IRON SPECIATION IN COASTAL RAINWATER: OXIDATION KINETICS AND ORGANIC COMPLEXATION

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TABLE OF CONTENTS

ABSTRACT

The redox kinetics and organic complexation of iron were investigated in rainwater collected from a coastal site in Wilmington, NC between September 2001 and September 2003. A series of authentic rain samples was irradiated with simulated sunlight to photoproduce Fe(II) and the kinetics of its reoxidation back to Fe(III) was monitored. The oxidation of Fe(II) by hydrogen peroxide during dark storage followed second order kinetics with an average rate constant of $0.024\mu M^{-1}h^{-1}$. Using sequential regression analysis the rate loss could be predicted accurately by the following equation (given that H_2O_2 is in µM and Fe(II) is in nM units):

$$\text{rate loss} = -16.6 + 1.1[H_2O_2] + .28[Fe(II)].$$

In addition to studying the redox kinetics of photoproduced Fe(II) in rainwater the importance of organic complexation on Fe speciation was also evaluated. After approximately 2 h the concentration of photochemically produced Fe(II) decreased until it reached levels at or near pre-irradiation values. A series of experiments demonstrated that the photochemically produced Fe(II) rapidly returned to initial concentrations, suggesting that essentially all the Fe(II) and most of the Fe(III) in rainwater in the absence of sunlight occurs organically complexed. When rainwater was UV oxidized the Fe(II) concentration declined to much lower concentrations than before irradiation, because the organic Fe(II) complex stabilizing Fe(II) in rainwater was destroyed. A second series of experiments demonstrated that Fe(II) present in authentic rainwater was stabilized for up to four hours once added to seawater. When the rain was UV oxidized prior to addition to seawater, the Fe(II) was oxidized almost immediately in the seawater again, suggesting essentially all the Fe(II) in rain is organically complexed.

In summary, the results presented in this study suggests that during the daytime when sunlight is present there is a dynamic interconversion between inorganic Fe(II) and Fe(III) species. Once solar irradiation is removed, there is a organically complexed form of Fe(II) which is stabilized against oxidation. Therefore, the concentrations of Fe(II) and Fe(III) measured in rainwater at any given time depends on the photochemical history of the sample.

ACKNOWLEDGEMENTS

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LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

Iron is one of the most abundant trace elements in atmospheric waters. It has been measured in fog, snow, cloudwater and rain. Many important redox reactions that occur in the troposphere such as the generation of hydrogen peroxide in cloudwater (Zuo and Hoigne 1992; Sedlack and Hoigne 1993) and fog (Zuo and Hoigne 1993) involve Fe species. Iron is also involved in the interconversion of S(IV) to S(VI) in the troposphere (Graedel et al. 1985; Jacob et al. 1986; Zuo and Hoigne 1993; Breytenbach et al. 1994; Grgic et al. 1999). It also contributes to the oxidizing capacity of the troposphere by its reactivity with several free radicals including $\bullet OH$, $\bullet HO_2$, and $\bullet O_2^-$ (Faust and Hoigne 1990; Faust and Zepp 1993; Sedlack and Hoigne 1993; Siefert and Hoffmann 1996). Reactions of several organic pollutant compounds in the troposphere (Erel et al. 1993; Faust and Zepp 1993; Zuo 1995) and in the study of redox chemistry in atmospheric waters must include analysis of several other factors besides Fe speciation.

Iron is thought to be the limiting nutrient in large areas of the world's oceans (Martin and Fitzwater 1988; Martin and Gordon 1988; Martin et al. 1990). The two main avenues for oceanic Fe input are rivers and atmospheric deposition. Rivers provide a particulate iron flux which is 3-4 times greater than atmospheric deposition of particulate Fe, however approximately three times as much dissolved iron enters the oceans through atmospheric processes relative to riverine dissolved Fe inputs (Duce and Tindale 1991).

