

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/7857478>

Oxidation of Fe(II) in Rainwater

ARTICLE in ENVIRONMENTAL SCIENCE AND TECHNOLOGY · MAY 2005

Impact Factor: 5.33 · DOI: 10.1021/es0404522 · Source: PubMed

CITATIONS

30

READS

25

4 AUTHORS, INCLUDING:



[Joan Willey](#)

University of North Carolina at Wilmington

96 PUBLICATIONS 2,006 CITATIONS

SEE PROFILE



[Robert F. Whitehead](#)

University of North Carolina at Wilmington

31 PUBLICATIONS 988 CITATIONS

SEE PROFILE



[Rance Hardison](#)

National Oceanic and Atmospheric Administr...

23 PUBLICATIONS 333 CITATIONS

SEE PROFILE

Oxidation of Fe(II) in Rainwater

J. D. WILLEY,* R. F. WHITEHEAD,
R. J. KIEBER, AND D. R. HARDISON

Department of Chemistry, University of North Carolina at
Wilmington, Wilmington, North Carolina 28403-3297

Photochemically produced Fe(II) is oxidized within hours under environmentally realistic conditions in rainwater. The diurnal variation between photochemical production and re-oxidation of Fe(II) observed in our laboratory accurately mimics the behavior of ferrous iron observed in field studies where the highest concentrations of dissolved Fe(II) occur in afternoon rain during the period of maximum sunlight intensity followed by gradually decreasing concentrations eventually returning to early morning pre-light values. The experimental work presented here, along with the results of kinetics studies done by others, suggests that the primary process responsible for the decline in photochemically produced Fe(II) concentrations is oxidation by hydrogen peroxide. This reaction is first order with respect to both the concentrations of Fe(II) and H_2O_2 . The second-order rate constant determined for six different authentic rain samples varied over an order of magnitude and was always less than or equal to the rate constant determined for this reaction in simple acidic solutions. Oxidation of photochemically produced ferrous iron by other oxidants including molecular oxygen, ozone, hydroxyl radical, hydroperoxyl/superoxide radical, and hexavalent chromium were found to be insignificant under the conditions present in rainwater. This study shows that Fe(II) occurs as at least two different chemical species in rain; photochemically produced Fe(II) that is oxidized over time periods of hours, and a background Fe(II) that is protected against oxidation, perhaps by organic complexation, and is stable against oxidation for days. Because the rate of oxidation of photochemically produced Fe(II) does not increase with increasing rainwater pH, the speciation of this more labile form of Fe(II) is also not controlled by simple hydrolysis reactions.

Introduction

Iron is one of the most abundant trace elements in atmospheric waters. It has been measured in fog, snow, cloudwater, and rain at several different locations (1–6). Iron is involved in many important redox reactions that occur in the troposphere such as the generation of hydrogen peroxide in cloudwater (7, 8) and fog (7, 9) and the interconversion of S(IV) to S(VI) in the troposphere (10–12). Iron also contributes to the oxidizing capacity of the troposphere by its reactivity with several free radicals including $\cdot\text{OH}$, $\cdot\text{HO}_2$, and $\cdot\text{O}_2^-$ (8, 13–15). Iron is also involved in the redox chemistry of several trace metals (16–18).

Despite the significance of Fe speciation in atmospheric waters, the precise mechanisms controlling that speciation are unclear. Earlier studies have demonstrated that iron

speciation undergoes a distinct diurnal variation in rainwater with a higher concentration of Fe(II) in rain received between noon and midnight (Table 1). The higher Fe(II)/Fe(III) ratio in afternoon rains indicates that Fe(II) is produced at the expense of Fe(III) during the course of the day (6). Recent laboratory studies have demonstrated that the increasing concentration of Fe(II) observed in field studies results from photochemical production of Fe(II) during the period of greatest sunlight intensity (19). Significant concentrations of Fe(II) (up to 144 nM) were produced upon irradiation of a wide variety of authentic rainwater samples (pH range from 3.73 to 5.47) with simulated sunlight (19). The magnitude of photoproduction of Fe(II) was dependent on initial Fe(II), Fe(III), and hydrogen ion concentrations of the rain (19).

One of the most important uncertainties remaining with respect to the redox chemistry of Fe in the troposphere is what mechanisms are responsible for the decrease in Fe(II) at night when the sunlight intensity diminishes. The most likely process responsible for the decrease in the ratio involves re-oxidation of the photochemically produced Fe(II) back to Fe(III). There are a variety of potentially important oxidants in rainwater that are in sufficiently high concentration and are stable enough to oxidize photochemically produced Fe(II) thereby causing the ratio of Fe(II)/Fe(III) to decline. These oxidants include Cr(VI), molecular oxygen, ozone, hydroxyl radicals, hydroperoxyl radical/superoxide radical, and hydrogen peroxide. The goal of this work is to compare rates of oxidation of Fe(II) by these rainwater oxidants using concentrations and pH values realistic for rainwater and to assess their relative importance as oxidants for Fe(II) in rain. This study therefore presents the first quantitative and comprehensive investigation of the oxidation of Fe(II) in authentic rain.

Materials and Methods

Reagents and Standards. All bottles and containers used for standards and samples were thoroughly cleaned before use employing trace metal clean protocols (20–22). Poretics polycarbonate filters used for filtration (0.4 μm) were first rinsed with deionized water (DI), placed in 6 M Optima HCl for at least 1 week, and thoroughly rinsed with DI water prior to use.

All reagents were Fisher Scientific reagent grade (Fairlawn, NJ) except for ferrozine, which was SigmaUltra (>99.9% pure) ferrozine (3-(2-pyridyl)-5,6-bis(4-phenylsulfonic acid)-1,2,4-triazine) obtained from Sigma Chemical Company (St. Louis, MO). All DI for standards and reagents was obtained from a Milli-Q/Milli-Q Ultra Plus (>18 $\text{M}\Omega\text{ cm}^{-1}$) water system (Millipore, Bedford, MA). Synthetic rainwater (SRW) for standard preparation (pH 4.5 H_2SO_4) was prepared daily by diluting 4 mL of 5 mM trace metal grade H_2SO_4 to 1 L with DI water. Nitric acid was omitted from the synthetic rain matrix to prevent oxidation from any generated NO_x .

All standards and samples for iron analysis were prepared and processed in a class 100 laminar flow clean bench to minimize contamination. An acidified secondary stock solution of 35.8 μM Fe was prepared gravimetrically each month from a dilution of a 0.0179 M iron standard (Fisher Scientific) and stored in the dark at 4 °C. Total iron standards were prepared gravimetrically daily from the secondary stock solution and diluted with pH 4.5 synthetic rain. An acidified Fe(II)(aq) primary stock solution (10 mM) was prepared by dissolving 0.4970 g of ferrous chloride tetrahydrate in 250.0 g of DI water followed by storage at 4 °C for up to 2 weeks. A Fe(II)(aq) secondary stock solution (10 μM) was prepared gravimetrically daily by diluting the primary stock solution.

