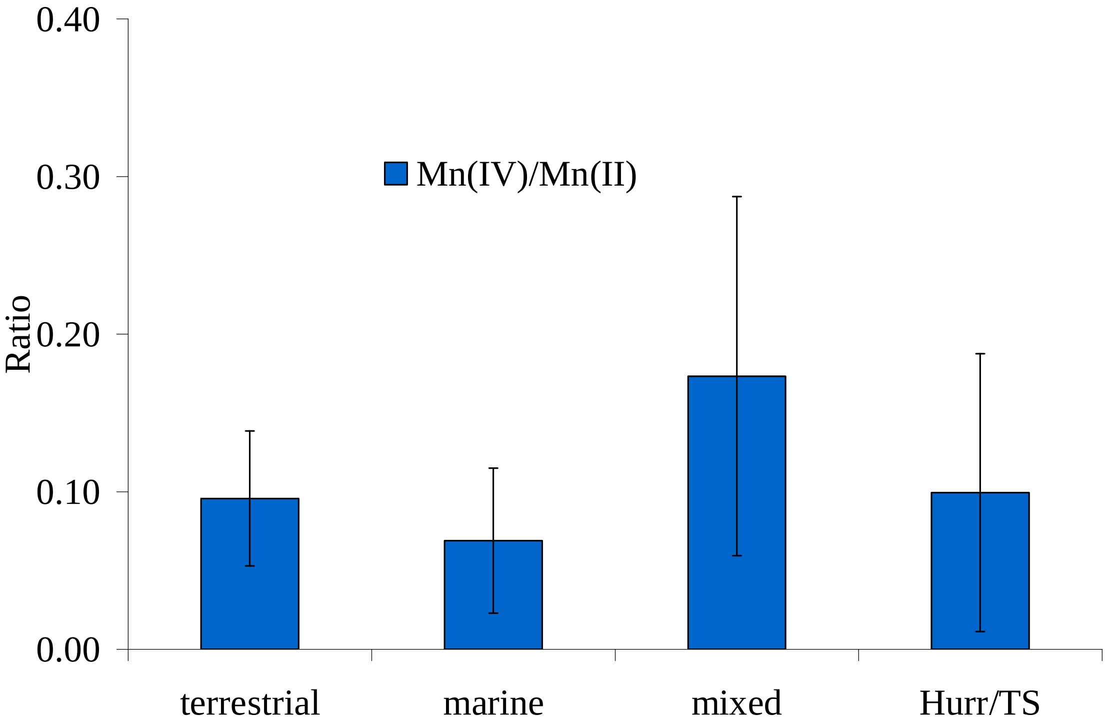
A. Mn_{total}, Mn(II), Mn(IV) and Mn(IV)/Mn(II)

	Mn_{total}	±	Mn(II)	±	Mn(IV)	±	Mn(IV)/Mn(II)	±	n
terrestrial	23	7.2	22	8	2.1	0.5	0.10	0.04	18
marine	4.4	1.2	4.9	1.3	0.34	0.21	0.07	0.05	15
mixed	13	5	11	5	1.9	0.9	0.17	0.11	23
Hurr/TS	2.9	1.5	2.8	1.2	0.28	0.22	0.099	0.088	5
marine – Hurr/TS	8.6	1.7	11	2	0.49	0.41	0.047	0.040	10

B. Fe_{total}, Fe_{diss}, Fe_{part} and Fe_{part}/Fe_{diss}

	Fe_{total}	±	Fe_{diss}	±	Fe_{part}	±	Fe_{part}/Fe_{diss}	±	n
terrestrial	136	32	77	18	63	18	0.82	0.31	18
marine	66	15	45	8.3	26	8.1	0.59	0.21	15
mixed	130	40	39	10	92	35	2.39	1.11	23
Hurr/TS	52	21	36	10	21	8.5	0.59	0.29	5
marine – Hurr/TS	107	20	69	13	41	16	0.59	0.25	10

A. Mn(IV)/Mn(II)



B. Fe_{part}/Fe_{diss}

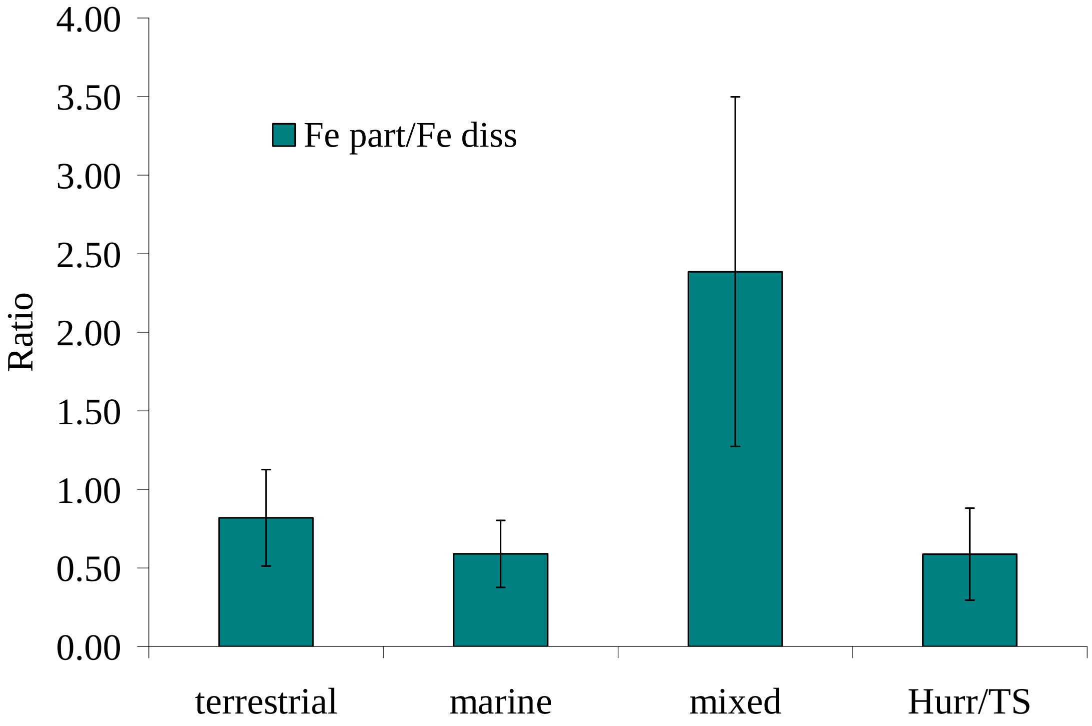


Figure 7. Ratio of Mn(IV)/Mn(II) and Fe_{part}/Fe_{diss} for terrestrial (trajectory 2), marine (contains hurricane and tropical storm data) (trajectory 5), mixed and hurricane and tropical storm rain events.