There have been many total Fe determinations in rainwater from marine areas. Quantifying total Fe concentration does not, however, predict the potential significance of atmospherically deposited iron to oceanic primary productivity because the bioavailability of Fe is critically dependent on the speciation of the soluble forms of the metal. Rich (1990), for example, has shown colloidal Fe and Fe oxides are not immediately available for use by phytoplankton. In addition, Fe(II) is much more soluble relative to Fe(III) and therefore more likely to be present in larger amounts for aquatic organisms (Anderson and Morel 1982; Martin and Fitzwater 1988; Martin and Gordon 1988; Banse 1990; Martin et al. 1990; Rich and Morel 1990; Martin et al. 1991).

A more relevant assessment of atmospheric deposition with respect to marine primary productivity will be obtained if the levels of individual Fe species are measured in rain. This is important because the speciation in rain may affect the speciation of Fe in seawater. It has been suggested that Fe in oxygenated systems, like rainwater, would be present primarily in the Fe(III) form (Moore et al. 1984; Zhuang et al. 1990). However, many studies have shown appreciable amounts of the Fe(II) exist in atmospheric waters including rain, aerosols, fog and cloudwater (Behra and Sigg 1990; Pehkonen et al. 1992; Erel et al. 1993; Siefert et al. 1998; Willey et al. 2000; Kieber et al 2001 a, b; Kieber et al 2003).

There have been several detailed studies of the temporal and spatial variability of the redox speciation of iron in rainwater (Kieber et al. 2001 a,b; Willey et al. 2000, Kieber et al. 2003). The degree of organic Fe complexation, however, remains an important uncertainty associated with iron chemistry in the atmosphere. Earlier studies have suggested a significant fraction of the Fe in rain may be organically complexed (Willey et al 2000, Kieber et al 2003). The existence of organic Fe has important ramifications with respect to the cycling of the Fe because evidence suggests the rates of interconversion between organically complexed and inorganic Fe are drastically different (Kieber et al. 2000). Other studies have suggested that organic complexation of $Fe(II)_{aq}$

stabilizes it against oxidation for more than four hours when added to oligotrophic seawater (Kieber et al. 2000). When authentic rainwater was UV oxidized prior to addition to seawater, the Fe(II) was rapidly oxidized to Fe(III) which the authors attributed to destruction of Fe(II) complexing ligands (Kieber et al 2001).

Despite the potential significance of organic complexation on the redox chemistry of iron both in atmospheric and marine systems, there have been no definitive iron complexation studies done in rainwater. The primary goal of this research therefore, is to quantify the degree of organic complexation of Fe(II) and Fe(III) in rainwater and evaluate the role of that complexation on both the photochemical production and reoxidation of rainwater Fe(II). A second goal was to simulate the behavior of organic iron in authentic rain using known ligands (potentially present in rainwater). Model ligands chosen included selected amino acids, EDTA, Cape Fear River humics, and rainwater humics, all of which are potentially effective Fe binding ligands.

EXPERIMENTAL

Trace Metal Clean Procedures

All Teflon, high-density polyethylene (HDPE), low-density polyethylene (LDPE), and fluorinated polyethylene bottles, tubing, and funnels were trace metal cleaned using the following procedures. First all bottles were rinsed with either methanol or ethanol to remove any residual organics. Each bottle was then thoroughly rinsed inside and out with deionized water (DIW). The bottles were then placed into a 2% Citranox (phosphate free acid cleaner and detergent) bath for one week. After one week bottles were well rinsed again with DIW, then placed into a 3 M HCl bath for at least two weeks.

Bottles were then rinsed well once again with DIW. All materials were then carefully transferred to the clean room. In the clean room everything was rinsed with 18.2 MΩ Milli-Q water (MQ). Materials, after rinsing, were then placed into a pH 2 bath, which was prepared by adding 1mL of Trace Metal grade HCl (Fisher) to 1L of MQ. Materials were stored in the bath until use or were rinsed with MQ and dried before use. Once dried, materials were placed into a doubled zip-lock bag. The interior bag was only opened inside a clean hood.

Sample Collection

Rainwater was collected on the UNCW campus on an event basis throughout the length of the project. 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 is on the UNCW campus, approximately 8.5 km from the Atlantic Ocean. Because of the 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.