* Corresponding author telephone: (910)962-3459; fax: (910)962-3013; e-mail: willeyj@uncw.edu.

TABLE 1. Time of Day of Fe(II) Maximum in Rainwater, Volume-Weighted Fe(II) Concentration at Maximum (in nM), Average Decrease in Fe(II) (in nM) during the 12 h after Maximum, and Average Rate of Oxidation over 12 h^a

max Fe(II), nM	$\Delta\text{Fe(II)}$, nM, 12 h	rate of oxidation, nM h ⁻¹	Fe(III), nM, at time of Fe(II) max	Fe _{TOT} , nM, at time of Fe(II) max	[H ₂ O ₂], μM , at time of Fe(II) max	time of Fe(II) max	study period	location	location	ref
48	24	2.0	42	558	25	noon–6 PM	summer 1997	Wilmington, NC	34.22° N 77.86° W	5
62	42	3.5	nd	191	8	noon–6 PM	summer 1999	South Island, New Zealand	45.85° S 170.50° E	4
118	92	7.7	171	465	24	noon–midnight	August 2000–2001	Wilmington, NC	34.22° N 77.86° W	this study +6
277	163	13.6	84	300	31	noon–midnight	August 1999	BATS	31.40° N 64.10° W	6

^a The concentration of Fe(III) at the time of the Fe(II) maximum is given in nM, along with the concentration of total Fe (nM) and hydrogen peroxide (μM) at this same time. Total Fe includes both dissolved and particulate iron. BATS = Bermuda Atlantic Time Series Station, collected from the R/V *Endeavor*. nd, none detected.

Working standards were prepared daily by dilutions of each secondary stock.

Sample Collection and Storage. Rain filtration, standard and sample preparation and reagent storage were all conducted using trace metal clean techniques. Rainwater samples were collected on an event basis using Aerochem Metrics (ACM) model 301 automatic sensing wet/dry precipitation collectors equipped with high-density polyethylene (HDPE) buckets. The collector used for Fe samples had a trace metal clean HDPE funnel placed in the wet deposition bucket. Tygon tubing with a fluoropolymer FEP (inert) liner connected the funnel to a trace metal clean 2 L Teflon bottle inside a closed HDPE bucket. After each event the Teflon bottle was replaced with a freshly washed bottle, and the funnel and tubing were thoroughly rinsed with DI water. The Teflon bottle containing the rain event was returned to the lab within 10 min of collection. DI water used in place of rainwater had undetectable Fe concentrations (<0.4 nM).

Analytical Methods. Fe(II) and Fe(III) were determined by a modification of the spectrophotometric ferrozine method (23). The 30 mL aliquots of rainwater were filtered through a precleaned 0.4 μm polycarbonate filter. To determine total dissolved Fe concentrations, 700 μL of 1.4 M hydroxylamine hydrochloride was added to a filtered sample and set aside for at least 1 h to ensure complete reduction of Fe(III)(aq) to Fe(II)(aq). Ferrozine (700 μL , 10 mM), a reagent that reacts with Fe(II)(aq) to form a colored complex, was added and thoroughly mixed with the sample followed by addition of 1.8 mL of pH 5.5 ammonium acetate buffer to adjust pH. Fe(II)(aq) concentrations were determined by the same procedure except hydroxylamine hydrochloride was not added to the filtered samples. Fe(III)(aq) was calculated from the difference between total dissolved Fe and Fe(II)(aq). Addition of the ferrozine reagent to Fe(III) standards resulted in no measurable Fe(II) signal after 1 h storage, indicating the reagent did not react with Fe(III) or reduce any Fe(III) to Fe(II) within the time frame of these analyses.

Absorbances of the iron ferrozine complex were read at 562 nm using a 1-m (Ocean Optics) or 5-m (World Precision Instruments) liquid waveguide capillary cell (LWCC) attached to an Ocean Optics SD2000 spectrophotometer and an Analytical Instrument Systems model DT 1000 CE UV/Vis light source. All iron analyses were conducted in triplicate. Absorbance measurements were referenced to a nonabsorbing wavelength (700 nm) in order to compensate for turbidity and instrument drift. This absorbance reading was typically less than 0.01 absorbance units (24). The reagent blank absorbance using the 1 m cell was 0.01 for Fe(II) versus an absorbance reading of 0.13 for a 50 nM standard, and the reagent blank absorbance for Fe_{total} including the hydroxylamine hydrochloride reducing agent was 0.06 versus 0.18 for a 50 nM Fe_{total} standard. The relative standard deviation

for absorbance readings for a 20 nM standard measured 10 times on different days during a 1-month time period was <1% for both Fe(II) and Fe_{total} using the 5-m cell. A conservative detection limit based on three times the signal-to-noise ratio for both Fe(II) and Fe(III) is 2 nM for the 1-m cell or 0.4 nM for the 5-m cell.

Supporting Data. Rainwater pH was determined using a Fisher Accumet model 50 m equipped with a Ross model 81-02 electrode. Orion low ionic strength buffers (6.97/4.10) were used to calibrate the instrument, and 50 μL of pH ionic strength adjuster was added to each 5 mL sample to match the ionic strength of samples to that of buffers. Hydrogen peroxide analyses were done using a scopoletin-induced fluorescence decay technique (4, 25). Inorganic anions were determined by ion suppressed chromatography (26). Dissolved organic carbon (DOC) was analyzed using a Shimadzu TOC 5000 (27).

Fe(II) Oxidation Studies. Reactive Fe(II) was generated for oxidation experiments by two methods. In experiments with authentic rain, Fe(II) was generated photochemically, similar to what would occur in nature, using 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 the solar spectrum at earth's surface ($\lambda < 300 \text{ nm}$) (19). The spectral quality and intensity of the solar simulator is very similar to that of midsummer, noontime solar irradiance for 34 °N latitude. Immediately after measurement of initial iron concentrations, filtered rainwater samples were apportioned into cylindrical quartz cells or Teflon bottles and irradiated for 2 h at 25 °C. A constant-flow temperature bath surrounded light-exposed cells to maintain the temperature at 25 °C for the 2 h irradiation, after which samples were stored in the dark at room temperature. In experiments using synthetic rain (pH 4.5 H₂SO₄) in place of authentic rain, Fe(II) was added from a 10 μM solution of FeCl₂ to provide Fe(II) for subsequent oxidation studies. The loss in photochemically produced Fe(II) in authentic rain and added Fe(II) in synthetic rain was then monitored with time, and various oxidants were evaluated including Cr(VI)(aq), O₂(aq), O₃(aq), •OH(aq), •HO₂/•O₂⁻(aq), and H₂O₂(aq).