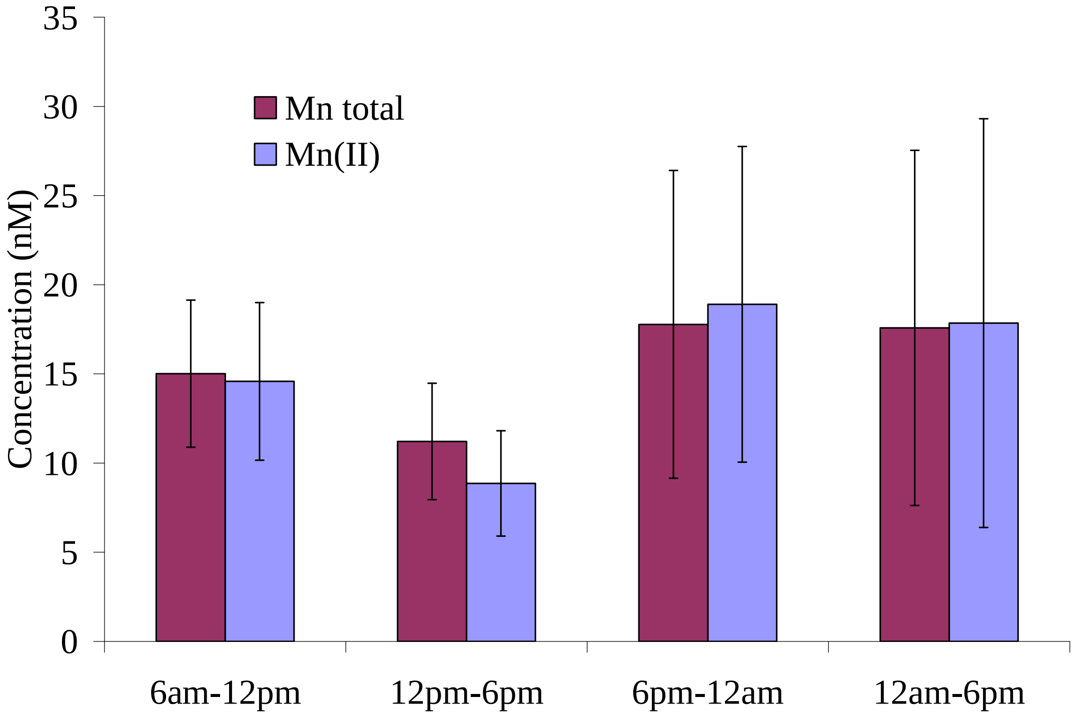
with Mn, Hg and Cu could explain the lack of observable difference in Cr concentration for terrestrial and marine storms.

Diurnal Variations

All rain events were subdivided based on time of day in which the rain occurred in order to assess potential diurnal oscillations in Mn speciation. Days were divided into four categories: 6 am – 12 pm, 12 pm – 6 pm, 6 pm – 12 am and 12 am – 6 pm. The time in which each rain event started was used to determine which of the four categories was used. Of the 56 rain samples analyzed, 10 occurred at 6am – 12 pm, 15 at 12 pm – 6 pm, 14 at 6 pm – 12 am and 12 at 12 am – 6 am (local time). Two rain samples from Hurricane Ophelia and three samples from Tropical Storm Tammy were omitted from data analysis because of their large volumes. Mn_{total} and Mn(II) concentrations were lowest during the 12 pm – 6 pm time period during which Mn(IV) was at a maximum (Figure 8). The ratio of Mn(IV)/Mn(II) also followed a diurnal trend with a maximum ratio at 12 pm – 6 pm with very similar ratios during the rest of the time periods (Figure 9A). This diurnal variation suggests some fraction of the Mn(II) is oxidized in the morning hours followed by a reduction of Mn(IV) in the evening.

The diurnal oscillation in the Mn(IV)/Mn(II) ratio may also be related to the speciation of Fe in these rain samples. The Fe_{part}/Fe_{diss} ratio shows the same diurnal trend with a maximum at 12 pm – 6am (Figure 9B). When both ratios are plotted together, a strong correlation is observed which suggests that when Fe_{part} concentrations are high, particulate Mn (as Mn(IV)) is also high (Figure 10). This pattern occurs even though the Fe_{part}/Fe_{diss} ratio is usually close to one or greater whereas the Mn(IV)/Mn(II) ratio is usually less than 0.5. The diurnal oscillation of Mn(IV)/Mn(II) is similar to the impact of time of day on other metals studied at this location. The ratio of Hg(II)/Hg(0) was also at a maximum during the 12 pm – 6 pm time period and at a

A. Mn_{total} and Mn(II)



B. Mn(IV)

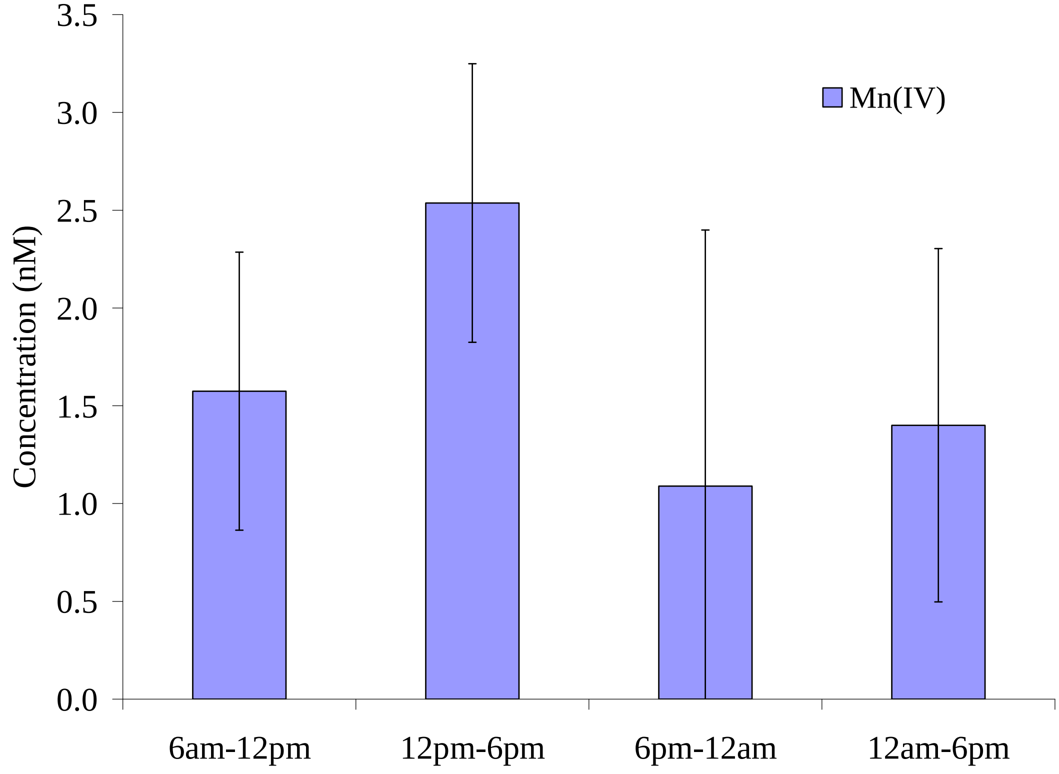
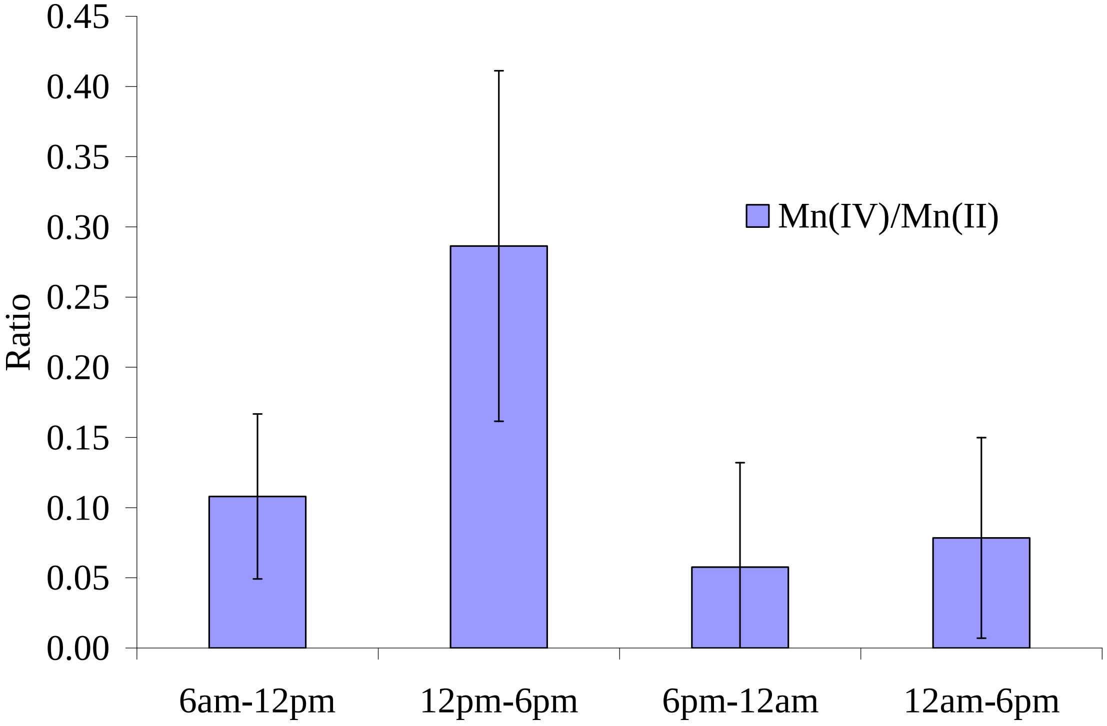


Figure 8. Volume weighted average concentrations and standard deviation (nM) for Mn_{total}, Mn(II) and Mn(IV) plotted as a function of time of day.