Event rain 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, inorganic ions and organic compounds were collected. The other collectors for trace metal samples held a 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).

Samples for Fe research were filtered using a trace metal cleaned 0.2 μm Millipore membrane filter and a trace metal cleaned 500 mL Nalgene polysulfone filtering apparatus. Between 60 and 120mL of sample was used for Fe(II) and Fe(T) concentrations. Two hundred and fifty milliliters to 1.5 L were stored in HDPE trace metal clean bottles in the freezer for organic Fe studies.

Analytical Methods

Iron analysis

Reagents for iron analysis were prepared as follows. Ferrozine was prepared by adding 0.514 g of ferrozine and MQ to make a 100 g solution. 10% Hydroxylamine Hydrochloride was prepared by adding 25 g of hydroxylamine hydrochloride and MQ to 250 g of total solution. Ammonium acetate buffer was prepared by adding 13.2 mL of NH_4OH, 2.4 mL glacial acetic acid, and MQ to 100 g total solution.

Iron(II) and Fe(III) in rainwater samples were determined by the ferrozine method modified from Stookey (1970). Absorbance measurements were made using a 1 m (Ocean Optics) or a 5 m (World Precision Instruments) liquid waveguide capillary cell (LWCC) attached to an Ocean Optics Inc. SD2000 spectrophotometer and an Analytical Instrument Systems Inc. Model DT 1000 CE UV/Vis Light Source (Hardison 2002). Iron(II) and the ligand ferrozine form a complex that absorbs visible light most strongly at 562 nm, so the absorbance at this point was recorded. To correct for baseline shifts and background absorbance, the absorbance readings at 685 nm were subtracted from the absorbance at 562 nm to give the correct absorbance for the Fe(II)-ferrozine complex.

The first step in the determination of the concentration of Fe(II) and Fe(III) was to prepare standard curves. Ferrozine forms a colorimetric complex with Fe(II) only.

Therefore, in order to determine Fe(T) (Fe(II) + Fe(III)), a 10% hydroxylamine hydrochloride solution was added to reduce Fe(III) in solution to Fe(II). Iron(III) concentrations were obtained by subtracting the Fe(II) concentration from the Fe(T). Two standard curves were prepared, one for Fe(II) and one for Fe(T). Iron(II) and Fe(T) standards for the 1m cell were prepared at concentrations of 0, 20, 100, and 200 nM, or 0, 20, 40, 80 nM for the 5 m cell. These standards were prepared as follows. First a primary stock Fe(II) solution was prepared by adding 0.4970 g $FeCl_2$, 2.0 mL Optima HCl and MQ to make 250 g total solution with an Fe(II) concentration of 0.010 M. Thirty microliters of primary stock was added to 30 g of pH 4.5 H_2SO_4 made in MQ to prepare a secondary stock with an Fe(II) concentration of 10.0 µM. Once the primary and secondary solutions were ready, eight 30 mL HDPE bottles were set aside for the standards (4 for Fe(II) and 4 for Fe(T)) prepared to the concentrations previously stated.

Once the rain was collected it had to be analyzed within 24 hrs for Fe(II) and Fe(III) concentrations (Kieber et al. 2001). All rain was analyzed in a class 100 laminar flow clean bench to minimize contamination. First the rain was filtered through a 0.2 µm Millipore Isopore membrane filter to remove any colloidal particles. For each rain event two 30g samples were weighed into two 30mL HDPE bottles. Seven-hundred microliters of Ferrozine was added to the Fe(II) sample and allowed to sit for 5 min. Next 1.8 mL of ammonium acetate buffer was added to the sample. The Fe(II) absorbance of the sample was then read in triplicate. The Fe(T) sample was spiked with 700 µL of 10% hydroxylamine hydrochloride, which had to sit for at least 1 h. After 1 h the ferrozine was added. After 5 min the ammonium acetate buffer was added to the sample and then the Fe(T) absorbance was read in triplicate. The Fe(II) and Fe(T) concentrations of the rain sample were calculated from their respective standard curves.