Results and Discussion

The concentration of dissolved Fe(II) shows a marked diurnal variation in rain with higher concentrations in the afternoons during periods of peak sunlight intensity (3, 4, 6). This pattern has been observed in rain collected in Wilmington, NC; on the South Island of New Zealand; and at the Bermuda Atlantic Time Series Station (BATS). The maximum Fe(II) concentration and the oxidative loss in Fe(II) ($\Delta\text{Fe(II)}$) 12 h after the maximum at these locations are reported in Table 1. All three

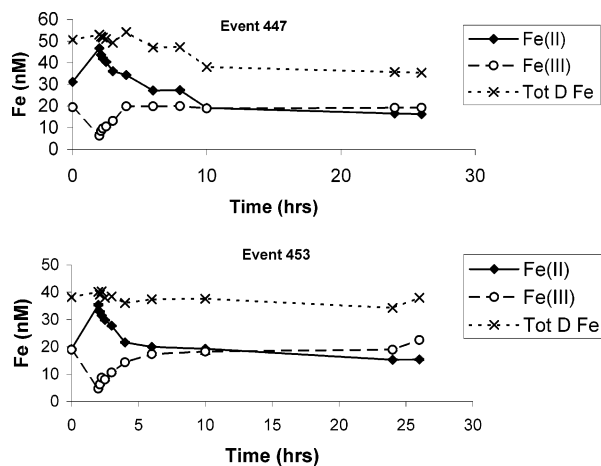


FIGURE 1. Concentrations of Fe(II), Fe(III), and total dissolved Fe in two authentic rainwater samples initially, after 2 h irradiation in a solar simulator (25 °C), and during 22 h of dark storage at room temperature following irradiation. Error bars represent one standard deviation based on triplicate analyses; error bars are approximately the same size as the symbols.

locations showed diurnal variation in the concentration of Fe(II) and in the ratio of the concentrations of Fe(II) to Fe(III) (Table 1). The fraction of photochemically active iron varied from 10% to approximately half the total iron in these studies. The magnitude of both the maximum and the loss in Fe(II) in rain from Wilmington, NC, and New Zealand were very similar, as were hydrogen peroxide concentrations. Fe(III) concentrations in New Zealand rain were completely depleted by photochemical reduction to Fe(II). The same diurnal pattern was observed in rainwater at BATS; however, there was a much larger maximum and greater loss in Fe(II) upon oxidation because of the much higher concentrations of Fe(II) and hydrogen peroxide (Table 1). The diurnal variation of Fe(II) observed in the field for Wilmington rainwater during these studies is very similar to the pattern observed in the controlled laboratory studies presented here.

The mechanism(s) responsible for the increase in the Fe(II)/Fe(III) ratio observed during these diurnal studies involves photoreduction of organic Fe(III) complexes with concomitant increases in dissolved Fe(II) (19). Rainwater photolyzed during this study also demonstrate that Fe(II) is photochemically produced upon exposure to simulated sunlight while Fe(III) decreases (Figure 1). The concentration

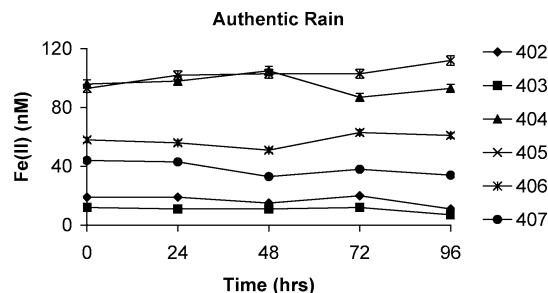


FIGURE 2. Concentration of Fe(II) in six different authentic rain samples as a function of time in hours of storage in the dark at room temperature. These rain samples were collected between December 20, 2002, and February 7, 2003 (Table 2), a time when sunlight intensity is very low; hence, any photochemically produced Fe(II) would have been a small part of the total Fe(II), so no concentration changes were observed during the first day of storage. Error bars represent 1 SD based on triplicate analyses; error bars are usually smaller than the symbols.

of Fe(II) increased an average of 26 nM (or 2.5 \times) in the six authentic rain samples (Samples 432–461 in Table 2) exposed to simulated sunlight for 2 h, with a concomitant decrease in Fe(III). The range of oxidation rate of photochemically produced Fe(II) in these six samples (0.9–7 nM h⁻¹) was similar to that observed for authentic rain over similar time periods (Table 1), which indicates that the Fe(II) produced in the solar simulator is the same species as that produced by sunlight in actual rain samples.

It is interesting to note that only recently photochemically produced Fe(II) oxidized within hours. The concentrations of Fe(II) did not approach zero in the dark, rather they returned to levels prior to irradiation. This indicates there are two forms of Fe(II) in rainwater, a labile Fe(II) produced photochemically that oxidizes within hours (Figure 1) and a much more stable form of Fe(II) that is stable for days (Figures 1 and 2). The rain samples presented in Figure 2 (Samples 402–407 in Table 2) were collected between December 20, 2002, and February 7, 2003 (Table 2), a time when sunlight intensity is at a minimum, and hence any photochemically produced Fe(II) would have been a small part of the total Fe(II), so no concentration changes were observed during the first day of storage. Both forms of Fe(II) in authentic rain oxidize much more slowly than inorganic Fe(II) in synthetic rain (Figure 3), suggesting that Fe(II) in authentic rain has a more complex speciation than simple inorganic Fe(II).

TABLE 2. Supporting Data for Rain Samples Used in Experiments^a

event	date	amount mm	Fe(II), nM	Fe(III), nM	pH init	pH exp i	H ₂ O ₂ init, μM	H ₂ O ₂ exp i, μM	H ₂ O ₂ exp f, μM	DOC, μM	Cl ⁻ , μM	NO ₃ ⁻ , μM	SO ₄ ²⁻ , μM	NH ₄ ⁺ , μM
343	5/11/2002	30	8	23	4.68	4.67	na	10	1	144	10	16	19	40
402	12/20/2002	15	19	1	4.84	4.84	11	11	na	64	127	14	22	4
403	1/1/2003	31	12	nd	5.94	5.94	5	5	na	17	56	5	8	3
404	1/22/2003	8	96	nd	4.14	4.14	4	4	na	267	23	54	29	18
405	1/31/2003	8	93	25	4.29	4.29	na	na	na	114	31	50	37	23
406	2/4/2003	7	58	32	4.61	4.61	22	22	na	267	43	31	36	15
407	2/7/2003	24	44	10	5.16	5.16	5	5	na	41	37	9	8	4
432	6/1/2002	46	32	62	4.26	5.63	22	20	20	469	12	18	28	62
435	6/17/2003	3	58	59	4.06	4.05	36	3	3	164	105	68	38	152
437	6/19/2003	12	16	na	4.43	4.40	33	7	na	64	21	15	13	2
447	7/24/2003	14	31	47	4.66	4.45	21	12	11	38	10	9	5	1
453	8/9/2003	8	19	19	4.75	4.42	2	13	11	42	40	10	9	3
461	9/10/2003	17	1	5	5.11	4.86	5	13	13	112	30	4	7	2

^a The first rain sample was used in the methanol experiment. Events 402–407 were used in the stability study. Events 432–461 were used in solar simulator experiments and in rate constant determinations. All rain samples were collected at the Wilmington, NC, site. init values indicate values at the time of collection. exp values indicate concentrations at the beginning (i) and end (f) of experiments. DOC, dissolved organic carbon. na, not analyzed. nd, none detected.