A. Mn(IV)/Mn(II)



B. Fe_{part}/Fe_{diss}

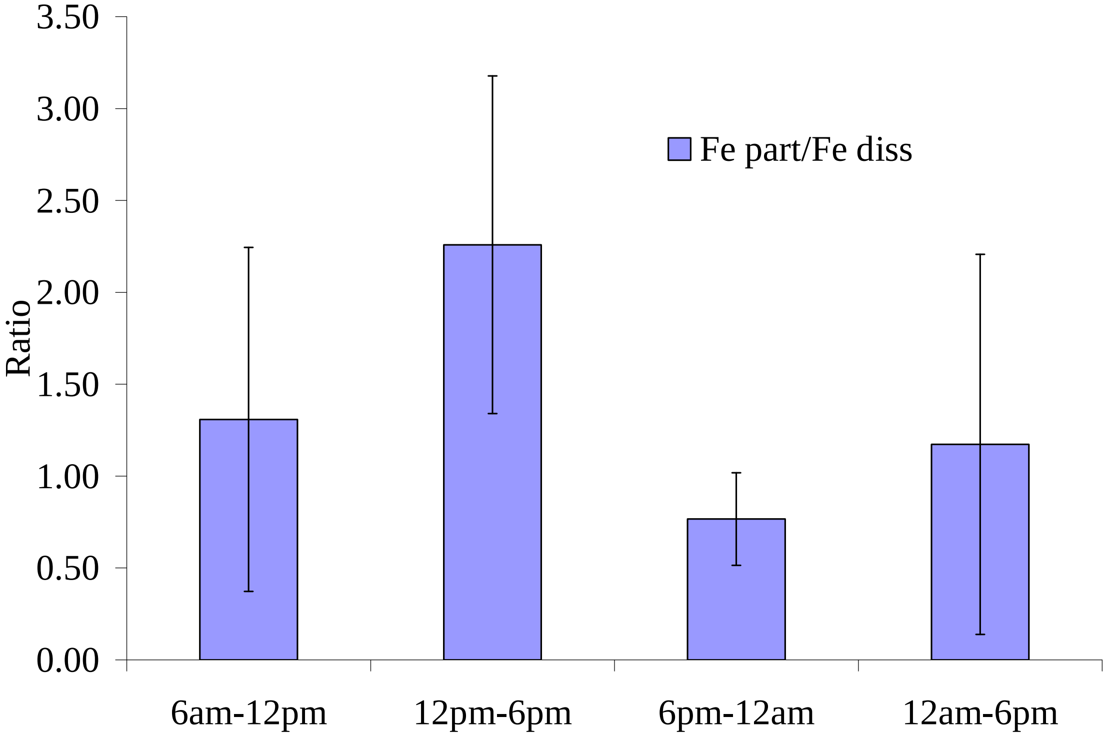


Figure 9. Volume weighed Mn(IV)/Mn(II) ratio and volume weighted Fe_{part}/Fe_{diss} ratio with standard deviations plotted as a function of time of day.

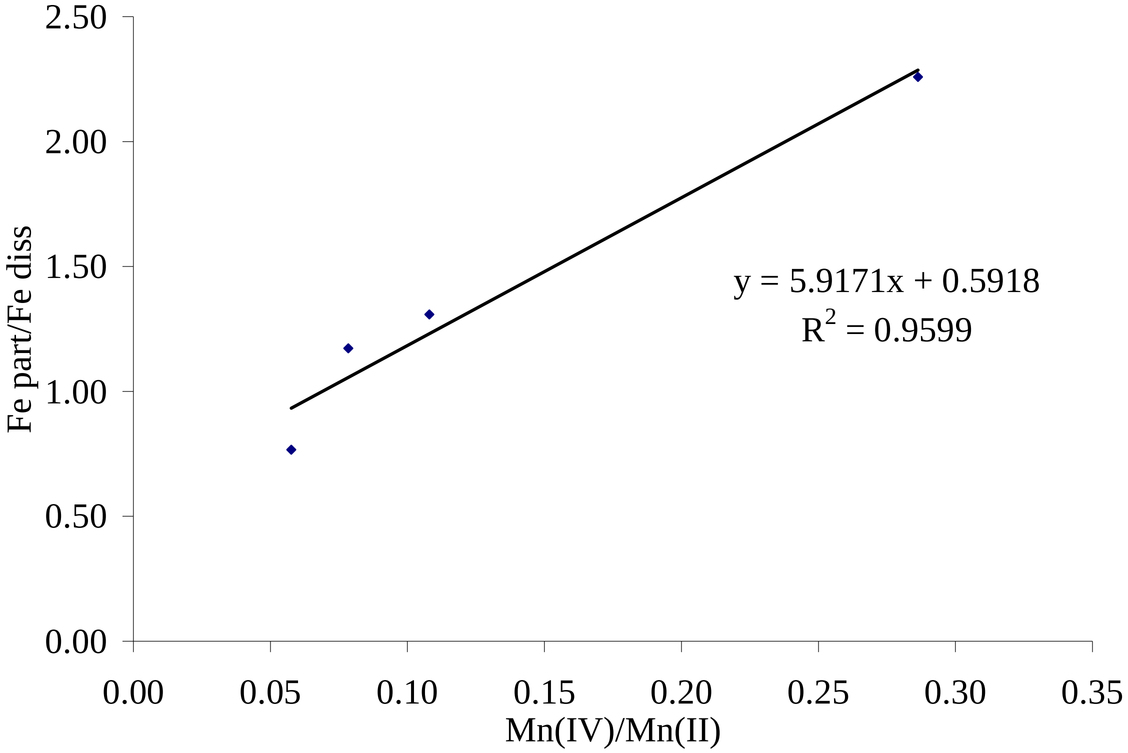


Figure 10. Volume weighted average comparison of Mn(IV)/Mn(II) ratio and Fe_{part}/Fe_{diss}.

minimum at 12 am – 6 am (Parler, 2005). The Mn(IV)/Mn(II) ratio also follows a similar trend as Cu(II)/Cu(I) with higher oxidized Cu during the 12 pm – 6 pm and 12 am – 6 am intervals and an increase in reduced Cu during 6am – 12pm and 6pm – 12am intervals (Kieber et al., 2004). The Cr(VI)/Cr(III) ratio was also comparable to the Mn(IV)/Mn(II) ratio with higher concentrations of reduced Cr(III) observed in the morning and increasing oxidation of Cr during the day, except the highest ratio was slightly later until 6 pm – 12 am (Kieber et al., 2002). The Fe(III)/Fe(II) ratio had a diurnal oscillation which is the mirror image of the other metals with the reduced form (Fe(II)) at a maximum during the 12 pm – 6 pm time period (Willey et al., 2000). The results of these earlier studies and this work suggest that most metals exist in their highest oxidation state during the period of peak sunlight intensity with the exception of Fe which is in the more reduced form during this time due to photoreduction of Fe(III) (Kieber et al., 2003).