pH, DOC, and H_2O_2 Analyses

Rainwater pH was determined using a Ross Model 81-02 electrode. Orion low ionic strength buffers (pH 6.97 and 4.10) were used to calibrate the instrument and 50 mL of pHisa ionic strength adjuster (Fisher) was added to each 5 mL sample to match the ionic strength of samples to that of buffers. Dissolved organic carbon (DOC) was determined using a Shimadzu 5000 TOC analyzer with an ASI 5000 autosampler (Willey et al. 2000). Hydrogen peroxide analyses were done using a scopoletin induced fluorescence decay technique (Kieber et al. 1986; Kieber et al. 2001).

Experimental Methods

Photochemical Production of Fe(II)

Photolysis experiments were performed 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 unwanted wavelengths. The spectral quality and intensity of the solar simulator is very similar to that of midsummer, noon-time solar irradiance for 34°N latitude (Reid et al. 2003). Temperature was controlled by water bath (25° C). After irradiation, samples were stored in the dark and room temperature.

Four hundred to 500 mL of a rainwater sample was poured into a Nalgene 1 L Teflon squeeze bottle. A H_2O_2 solution (10 mM), was added to the sample to a final concentration of 10 µM. Two 15 mL aliquots were taken for initial Fe(II) and Fe(T) by ferrozine analysis as described earlier. A 20 mL aliquot was taken for pH and H_2O_2 analyses. The nozzle of the squeeze bottle was plugged by a knotted piece of tubing to prevent sample loss. The sample was then placed in a 25° C water bath inside the solar simulator, centered so that the sample would receive the maximum light intensity and irradiated for two hours. Fifteen milliliter aliquots of the sample were taken at the following times: 0, 0.12, 0.25, 0.5, 1, 2, 4, 8, 24hrs for Fe(II) and Fe(T). 20mL aliquots were taken at 4 and 24 hr for pH and H_2O_2 analyses.

Fe/Hydrogen Peroxide Redox Chemistry

All samples were stored in the dark at room temperature. For Fe(III)-hydrogen peroxide experiments $FeCl_3$ was used to prepare a 10 µM solution of Fe(III). Stock solutions of Fe(III) were prepare daily. Two 250 mL samples of synthetic rain were spiked with Fe(III) to a concentration of 100 nM. One sample was spiked with H_2O_2 to a concentration of 20-30 µM. No H_2O_2 was added to the second sample. Fifteen milliliter aliquots from each sample were taken initially and at 1, 2, 4, 6, and 24 hours and analyzed in triplicate for Fe(II) and Fe(T). Twenty milliliter aliquots were taken initially at 4 and 24 h for pH and hydrogen peroxide analysis. For Fe(II) peroxide experiments $FeCl_2$ was used to prepare a 10 µM solution of Fe(II). Two 250 mL samples of synthetic rain were spiked with Fe(II) to a concentration of 100 nM. One sample was spiked with H_2O_2 to a concentration of 20-70 µM. No H_2O_2 was added to the second sample. Fifteen milliliter aliquots from each sample were taken at the same times, and analyzed the same way.

Fe (II) Addition

Rain events used in Fe addition experiments were divided into three samples of equal volume of a minimum of 120 mL per sample. Iron(II), from a 10 µM $FeCl_2$ solution, was added into two of these samples to final concentrations of 40 nM and 80 nM (analysis by 1 m LWCC) and 20 nM and 40 nM (analysis by 5 m LWCC). Iron(II) and Fe(T) analyses were performed initially and at 0.5, 1, 4, and 24 hours on 15mL aliquots with triplicate absorbance readings. H_2O_2 and pH were analyzed initially and after 4 and 24 h on 20 mL aliquots.

Control samples for the Fe (II) titrations were performed using synthetic rain. Synthetic rain is DIW which has its pH lowered to 4.5 using sulfuric acid. Hydrogen peroxide concentrations and pH were adjusted to that of actual rain events. Iron(II) was spiked into the samples to a final concentration consistent with a rain event being analyzed. Samples were analyzed initially and at 0.5, 1, 4 and 24 h.