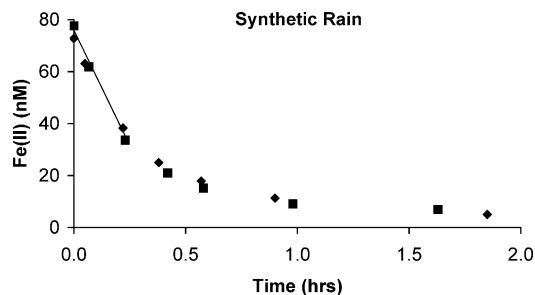


FIGURE 3. Concentration of Fe(II) (nM) in synthetic rain initially containing 80 nM Fe(II) and 10 μ M hydrogen peroxide at pH 4.5 as a function of time in hours. The experiment was performed in duplicate; samples were kept in the dark and at room temperature. The solid line was used to calculate the initial reaction rate. Error bars represent 1 SD based on triplicate analyses; error bars are usually smaller than the symbols.

One of the most important questions remaining with respect to the redox chemistry of Fe in these samples is what is the dominant mechanism responsible for the oxidation of photochemically produced Fe(II). There are a variety of potentially important oxidants present in rainwater that are in sufficiently high concentration and are stable enough to oxidize photochemically produced Fe(II). Potential oxidants include Cr(VI), molecular oxygen, ozone, hydroxyl radicals, hydroperoxyl/superoxide radicals, and hydrogen peroxide. Calculations and experiments were conducted to assess the relative importance of each of these oxidants under environmentally realistic conditions and concentrations found in rainwater.

Cr(VI). Cr(VI) is an effective oxidant of Fe(II) in certain natural waters including fresh, estuarine, and marine systems (28, 29). An earlier kinetic model developed for chromium speciation in cloudwaters and aerosols (30) indicated that Fe(II) may be important in the reduction of Cr(VI) in rainwater, where Cr(VI) concentrations can be up to 4 nM (31). The model predicted that the reaction of Fe(II) with Cr(VI) would occur over time periods of hours to days in cloud droplets, which is an appropriate time frame for the loss of rainwater Fe(II) observed in field studies (Table 1) and in Figure 1. Other reductants considered in this model included As(III), V(II), V(IV), and HSO_3^- , and Mn(III) and Mn(IV) were included as potential oxidants for Cr(III).

To determine if this mechanism is important in our rainwater samples, iron (II) was added (40 nM) to solutions containing Cr(VI) at a realistic concentration (2 nM) over a range of environmentally relevant rainwater pH values (3.5–5.5) (31). The Fe(II) concentration with and without Cr(VI) present was measured initially and as a function of time (Figure 4). The decrease of Fe(II) with time is the same in the presence and absence of Cr(VI) over the entire pH range, indicating that Cr(VI) is not an effective oxidant of Fe(II) at these concentrations and pH values.

A second experiment was conducted at greatly elevated concentrations and Cr(VI)/Fe(II) ratio (approximately 100 nM Fe(II) and 40 nM Cr(VI)) at pH 4.5 in order to determine if reactant concentration and ratio influenced the oxidation of ferrous iron by hexavalent chromium (Figure 4). Even at this higher concentration of Cr(VI) there was no effect on the oxidation of Fe(II). Therefore oxidation of Fe(II) by Cr(VI) is too slow to be environmentally relevant in rainwater. This process may, however, be important in other atmospheric samples with different pH values such as acidic aerosols (32).

Calculations using rate constants in an earlier kinetic model (30) indicate the maximum rate of oxidation for Fe(II) by Cr(VI) under the conditions used in these experiments is approximately 0.5 nM d⁻¹, too small of a change to be observed in our experiments. Fe(II) is therefore not the

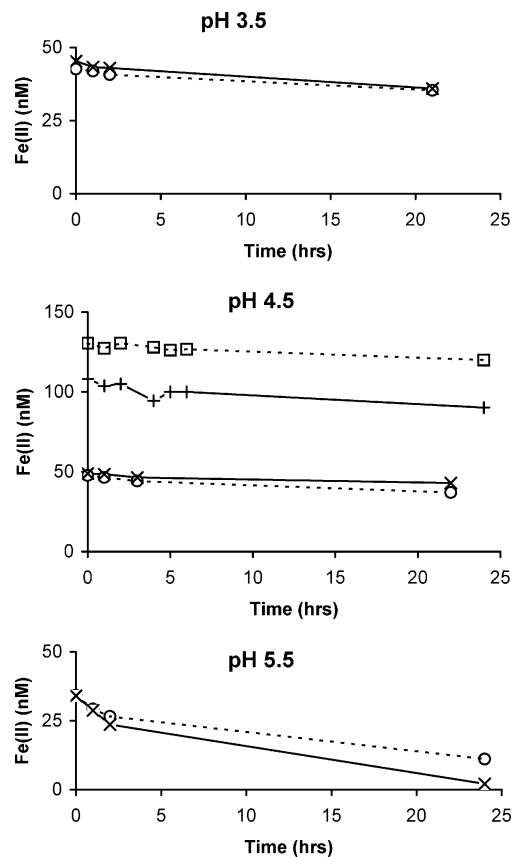


FIGURE 4. Concentration of Fe(II) (nM) in synthetic rain containing 40 nM Fe(II) alone (○) and with 2 nM Cr(VI) (×) as a function of time at pH 3.5, 4.5, and 5.5. Concentration of Fe(II) (nM) in synthetic rain containing 100 nM Fe(II) alone (□) or with 40 nM Cr(VI) (+) as a function of time at pH 4.5. Solid lines are synthetic rain with both Fe(II) and Cr(VI) added, and dotted lines are synthetic rain with Fe(II) alone.

predominant reductant for Cr(VI) in rain; V(II) and HSO_3^- are probably more important in carrying out this reaction; and Cr(VI) is not an important oxidant for Fe(II) in rainwater. This model predicts that, under the humid conditions prevailing in eastern North Carolina, chromium should exist predominantly as Cr(III) in rain; however, a recent study reported an average concentration of 1.2 nM for Cr(VI) and 0.8 nM for Cr(III) (31). Clearly more research is needed in the area of chromium speciation in rain.