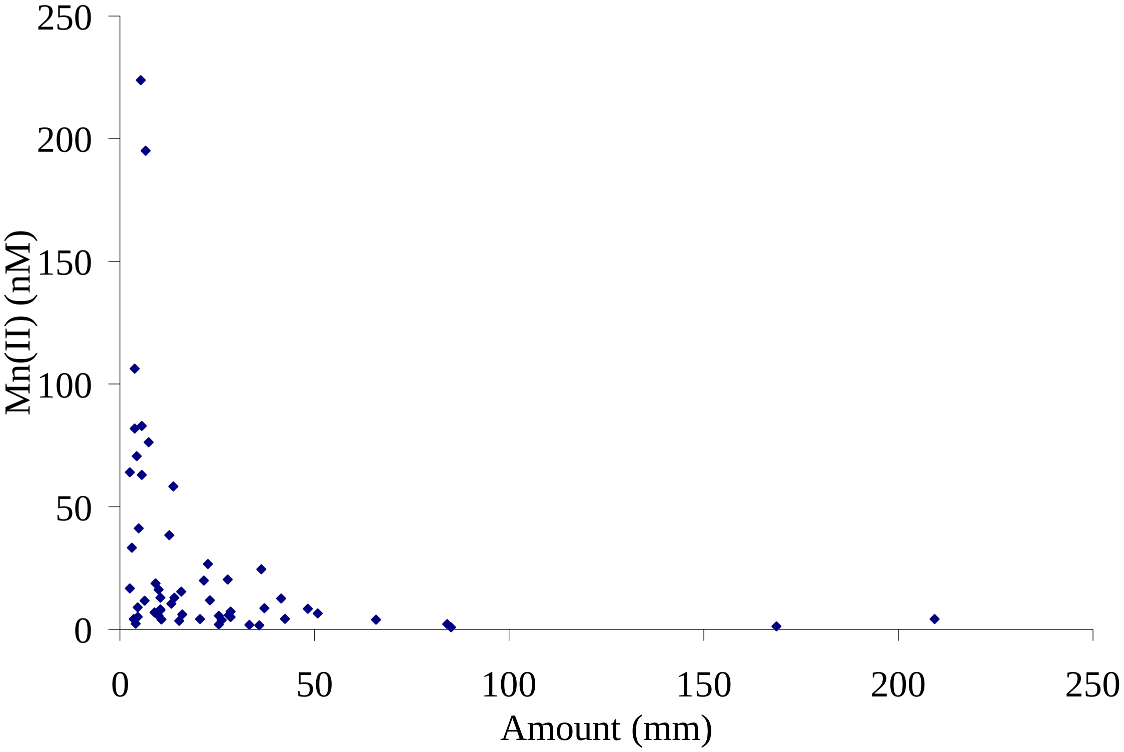
Correlation Analysis

Correlation analysis was performed between Mn species and other rainwater components in order to evaluate possible relationships using a Pearson product moment correlation with Sigma Stat. A complete list of analytes is shown in Table 8. No correlation was found between Mn(II) and Mn(IV) (Table 8) suggesting these two forms behave as independent variables in rainwater with different source strengths. A negative correlation was observed between Mn(II) and rainfall amount suggesting that dissolved Mn is effectively washed out of the atmosphere (Figure 11A). No significant correlation was observed for Mn(IV) and rainfall amount although the highest Mn(IV) occurred in small volume rains, and lowest concentrations in high volume events (Figure 11B). Similar washout behavior has been observed for dissolved Hg and Cu at this location suggesting these metals are also being washed out of the atmosphere (Parler, 2005;

Table 8. Correlation between Mn(IV), Mn(II), H_2O_2, DOC, H^+, Cl^-, NO_3^-, NSS, amount, Fe_{part} and Fe_{diss}. Values given in order of correlation coefficient, p value and number of samples. P values below 0.050 are considered significant.

	Mn(II)	H_2O_2	DOC	H^+	Cl^-	NO_3^-	NSS	Amount	Fe_{part}	Fe_{diss}
Mn(IV)	0.15 0.27 56	0.049 0.72 55	0.19 0.18 54	0.057 0.67 56	0.73 1.4E-10 56	0.25 0.068 54	0.096 0.48 56	-0.15 0.28 56	0.35 7.4E-3 56	0.22 0.098 56
Mn(II)		5.7E-3 0.97 55	0.34 0.011 54	0.47 2.6E-4 56	0.14 0.29 56	0.54 2.5E-5 54	0.50 8.9E-5 56	-0.27 0.042 56	0.28 0.039 56	0.80 1.9E-13 56
H_2O_2			0.33 0.016 53	0.056 0.68 55	0.12 0.39 55	-0.022 0.88 53	0.21 0.13 55	-0.22 0.10 55	0.29 0.035 55	0.16 0.23 55
DOC				0.44 9.2E-4 54	0.25 0.072 54	0.58 7.5E-6 52	0.70 3.3E-9 54	-0.28 0.038 54	0.60 1.3E-6 54	0.52 6.6E-5 54
H^+					0.021 0.88 56	0.52 6.1E-5 54	0.54 1.8E-5 56	-0.28 0.034 56	0.36 5.9E-3 56	0.62 3.1E-7 56
Cl^-						0.22 0.11 54	0.22 0.10 56	0.083 0.54 56	0.34 9.9E-3 56	0.23 0.091 56
NO_3^-							0.63 3.2E-7 54	-0.28 0.042 54	0.36 6.9E-3 54	0.56 8.7E-6 54
NSS								-0.14 0.32 56	0.66 3.6E-8 56	0.59 1.4E-6 56
Amount									-0.20 0.13 56	-0.28 0.038 56
Fe_{part}										0.44 6.4E-4 56

A. Mn(II)



B. Mn(IV)

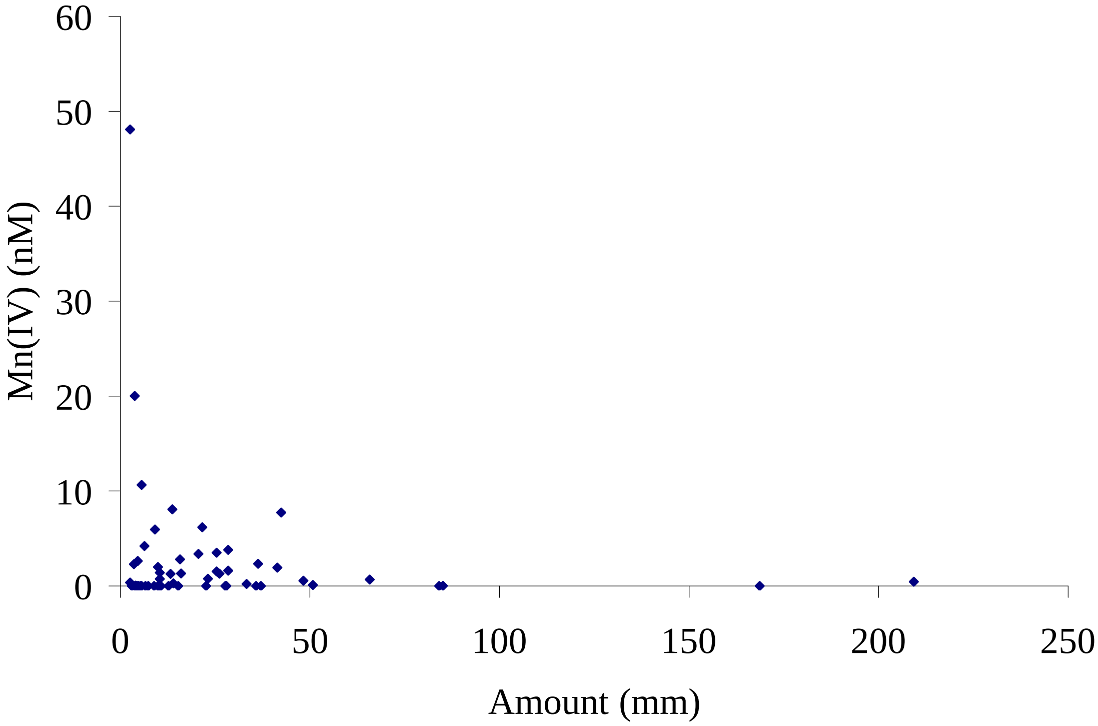


Figure 11. Mn(II) and Mn(IV) concentrations (nM) plotted as a function of rain amount (mm) measured in Wilmington, NC rainwater.