Stability Experiments

Two hundred and fifty milliliter rain samples were removed from the freezer and given time to thaw. Thirty milliliter aliquots were removed from each sample for Fe(II) and Fe(T) analysis. Samples were stored in the dark at ambient temperature overnight. After the 24 h time period, 30 mL aliquots were removed from each sample for Fe(II) and Fe(T) analysis.

UV Oxidation Experiments

UV oxidation studies utilized an Ace Glass UV oxidation system with a 1.2 kilowatt mercury arc lamp. Two hundred and fifty milliliters of synthetic and authentic rainwater samples for UV oxidation studies were first filtered through a 0.05 µm Whatman Nuclepore membrane using a plastic Nalgene 500 mL filtering apparatus. Samples were then split into two parts. The first sample was stored in the dark at ambient temperature these were marked “pre” for before UV oxidation. The second sample was placed into the UV oxidation system and UV irradiated for 6 h. These samples were designated “post” for after UV oxidation. After the six hours of UV irradiation, samples were allowed to sit in the dark in the apparatus overnight at room temperature to allow radicals generated by UV irradiation to decompose.

The next day both the pre and post samples were spiked with Fe(II) from a 10 µM $FeCl_2$ solution to a final concentration of 80 nM. Samples were again stored in the dark at room temperature. The ferrozine method was used for Fe(II) and Fe(T) analyses which were performed initially and at 4 and 24 h after addition of Fe(II).

EDTA as a Model Ligand

Samples for EDTA model ligand experiments were analyzed using a Milton Roy Spectronic 1001+ and a 10 cm quartz cell. Thirty-milliliter samples of SRW (pH 4.5) were spiked with EDTA to final concentrations of 0, 50, 100, 200, and 400 nM. These samples were then spiked with Fe(II) to final concentration of 100 nM. Samples then were spiked with 700 µL of Ferrozine. After 5 min buffer was added to the sample. Samples were then poured into a clean 10 cm quartz cell and the absorbance was read.

UV Oxidation of the EDTA-Fe(II) Complex

Two samples of 120mL of SRW (pH 4.5) were spiked with EDTA to a final concentration of 100 µM. These two samples were spiked with Fe(II) from a 10 µM $FeCl_2$ solution to a final concentration of 100 nM. A 30 mL aliquot of each sample was analyzed for Fe(T). The remaining sample was UV oxidized for 6 h inside the UV oxidation system. The sample was allowed to sit in the dark inside the apparatus at ambient temperature overnight. The next day 30 mL aliquots of both samples were analyzed for Fe(T). After analysis was complete the remaining sample was spiked once again with 100μM EDTA. Thirty-milliliter aliquots of each sample were again analyzed for Fe(T).

Fe(II) Stability in Synthetic Rain with Thiourea

Three 250 mL synthetic rain samples were spiked with thiourea (CH_4N_2S) to final concentrations of 250 μM and 2.5 mM. The third sample was not spiked with thiourea and was used as a control. All three samples were spiked with Fe(II) from a 10 μM $FeCl_2$ solution to a final concentration of 80 nM. Thirty-milliliter aliquots of sample were removed for Fe(II) and Fe(T) analyses by the ferrozine method. Fe(II) and Fe(T) concentrations were measured initially and at 2, 4, and 24 h.

Fe(II) Stability in Synthetic Rain with Methanesulfonic Acid

Four 250 mL synthetic rain samples were spiked with methanesulfonic acid (CH_4O_3S) to final concentrations of 250 μM, 2.5 and 25 mM. The fourth sample was not spiked with methanesulfonic acid and was used as a control. All four samples were spiked with Fe(II) from a 10μM $FeCl_2$ solution to a final concentration of 80 nM. Thirty-milliliter aliquots of sample were used for Fe(II) and Fe(T) analyses by the ferrozine method. Fe(II) and Fe(T) concentrations were measured initially and at 2, 4, and 24 h.