Molecular Oxygen. Molecular oxygen is an important oxidant for Fe(II) in lake water (33). Dissolved oxygen is also present in fairly high concentrations in rainwater (approximately 0.25 mM); therefore, oxygen was investigated as a potential oxidant of Fe(II) in rain. On the basis of earlier work (34, 35), the rate of oxidation of Fe(II) by molecular oxygen is expressed by

$$-d[\text{Fe(II)}]/dt = k[\text{Fe(II)}][\text{P}_{\text{O}_2}][\text{OH}^-]^2 \text{ where } k = 8 \times 10^{13} \text{ min}^{-1} \text{ atm}^{-1} \text{ M}^{-2} \quad (1)$$

For rainwater with 100 nM Fe(II) at pH 4.5 in equilibrium with air, the rate of oxidation would be on the order of 0.2 nM Fe(II) per day. This is much too slow to be observed in our experiments (Figure 1), hence molecular oxygen is not a significant oxidant of ferrous iron in rainwater.

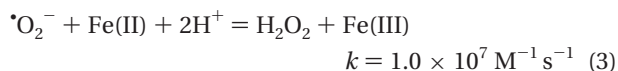
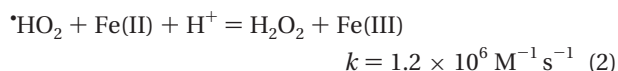
Ozone. Ferrous ions can be effectively oxidized by ozone in acidic (pH 0–2) solutions at highly elevated concentrations of iron and O_3 (36). The importance of ozone in the oxidation of Fe(II) under environmentally relevant conditions typical of rainwater depends on several factors. The Henry's law

constant for ozone is $9.4 \times 10^{-3} \text{ M atm}^{-1}$ at 25°C . Using the 8 h gas phase maximum average summer concentration of 40 ppbv (40 natm) for this region of North Carolina (North Carolina Department Environment and Natural Resources, 2003 data), the aqueous phase concentration would be approximately 0.4 nM, with occasional higher values to 0.8 nM and lower concentrations at night and during the winter. This concentration is substantially lower than the average concentration of Fe(II) in rain of 40 nM (5). Because of the significantly lower ozone concentrations relative to ferrous iron, oxidation of Fe(II) by O_3 would be limited by the rate of replenishment of ozone into rain from the gas phase, which is a slow heterogeneous process; therefore, ozone is unlikely to be an important oxidant of ferrous iron in rainwater.

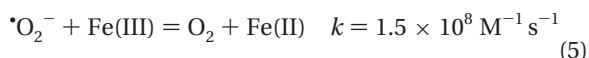
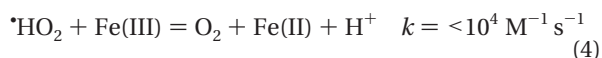
Hydroxyl Radical. Hydroxyl radical ($\cdot\text{OH}$) is a powerful oxidant produced in significant quantities upon relatively short term exposure of surface waters to ambient sunlight (37, 38). It is difficult to assess the importance of hydroxyl radical as an oxidant for Fe(II) in rain by calculation because the concentration of this radical is highly variable in natural waters, and rainwater contains many components that compete with Fe(II) for the hydroxyl radical including DOC, which is not well-characterized in rain. Therefore, to assess the potential importance of hydroxyl radicals in the oxidation of photochemically produced Fe(II) in rain, an experiment was conducted in the presence and absence of photochemically produced hydroxyl radicals. Hydroxyl radicals were removed from one sample by addition of 40 mM methanol, which is an effective scavenger of photochemically produced hydroxyl radicals (39). An authentic rain sample (event 343 in Table 2) was irradiated in the light for 2 h to generate Fe(II) followed by 22 h dark incubation at pH 4.5 in the presence of $10 \mu\text{M H}_2\text{O}_2$ (a typical hydrogen peroxide value for rain in this area).

The ferrous iron concentration in the presence and absence of methanol and hence also hydroxyl radicals decreased the same amount (23 nM) after 22 h dark incubation (Figure 5). These results suggest that hydroxyl radicals are not a significant oxidant of Fe(II) in rainwater. This may result from competition for the hydroxyl radical by other rainwater components, for example, chloride which occurs in tens of micromolar concentrations, or dissolved organic material in rainwater, which is often higher than $100 \mu\text{M C}$ and probably contains some methanol.

Superoxide/Hydroperoxyl Radicals. Hydroperoxyl radical ($\cdot\text{HO}_2$) and the deprotonated superoxide radical ($\cdot\text{O}_2^-$) should occur in rain in approximately equal concentrations because the pK_a of the hydroperoxyl radical of 4.8 is near the average pH of rainwater at this location. Both forms of this radical can act as effective oxidants for Fe(II) as demonstrated in eqs 2 and 3 (35, 40):



These radicals are also effective reducing agents of Fe(III) as shown below (35, 40):



Of the four possible reactions, the rate constant for reduction of Fe(III) by superoxide (eq 5) is the largest number by more than an order of magnitude. Therefore, in rainwater con-

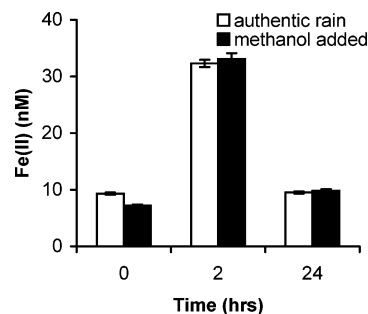


FIGURE 5. Concentration of Fe(II) (nM) in authentic rain (event 343 in Table 2) initially, after 2 h irradiation in a solar simulator (25°C), and after 22 h of dark storage at room temperature in rain samples with and without 40 mM methanol, which scavenges hydroxyl radicals. Each sample contained $10 \mu\text{M}$ hydrogen peroxide. Error bars represent 1 SD based on triplicate analyses.

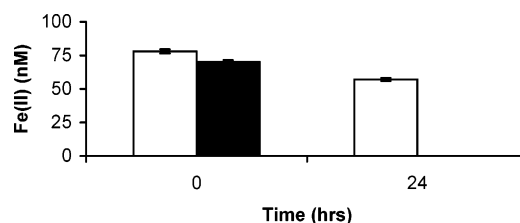


FIGURE 6. Concentration of Fe(II) in pH 4.5 synthetic rain containing 80 nM Fe(II) with ambient hydrogen peroxide ($0.5 \mu\text{M}$, white bars) or with $10 \mu\text{M}$ hydrogen peroxide (black bars), initially and after 24 h of room-temperature dark storage. Fe(II) was undetectable in the synthetic rain with $10 \mu\text{M}$ hydrogen peroxide after 24 h. Error bars represent 1 SD based on triplicate analyses.

taining approximately equal concentrations of Fe(II) and Fe(III) (3, 5), reduction of Fe(III) by superoxide should be the predominant reaction rather than oxidation of Fe(II).

An additional consideration in rainwater is competition for superoxide and hydroperoxyl radicals by other rainwater components. For example, even though Cu concentrations are smaller than iron concentrations in rain (dissolved Cu concentrations are up to 4 nM with approximately 25% as Cu(I) (41)), the rate constants for reactions between Cu(I), Cu(II), superoxide, and hydroperoxyl radicals are 2 orders of magnitude greater than the comparable rate constants with iron (35) indicating that most of superoxide/hydroperoxyl radicals will react with copper rather than iron.