Kieber et al., 2004). In contrast to Hg, Cu and Mn, Fe and Cr showed no correlations with rainfall amount suggesting that these trace metals are not simply washed out of the atmosphere (Kieber et al., 2001; Kieber et al., 2002). Contrary to previous studies of Fe at this location, this study showed a negative correlation between Fe_{diss} and rainfall amount suggesting that dissolved Fe is effectively washed out of the atmosphere (Figure 12A). Although no significant correlation was observed for Fe_{part} and rainfall amount, highest Fe_{part} occurred in small volume rains and lowest concentrations in high volume rains (Figure 12B).

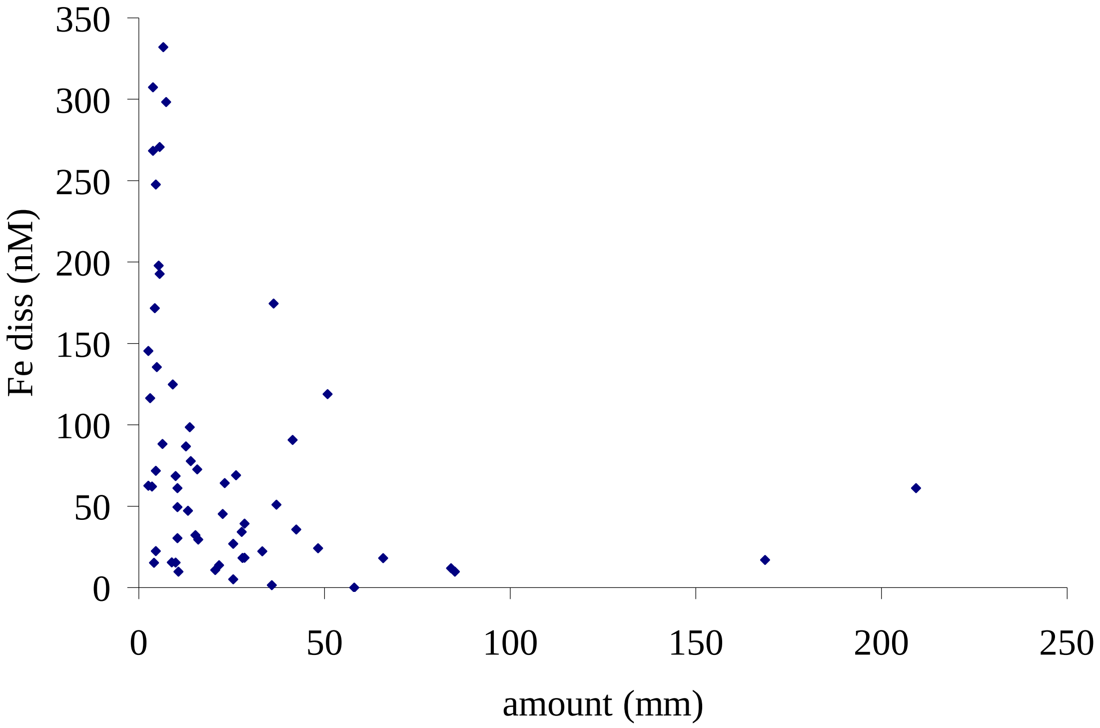
Manganese species were also correlated with other rainwater components in addition to rainfall amount. Mn(II) showed a positive correlation with H^+ whereas Mn(IV) showed no correlation with acidity. Mn(II), Fe_{diss}, H^+, NO_3^-, and non-seasalt sulfate (NSS) were all highly correlated ($p<0.001$, Figures 13 and 14, Table 8). NSS is sulfate that does not come from seaspray, and hence is primarily derived from pollutant sources. It is calculated as follows, based on the constant composition of seawater:

$$\mathrm{NSS} = [SO_4^{2-}] - 0.0517[Cl^-]. \qquad (5)$$

This association of H^+, NO_3^- and NSS is generally interpreted as coming from anthropogenic sources and is often used as a pollution indicator. The correlation between Mn(II) and these pollutant indicators implies a strong anthropogenic source for Mn at this location. Mn(II) and Fe_{diss} also showed positive correlations with DOC suggesting that Mn(II) increases with dissolved organic carbon in rainwater possibly due to complexation with organic ligands as has been observed for Fe_{diss} (Kieber et al., 2005).

Manganese species were analyzed for correlation with Fe_{part} and Fe_{diss}. Mn(IV) showed a positive correlation with Fe_{part} suggesting Mn(IV) increases with Fe_{part} (Figure 15) as was suggested in equation 4. Mn(II), Fe_{diss} and Fe_{part} covary (Figures 16 and 17, Table 8) which is

A. Fe$_{\text{diss}}$



B. Fe$_{\text{part}}$

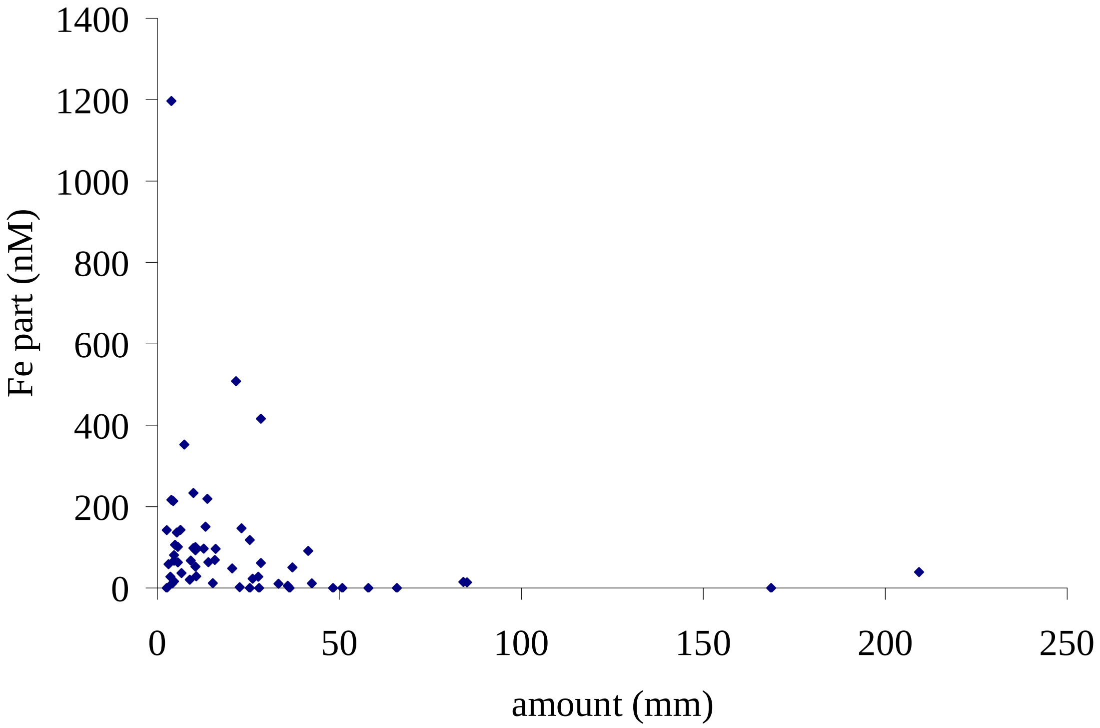


Figure 12. Fe$_{\text{diss}}$ and Fe$_{\text{part}}$ concentrations (nM) plotted as a function of rain amount (mm) measured in Wilmington, NC rainwater.