Fe(II) and Stability, Mixing Synthetic Rain with Ferrozine to Seawater

Three 125 mL samples of synthetic rain were spiked with Fe(II) from a 10 μM solution of $FeCl_2$ to a final concentration of 200 nM. Each sample was mixed with 125 mL of ogliotrophic seawater to make a final solution of 250 mL with 100 nM Fe(II). Samples were then spiked with ferrozine to a final concentration of 250 μM. Iron(II) and Fe(T) analyses were preformed initially and at 1, 2, and 4 h by the ferrozine method.

Fe(II) Stability, Mixing Synthetic Rain with Thiourea to Seawater

Three 125 mL samples of synthetic rain were spiked with thiourea to a final concentration of 1 μM. Samples were then spiked with Fe(II) from a 10 μM solution of $FeCl_2$ to a final concentration of 200 nM. Each sample was mixed with 125 mL of ogliotrophic seawater to make a final solution of 250 mL with 100 nM Fe(II). Thirty-milliliter aliquots of sample were removed initially, and at 1, 2, and 4 h for Fe(II) and Fe(T) analysis by the ferrozine method.

Fe(II) Stability, Mixing Synthetic Rain with Methanesulfonic Acid to Seawater

Three 125mL samples of synthetic rain were spiked with methanesulfonic acid to a final concentration of 1 μM. Samples were then spiked with Fe(II) from a 10 μM solution of $FeCl_2$ to a final concentration of 200 nM. Each sample was mixed with 125 mL of ogliotrophic seawater to make a final solution of 250mL with 100nM Fe(II). Thirty-milliliter aliquots of sample were removed initially, and at 1, 2, and 4 h for Fe(II) and Fe(T) analysis by the ferrozine method.

Fe(II) Stability, Mixing Synthetic Rain with Amino Acids to Seawater

Four 125 mL samples of synthetic rain were spiked with glycine, cysteine, serine, and histidine to a final concentrations of 1 μM. Samples were then spiked with Fe(II) from a 10 μM solution of $FeCl_2$ to a final concentration of 200 nM. Each sample was mixed with 125 mL of ogliotrophic seawater to make a final solution of 250 mL with 100 nM Fe(II). Thirty-milliliter aliquots of sample were removed initially, and at 1, 2, and 4 h for Fe(II) and Fe(T) analysis by the ferrozine method.

RESULTS

Photochemical Production of Fe(II) in Authentic Rain

Four rain events were irradiated in the laboratory with simulated sunlight for two hours and then stored in the dark for twenty-four hours at room temperature. In each sample a fraction of the original Fe(III) was rapidly photoreduced to Fe(II) during the two hours in the solar simulator (Figures 1-4). This is similar to what was observed by Kieber et al. (2003) who also demonstated that Fe(II) was photochemically produced from Fe(III) in a variety of authentic rainwater samples. The authors found the magnitude of production of Fe(II) was directly related to the initial Fe(III) and H^+ concentrations and inversely related to initial Fe(II) concentrations.

In the current study the photochemically produced Fe(II) rapidly oxidized back to Fe(III) during the first 2 h of dark storage . After the first 2 h of dark storage, Fe(II) concentrations began to stabilize. The final Fe(II) concentration after 24 h was at or near the original concentration of Fe(II). The decrease in Fe(II) concentration was mirrored by an increase in Fe(III) concentration. The concentration of Fe(III) also appeared to stabilize after approximately 2 h.

Fe(II) Oxidation in Authentic and Synthetic Rain

In order to understand the fate of photochemically produced Fe(II) in rainwater a series of controlled laboratory experiments were conducted following the oxidation of Fe(II) in SRW (pH 4.5 H_2SO_4). Synthetic rain was chosen initially as the matrix because it does not contain additional Fe(II) competing components which may be present in authentic rain. The synthetic rain did contain hydrogen peroxide at varying concentrations because it is an important reductant (Equation 1) and oxidant (Equation 2)