Hydrogen Peroxide. Earlier studies have suggested that hydrogen peroxide is a very effective oxidant of ferrous iron in atmospheric waters including aerosols and fog (42). To determine if hydrogen peroxide is also an effective oxidant in rainwater, a synthetic rain sample with 80 nM Fe(II) was prepared with $10 \mu\text{M}$ added hydrogen peroxide, a typical concentration in rainwater in this area, and without added hydrogen peroxide (ambient background approximately $0.5 \mu\text{M}$). The concentration of Fe(II) in each sample was measured initially and after 24 h dark storage. Fe(II) in the synthetic sample without added hydrogen peroxide decreased 22 nM (Figure 6). The synthetic rain sample with $10 \mu\text{M}$ hydrogen peroxide added had undetectable Fe(II) after the 24 h incubation. The oxidation of the synthetic sample with added peroxide occurred so rapidly that 10 nM Fe(II) oxidized before initial measurements could be conducted. The relatively small loss in the sample with no added peroxide is the result of oxidation by the ambient peroxide present in the deionized water used to prepare samples. This background H_2O_2 signal is extremely difficult to reduce further without introducing iron contamination (25, 43). The results presented in Figure 6 suggest that H_2O_2 is the dominant oxidant for Fe(II) in synthetic rain (pH 4.5 H_2SO_4).

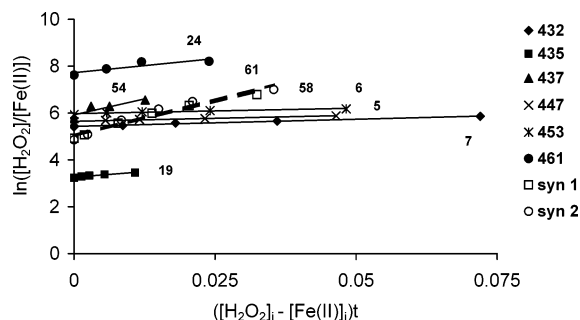
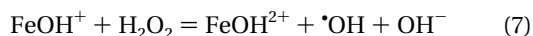
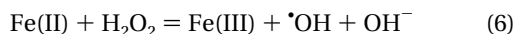


FIGURE 7. Plot of $\ln([H_2O_2]/[Fe(II)])$ vs $([H_2O_2]_{\text{initial}} - [Fe(II)]_{\text{initial}})/t$ in accordance with eq 8 for six authentic rain samples (Table 2) and two synthetic rain samples. Brackets indicate concentrations in M, and t is time in s. The second-order rate constants were determined from the slope of the linear regression, and these are given in $M^{-1} s^{-1}$ for each of the six authentic rain samples (solid symbols and solid lines) and for two synthetic rain samples (open symbols and dashed lines).

The most likely mechanisms of Fe(II) oxidation by hydrogen peroxide in atmospheric waters proceed as follows (42, 44):



These reactions follow second-order kinetics with the rate depending on both the concentration of Fe(II) and hydrogen peroxide. The second-order rate constant for reaction 6 has been measured many times in acidic solutions, and reported values range from 50 to 83 $M^{-1} s^{-1}$ (44–47). Our experimentally determined values for replicate determinations in synthetic rain are 58 and 61 $M^{-1} s^{-1}$ (Figure 7). The rate constant for reaction 7 was determined to be $3.8 \times 10^{+5} M^{-1} s^{-1}$ in pure water (44). The relative importance of these two reactions is very dependent upon pH because the speciation of Fe(II) is so pH dependent. At pH 4, oxidation of Fe(II) by reaction 7 is insignificant relative to oxidation via reaction 6, at pH 5 the oxidation rate from reaction 7 is approximately 10% of the rate for reaction 6, and at pH 6 the oxidation rate via reaction 7 is approximately twice that for reaction 6 under conditions used in these experiments. An initial Fe(II) oxidation rate of 173 $nM h^{-1}$ in pH 4.5 synthetic rain is calculated using eq 6 with an average rate constant of 60 $M^{-1} s^{-1}$ and with initial hydrogen peroxide and Fe(II) concentrations of 10 μM and 80 nM, respectively. The average measured loss of Fe(II) in two separate synthetic rain samples containing these initial iron and hydrogen peroxide concentrations was 175 $nM h^{-1}$ (Figure 3). The remarkably close agreement between the experimentally determined iron oxidation rate in Figure 3 with the predicted rate suggests that the reaction represented in eq 6 is important in the oxidation of Fe(II) in synthetic rainwater at pH 4.5.

The oxidative loss of Fe(II) was also examined in authentic rain samples and compared to oxidation rates in synthetic rain. The oxidation of photochemically produced Fe(II) observed in authentic rain (Figure 1) obeyed second-order kinetics where the oxidation rate depended on both the concentrations of Fe(II) and hydrogen peroxide (Figure 7). The following second-order integrated rate law equation was used to determine rate constants (k) for the oxidation of photochemically generated Fe(II) in authentic rain samples and in synthetic rain with added Fe(II):

$$\ln([H_2O_2]/[Fe(II)]) = \frac{([H_2O_2]_0 - [Fe(II)]_0)kt + \ln([H_2O_2]_0/[Fe(II)]_0)}{([H_2O_2]_0 - [Fe(II)]_0)} \quad (8)$$

The first several data points (between 4 and 6) in the linear

range were used in the determination of rate constants for each of the six authentic rain samples and two synthetic rain samples in Figure 7 ($p \leq 0.02$ for each line in Figure 7). In each case, the y-intercept agreed with the theoretical value of $\ln([H_2O_2]_0/[Fe(II)]_0)$ predicted from eq 8 based on initial concentrations of Fe(II) and hydrogen peroxide to within ± 0.2 . After these initial time points, there was little net reaction, and the value for the rate constants became $\leq 1 M^{-1} s^{-1}$.

The rate constants determined for the oxidation of photochemically produced Fe(II) in authentic rain by hydrogen peroxide ($5\text{--}54 M^{-1} s^{-1}$) via eq 8 were always less than the rate constant determined in synthetic rain. The value of the rate constant was not greater in high pH rain samples (range of 4.06–5.63) as predicted by formation of $FeOH^+$ at higher pH values (Table 2 and Figure 7), which suggests that the oxidation rate is not controlled by simple hydrolysis reactions of photochemically produced Fe(II) with water. This implies that some component(s) of authentic rain complexes iron(II) causing its oxidation rate to slow relative to that in synthetic rain. Previous research has shown that non-photochemically produced Fe(II) in rain is almost entirely complexed by stable organic ligands (6). These complexed iron species resist oxidation even when the rain is added to seawater at pH 8 (5, 6). Because rate constants for the oxidation of Fe(II) in authentic rain are always less than in simple inorganic solutions (Figure 7), the photochemically produced iron must exist as a complex, probably organic, once the irradiation is removed. This somewhat labile complex slows the oxidation of Fe(II) by hydrogen peroxide relative to synthetic rain. Previous studies in lake water and seawater have shown that organic complexation can either enhance or inhibit oxidation of Fe(II) depending upon the nature of the complexing ligand (48–51).