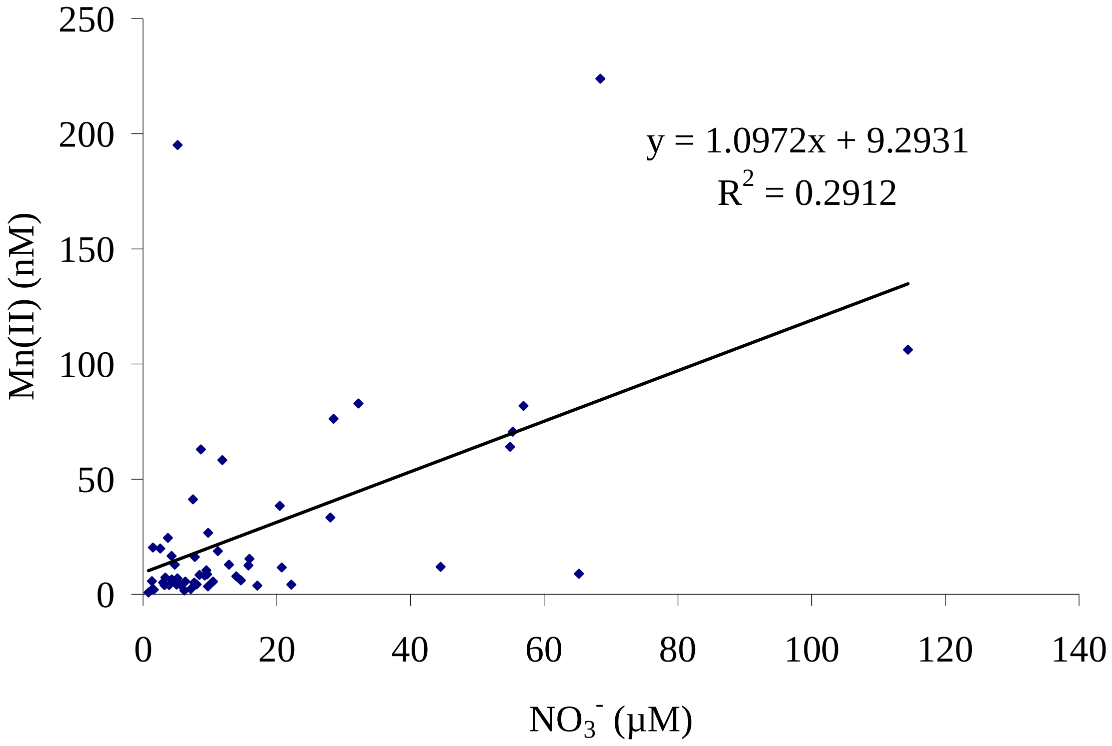


Figure 13. Mn(II) concentrations (nM) as a function of NO_3^- concentrations (µM) in Wilmington, NC rainwater.

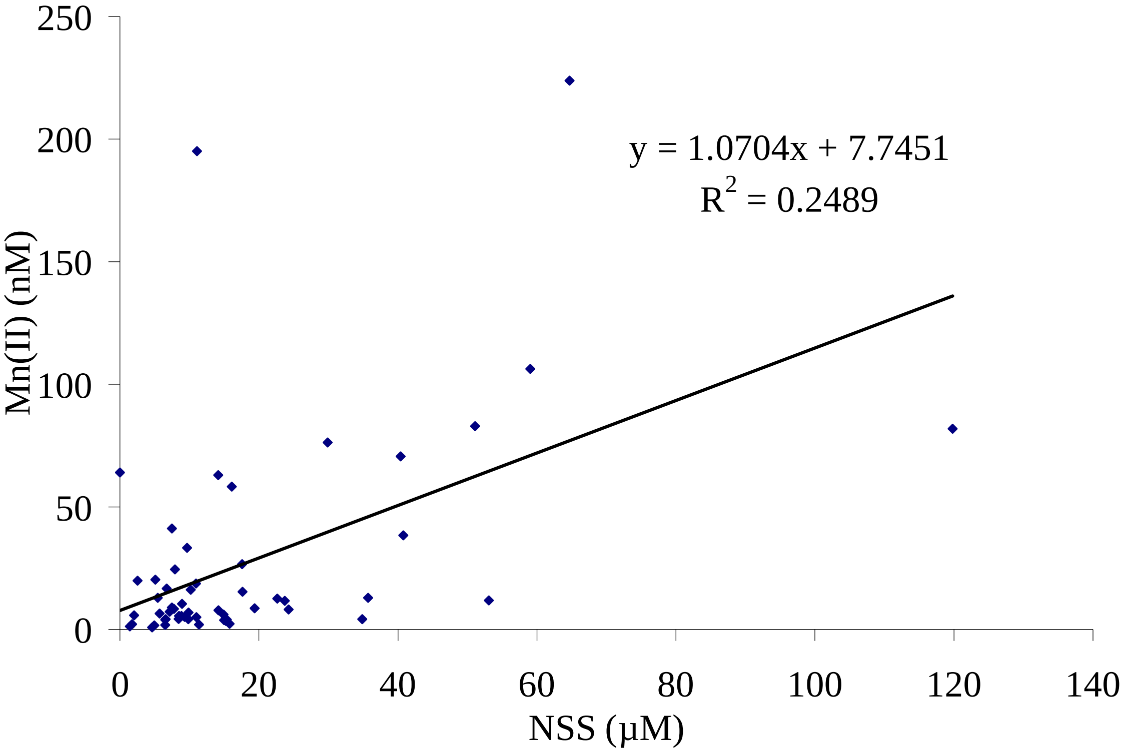


Figure 14. Mn(II) concentrations (nM) as a function of NSS concentrations (µM) in Wilmington, NC rainwater.

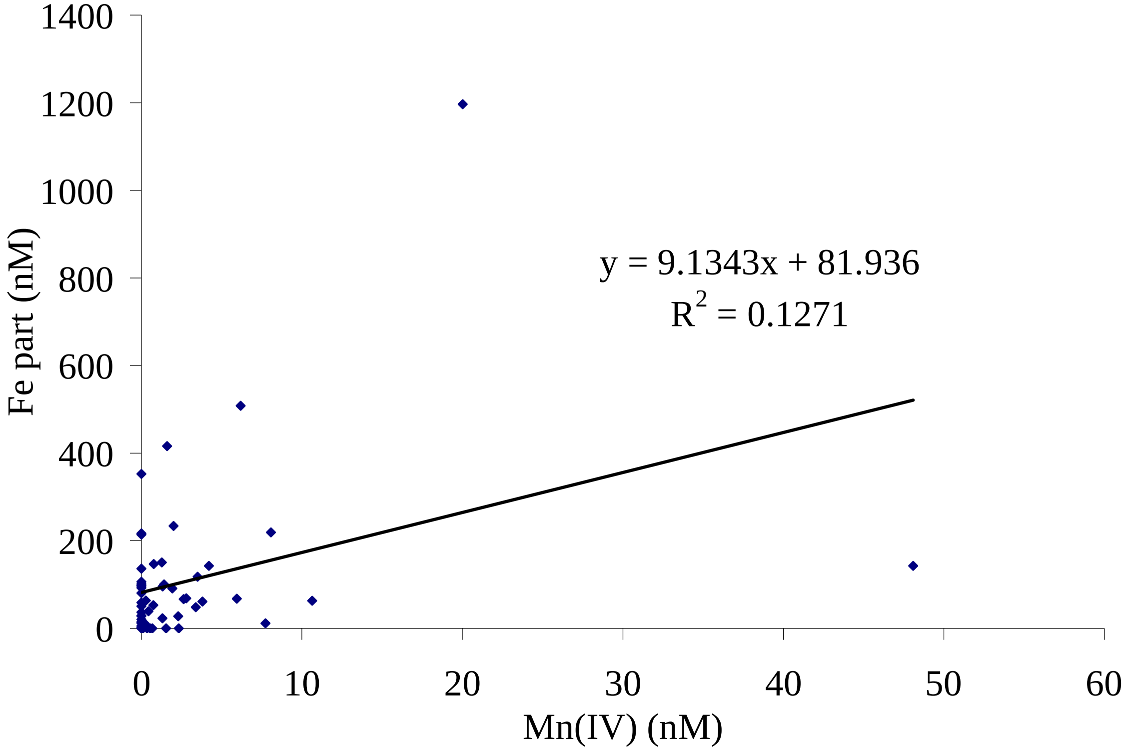


Figure 15. Mn(IV) concentrations (nM) as a function of Fe_{part} concentrations (nM) in Wilmington, NC rainwater.

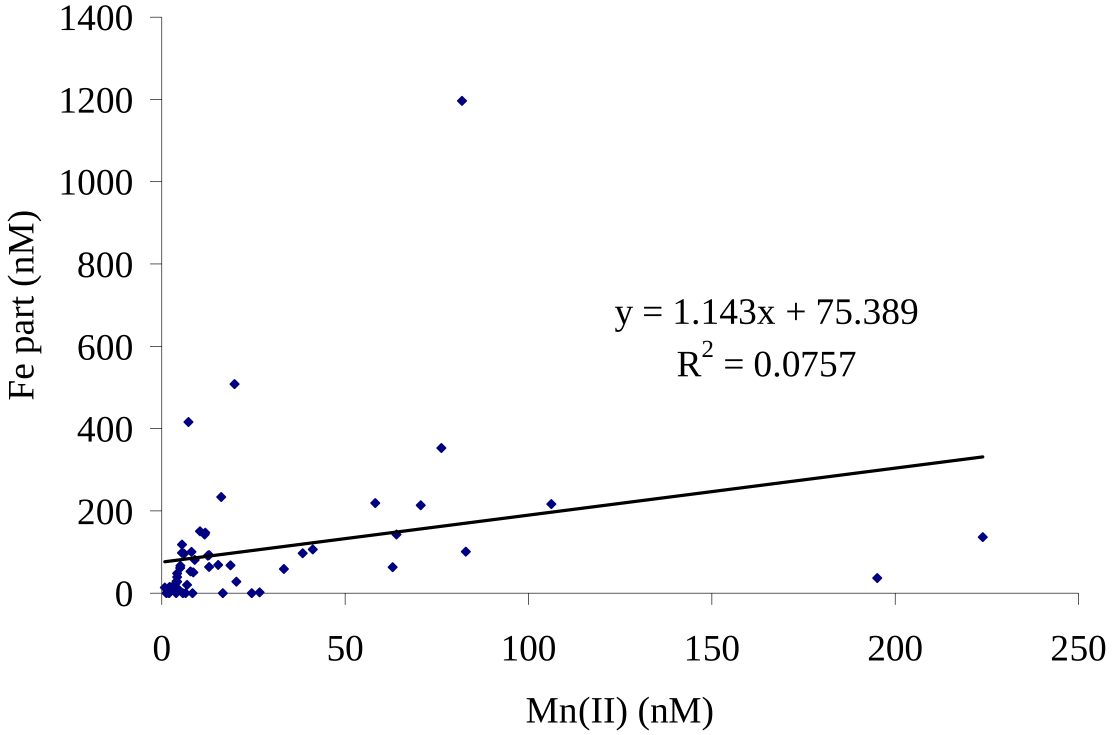


Figure 16. Mn(II) concentrations (nM) as a function of Fe_{part} concentrations (nM) in Wilmington, NC rainwater.

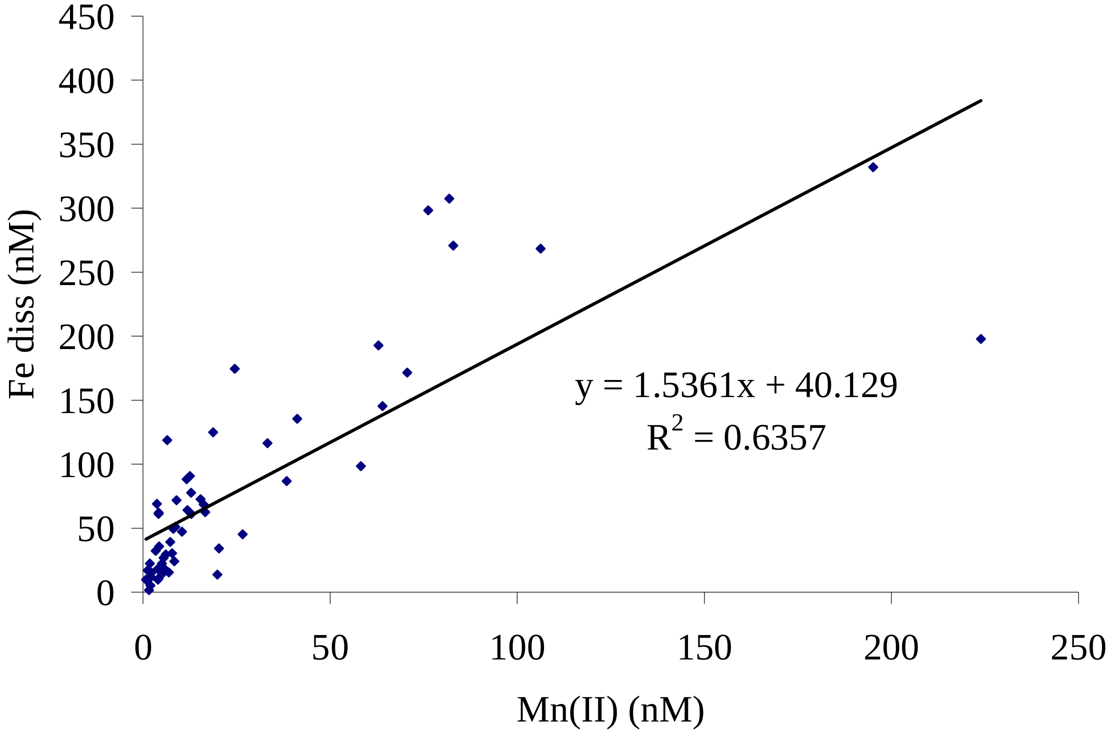


Figure 17. Mn(II) concentrations (nM) as a function of Fe_{diss} concentrations (nM) in Wilmington, NC rainwater.

also consistent with the reaction described by equation 4. The correlation of Mn(II) with Fe_{diss} is strong ($p<0.001$) indicating that these species respond to similar chemical processes in the atmosphere.

Photochemistry

Photochemistry experiments were performed to evaluate the role of sunlight on Mn speciation. Two rain samples were irradiated for 6 h and compared to dark controls. No significant difference ($p>0.05$) was observed between irradiated samples and dark controls for either rain event (Figure 18) suggesting photochemical reduction of Mn(IV) to Mn(II) is not a significant process in rainwater. The observed seasonality (Figure 2) and diurnal variability (Figure 8 and 9) in Mn speciation are therefore not driven by photochemical processes but may rather be the result of temporal and seasonal changes in particulate Fe abundances in rainwater. Fe(III) and Fe(II) species show dynamic interconversion during the daylight in which Fe(III) is rapidly photoreduced to Fe(II) (Kieber et al., 2005). The photochemical reactivity of Mn(IV) is therefore much less than that observed for Fe(III).