It is possible organic peroxides may also oxidize Fe(II) in our authentic rainwater samples. Earlier studies have shown that the reaction rate constants for the oxidation of Fe(II) by methylhydroperoxide and ethylhydroperoxide are similar to the rate constants for oxidation by hydrogen peroxide in liquid aerosols (52). Small amounts of organic peroxides could be present in these rain samples (53, 54) implying that organic peroxides may contribute to the oxidation of Fe(II) in authentic rain samples.

It is clear from this study that Fe(II) occurs in at least two different chemical species in rain; photochemically produced Fe(II) that is oxidized over time periods of hours (Figure 1 and Table 1), and a background Fe(II) that is protected against oxidation, most likely by organic complexation, and is stable for days (Figure 2). The rate of oxidation of Fe(II) is greatest for inorganic Fe(II) added to synthetic rain, slower and more variable for photochemically produced Fe(II) in authentic rain, and much slower for the background or ambient Fe(II) in authentic rain that was not produced photochemically, at least within the few hours prior to the rain event. This slower oxidation rate most likely results from complexation by rainwater organic material, which still remains poorly characterized and is currently being investigated in our laboratory.

Acknowledgments

This work was supported by NSF Grants ATM-0096878 and ATM-0342420. B. Jason Smith assisted with several experiments. The Marine and Atmospheric Chemistry Research Laboratory group at UNC Wilmington assisted with sampling and analyses.

Literature Cited

- (1) Zhuang, G.; Yi, Z.; Wallace, G. T. Iron(II) in rainwater, snow, and surface seawater from a coastal environment. *Mar. Chem.* **1995**, *50*, 41–50.
- (2) Siefert, R. L.; Johansen, A. M.; Hoffmann, M. R. Measurements of trace metal (Fe, Cu, Mn, Cr) oxidation states in fogs and stratus clouds. *J. Air Waste Manage. Assoc.* **1998**, *48*, 128–143.