Atmospheric Flux of Mn

Natural sources contribute 3.17×10^{11} g of Mn into the atmosphere annually, whereas anthropogenic sources provide 1.1×10^{10} g annually for a total of 3.28×10^{11} g per year or 6.0×10^{9} moles per year (Pacyna and Pacyna, 2001). The average total concentration of Mn found in Wilmington rainwater is 11 ± 3 nM (Table 3). Using the precipitation value from Elliott and Reed (1984) for total global rainfall, 4.1×10^{17} liters per year, and assuming that the Wilmington concentration is representative of rainfall concentrations worldwide, the total global flux of Mn removed by wet deposition is 4.5×10^{9} moles per year. This suggests that approximately 75% of atmospheric Mn is removed by wet deposition with the remaining 25% removed by dry

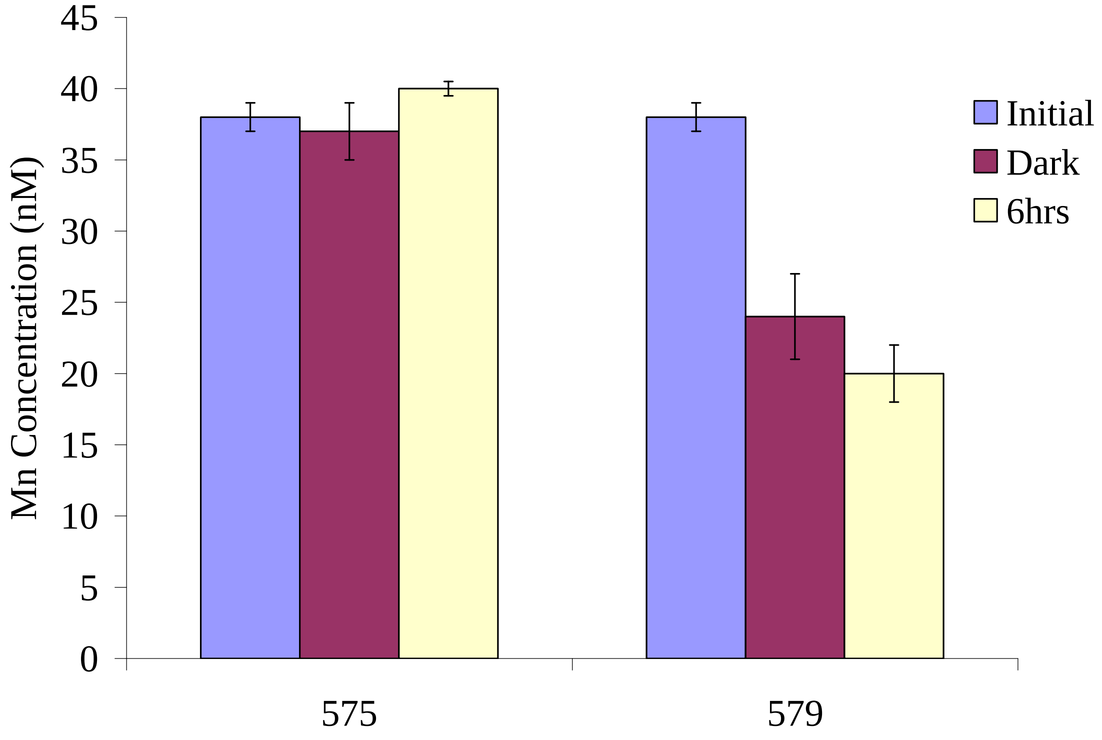


Figure 18. Manganese concentrations (nM) for initial, dark and 6 hr irradiance for rain samples 575 and 579. Initial represents Mn_{total}. Dark and 6hrs represents Mn(II). Error bars represents the range of data where n=2.

deposition.

The atmospheric flux can be compared to the riverine flux, which is also considered to be a major source of trace metals to the world's oceans. An average total Mn concentration in rivers is 0.15 µM (Martin and Meybeck, 1979). Using a global riverine discharge of 3.6×10^{16} liters per year (Broecker and Peng, 1982), the total global flux of Mn delivered to the oceans is 5.4×10^{9} moles per year. Considering that 74% of the global rain falls over the oceans (Elliott and Reed, 1984), then 3.3×10^{9} moles per year of Mn removed by wet deposition (of the 4.5×10^{9} moles per year global total) is delivered to the oceans. This suggests that the amount of Mn removed by wet deposition deposited to the oceans is slightly less but of the same order of magnitude as riverine discharge.

Seawater Mixing Experiment

One important consequence of atmospheric Mn delivered to the oceans is potential changes in speciation, which might occur when rainwater is mixed with seawater of pH 8.1. A series of mixing experiments were therefore conducted in order to assess the possibility of oxidation of Mn(II) to Mn(IV) (Figure 1). Based on simple dilution of the two solutions in Table 9 one would expect a Mn concentration for sample E633 and the synthetic rain water after mixing with seawater in a 1:1 ratio to be 48 nM and 37 nM respectively if no chemical reaction occurred (Table 9). When the experiment was conducted, similar results to those predicted were obtained suggesting that there was no observable oxidation of Mn(II) to Mn(IV) within 4 h after mixing with seawater (Table 9). Therefore, Mn(II) is thermodynamically stable under these experimental conditions and a longer time frame is required to oxidize Mn(II) to Mn(IV) based solely on pH and salinity changes.

Table 9. Average Mn concentration and standard deviation (±) (nM) of rain event 633 initial, synthetic rain water (SRW) initial, seawater (SW) initial, 633 + SW 4 h and SRW + SW 4 h.

Sample	Mn(II)	pH
633 initial	70 ± 1	4.70
SRW initial	48 ± 9	4.30
SW initial	26 ± 3	8.46
Predicted 633 mix	48	-
Predicted SRW mix	37	-
633 + SW 4 h	36 ± 9	8.54
SRW + SW 4 h	44 ± 9	8.48

CONCLUSIONS

1. Dissolved Mn accounts for 97% of the total Mn in Wilmington, NC rainwater. The other 3% is particulate (operationally defined as Mn(IV)) with a negligible colloidal fraction.
2. There was a distinct seasonality to Mn speciation with higher concentrations of Mn_{total} and Mn(II) in winter relative to summer season and no observable difference in Mn(IV) between these seasons. During the spring months, no difference was observed for all Mn species in comparison to summer and winter seasons although Mn species were considerably lower during the fall season.
3. There was an impact of air mass back trajectory on Mn speciation with higher concentrations of Mn_{total} and Mn(II) in terrestrial storms relative to marine storms with no significant difference in Mn(IV) between storm types.
4. The speciation of Mn underwent diurnal oscillations in which Mn_{total} and Mn(II) concentrations were lowest during the afternoon hours when Mn(IV) was at a maximum. The ratio of Mn(IV)/Mn(II) also had diurnal variability with a maximum at 12 pm – 6 pm with very similar ratios during the rest of the day, suggesting some fraction of the Mn(II) is oxidized in the morning hours followed by reduction of Mn(IV) in the evening.
5. The ratio of dissolved to particulate Fe (Fe_{part}/Fe_{diss}) underwent a diurnal trend as well with a maximum at 12 pm – 6am. The ratio (Fe_{part}/Fe_{diss}) was strongly correlated with the Mn(IV)/Mn(II) ratio.
6. Correlations were found between Mn(II) and the pollutant indicators H^+, NO_3^-, and NSS which implies a strong anthropogenic source for Mn at this location. Mn(IV) showed a positive correlation with Fe_{part} whereas Mn(II) correlated with Fe_{diss} and Fe_{part}, suggesting

a tight coupling between Fe and Mn phases in precipitation. No correlation was found between Mn(II) and Mn(IV).

7. The comparison between the total global input of Mn and the calculated flux of Mn removed via wet deposition suggests that approximately 75% of Mn released by both natural and anthropogenic sources into the atmosphere is removed by wet deposition with the remaining 25% removed by dry deposition.