- (3) Willey, J. D.; Kieber, R. J.; Williams, K. H.; Crozier, J. S.; Skrabal, S. A.; Avery, G. B. Temporal variability of iron speciation in coastal rainwater. *J. Atmos. Chem.* **2000**, *37*, 185–205.
- (4) Kieber, R. J.; Peake, B.; Willey, J. D.; Jacobs, B. Iron speciation and hydrogen peroxide concentrations in New Zealand rainwater. *Atmos. Environ.* **2001**, *35*, 6041–6048.
- (5) Kieber, R. J.; Williams, K. H.; Willey, J. D.; Skrabal, S. A.; Avery, G. B. Iron speciation in coastal rainwater: concentration and deposition to seawater. *Mar. Chem.* **2001**, *73*, 83–95.
- (6) Kieber, R. J.; Willey, J. D.; Avery, G. B. Temporal variability of rainwater iron speciation at the Bermuda Atlantic Time Series Station. *J. Geophys. Res.* **2003**, *108*, 1–7.
- (7) Zuo, Y.; Hoigne, J. Formation of hydrogen peroxide and depletion of oxalic acid in atmospheric waters by photolysis of iron(III)–oxalato complexes. *Environ. Sci. Technol.* **1992**, *26*, 1014–1022.
- (8) Sedlak, D. L.; Hoigne, J. The role of copper and oxalate in the redox cycling of iron in atmospheric waters. *Atmos. Environ.* **1993**, *27A*, 2173–2185.
- (9) Zuo, Y.; Deng, D. Evidence for the production of hydrogen peroxide in rainwater by lightning during thunderstorms. *Geochim. Cosmochim. Acta* **1999**, *63*, 3451–3455.
- (10) Graedel, T. E.; Weschler, C. J.; Mandich, M. L. Influence of transition metal complexes on atmospheric droplet acidity. *Nature* **1985**, *317*, 240–242.
- (11) Jacob, D. J.; Waldman, J. M.; Munger, J. W.; Hoffmann, M. R. The H_2SO_4 – HNO_3 – NH_3 system at high humidities and in fogs. 2. Comparison of field data with thermodynamic calculations. *J. Geophys. Res.* **1986**, *91*, 1089–1096.
- (12) Breytenbach, L. W.; Vanparen, W.; Pienaar, J. J.; van Eldik, R. The role of organic acids and metal ions on the kinetics of the oxidation of S(IV) by hydrogen peroxide. *Atmos. Environ.* **1994**, *28*, 2451–2459.
- (13) Faust, B.; Hoigne, J. Photolysis of Fe(III)–hydroxy complexes as sources of OH radicals in clouds, fog and rain. *Atmos. Environ.* **1990**, *24A*, 79–89.
- (14) Faust, B. C.; Zepp, R. G. Photochemistry of aqueous iron(III)–polycarboxylate complexes: roles in the chemistry of atmospheric and surface waters. *Environ. Sci. Technol.* **1993**, *27*, 2517–2522.
- (15) Siefert, R. L.; Hoffmann, M. R. Determination of photochemically available iron in ambient aerosols. *J. Geophys. Res.* **1996**, *101*, 14441–14449.
- (16) Faust, B.; Zepp, R. G. Photochemistry of aqueous iron(III)–polycarboxylate complexes: roles in the chemistry of atmospheric and surface waters. *Environ. Sci. Technol.* **1993**, *27*, 2517–2522.
- (17) Erel, Y.; Pehkonen, S. O.; Hoffman, M. R. Redox chemistry of iron in fog and stratus clouds. *J. Geophys. Res.* **1993**, *98*, 18,418–18,434.
- (18) Zuo, Y. Kinetics of photochemical/chemical cycling of iron coupled with organic substances in cloud and fog droplets. *Geochim. Cosmochim. Acta* **1995**, *59*, 3123–3130.
- (19) Kieber, R. J.; Hardison, D. R.; Whitehead, R. F.; Willey, J. D. Photochemical production of Fe(II) in rainwater. *Environ. Sci. Technol.* **2003**, *37*, 4610–4616.
- (20) Bruland, K. W.; Franks, R. P.; Knauer, G. A.; Martin, J. H. Sampling and analytical methods for the determination of copper, cadmium, zinc, and nickel at the nanogram per liter level in seawater. *Anal. Chim. Acta* **1979**, *105*, 223–245.
- (21) Bruland, K. W. Oceanographic distributions of cadmium, zinc, nickel and copper in the North Pacific. *Earth Planet. Sci. Lett.* **1980**, *47*, 176–198.
- (22) Tramontano, J. M.; Scudlark, J. R.; Church, T. M. A method for the collection, handling and analysis of trace metals in precipitation. *Environ. Sci. Technol.* **1987**, *21*, 749–753.
- (23) Stookey, L. C. Ferrozine—a new spectrophotometric reagent for iron. *Anal. Chem.* **1970**, *42*, 779–781.
- (24) Waterbury, R. D.; Wensheng, Y.; Byrne, R. H. Long pathlength absorbance spectroscopy: trace analysis of Fe(II) using a 4.5 meter liquid core waveguide. *Anal. Chim. Acta* **1997**, *357*, 99–102.
- (25) Kieber, R. J.; Helz, R. G. Two method verification of hydrogen peroxide determinations in natural waters. *Anal. Chem.* **1986**, *58*, 2312–2315.
- (26) Fitchett, A. W. *Analysis of Rain by Ion Chromatography*; ASTM Special Technique Publication: ASTM: Philadelphia, 1983.
- (27) Willey, J. D.; Kieber, R. J.; Eyman, M. S.; Avery, G. B. Rainwater dissolved organic carbon: concentrations and global flux. *Global Biogeochem. Cycles* **2000**, *14*, 139–148.
- (28) Kieber, R. J.; Helz, G. R. Indirect photoreduction of aqueous chromium(VI). *Environ. Sci. Technol.* **1992**, *26*, 307–312.
- (29) Kaczynski, S. E.; Kieber, R. J. Aqueous trivalent chromium photoproduction in natural waters. *Environ. Sci. Technol.* **1993**, *27*, 1572–1576.
- (30) Seigneur, C.; Constantinou, E. Chemical kinetic mechanism for atmospheric chromium. *Environ. Sci. Technol.* **1995**, *29*, 222–231.
- (31) Kieber, R. J.; Willey, J. D.; Zvalaren, S. D. Chromium speciation in rainwater: temporal variability and atmospheric deposition. *Environ. Sci. Technol.* **2002**, *36*, 5321–5327.
- (32) Pettine, M.; D'Ottone, L.; Campanella, L.; Millero, F. J.; Passino, R. The reduction of chromium(VI) by iron(II) in aqueous solutions. *Geochim. Cosmochim. Acta* **1998**, *62*, 1509–1519.
- (33) Emmenegger, L.; King, D. W.; Sigg, L.; Sulzberger, B. Oxidation kinetics of Fe(II) in a Eutrophic Swiss Lake. *Environ. Sci. Technol.* **1998**, *32*, 2990–2996.
- (34) Singer, P. C.; Stumm, W. The solubility of ferrous iron in carbonate bearing waters. *J. Am. Water Works Assoc.* **1970**, *62*, 198–202.
- (35) Faust, B. In *Aquatic and Surface Photochemistry*; Helz, G. R., Zepp, R. G., Crosby, D. G., Eds.; Lewis Publishers/CRC Press: Boca Raton, FL, 1994; pp 3–39.
- (36) Logager, T.; Holcman, J.; Sehested, K.; Pedersen, T. Oxidation of ferrous ions by ozone in acidic solutions. *Inorg. Chem.* **1992**, *31*, 3523–3529.
- (37) Mopper, K.; Zhuo, X. Hydroxyl radical photoproduction in the sea and its potential impact on marine processes. *Science* **1990**, *250*, 661–664.
- (38) King, D. W.; Aldrich, R. A.; Charnecki, S. E. Photochemical redox cycling of iron in NaCl solutions. *Mar. Chem.* **1993**, *44*, 105–120.
- (39) Zhu, X. R.; Mopper, K. Determination of photochemically produced hydroxyl radicals in seawater and freshwater. *Mar. Chem.* **1990**, *30*, 71–88.
- (40) Bielski, B. H.; Cabelli, D. E.; Arudi, R. L. Reactivity of HO_2/O_2^- radicals in aqueous solution. *J. Phys. Ref. Data* **1985**, *14*, 1041.
- (41) Kieber, R. J.; Skrabal, S. A.; Smith, C.; Willey, J. D. Redox speciation of copper in rainwater: temporal variability and atmospheric deposition. *Environ. Sci. Technol.* **2004**, *38*, 3587–3594.
- (42) Seifert, R. L.; Johansen, A. M.; Hoffmann, M. R.; Pehkonen, S. O. Measurements of trace metals (Fe, Cu, Mn, Cr) oxidation states in fog and stratus clouds. *J. Air Waste Manage. Assoc.* **1998**, *48*, 128–143.
- (43) Cooper, W. J.; Moegling, J. K.; Kieber, R. J.; Kiddle, J. J. A chemiluminescence method for the analysis of H_2O_2 in natural waters. *Mar. Chem.* **2000**, *70*, 191–200.
- (44) King, D. W.; Farlow, R. Role of carbonate speciation on the oxidation of Fe(II) by H_2O_2 . *Mar. Chem.* **2000**, *70*, 201–209.
- (45) Wells, C. F.; Salam, M. A. Complex formation between Fe(II) and inorganic anions. *Trans. Faraday Soc.* **1967**, *63*, 620–629.
- (46) Millero, F. J.; Sotolongo, S.; Izaguirre, M. The oxidation of Fe(II) with hydrogen peroxide in seawater. *Geochim. Cosmochim. Acta* **1989**, *53*, 1867–1873.
- (47) Christensen, H.; Sehested, K.; Logager, T. The reaction of hydrogen peroxide with Fe(II) ions at elevated temperatures. *Radiat. Phys. Chem.* **1993**, *41*, 575–578.
- (48) Theis, T. L.; Singer, P. C. Complexation of iron(II) by organic matter and its effect on iron(II) oxygenation. *Environ. Sci. Technol.* **1974**, *8*, 569–573.
- (49) Santana-Casiano, J. M.; Gonzalez-Davila, M.; Rodriguez, M. J.; Millero, F. The effect of organic compounds in the oxidation kinetics of Fe(II). *Mar. Chem.* **2000**, *70*, 211–222.
- (50) Santana, J. M.; Gonzalez-Davila, M.; Millero, F. The oxidation of Fe(II) in NaCl – HCO_3^- and seawater solutions in the presence of phthalate and salicylate ions: a kinetic model. *Mar. Chem.* **2004**, *27*, 27–40.
- (51) Voelker, B. M.; Sulzberger, B. Effects of fulvic acid on Fe(II) oxidation by hydrogen peroxide. *Environ. Sci. Technol.* **1996**, *30*, 1106–1114.
- (52) Chevallier, E.; Jolibois, R. D.; Meunier, N.; Carlier, P.; Monod, A. Fenton like reactions of methylhydroperoxide and ethylhydroperoxide with Fe^{2+} in liquid aerosols under tropospheric conditions. *Atmos. Environ.* **2004**, *38*, 921–933.
- (53) Kelly, T. J.; Daum, P. H.; Schwartz, S. E. Measurements of peroxides in cloudwater and rain. *J. Geophys. Res.* **1985**, *90*, 7861–7871.
- (54) Hewitt, A. D.; Kok, G. L. Formation and occurrence of organic hydroperoxides in the troposphere: laboratory and field observations. *J. Atmos. Chem.* **1991**, *12*, 181–194.

Received for review June 25, 2004. Revised manuscript received December 8, 2004. Accepted January 19, 2005.

ES0404522