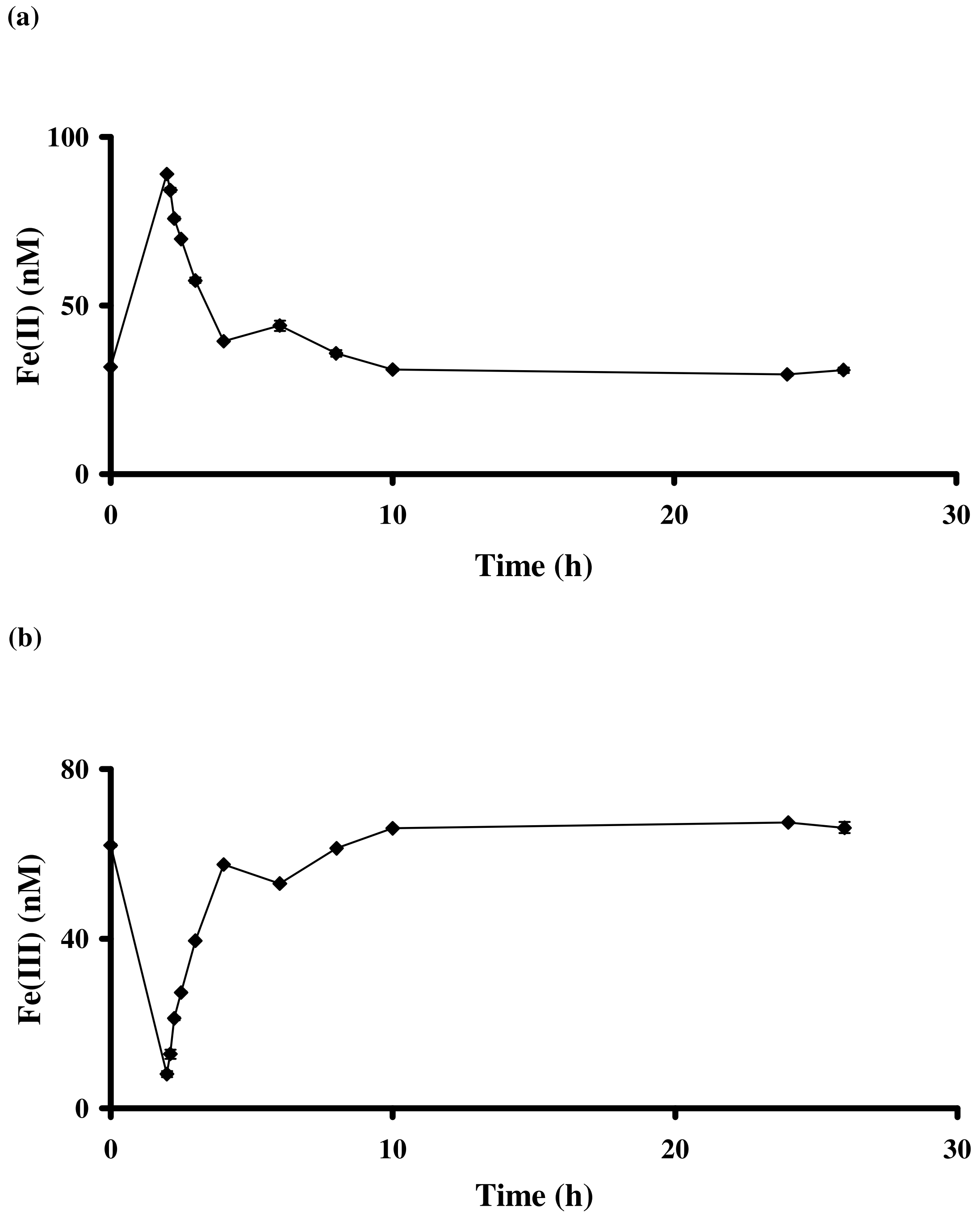

Figure 1-a and b. Concentration of Fe(II) and Fe(III) (nM) as a function of time (h) in an authentic rain sample (Event # 432) irradiated for two 2 h and then stored dark for the remainder of the experiment. The initial pH was 5.63 with a hydrogen peroxide concentration of 20.0 μM.

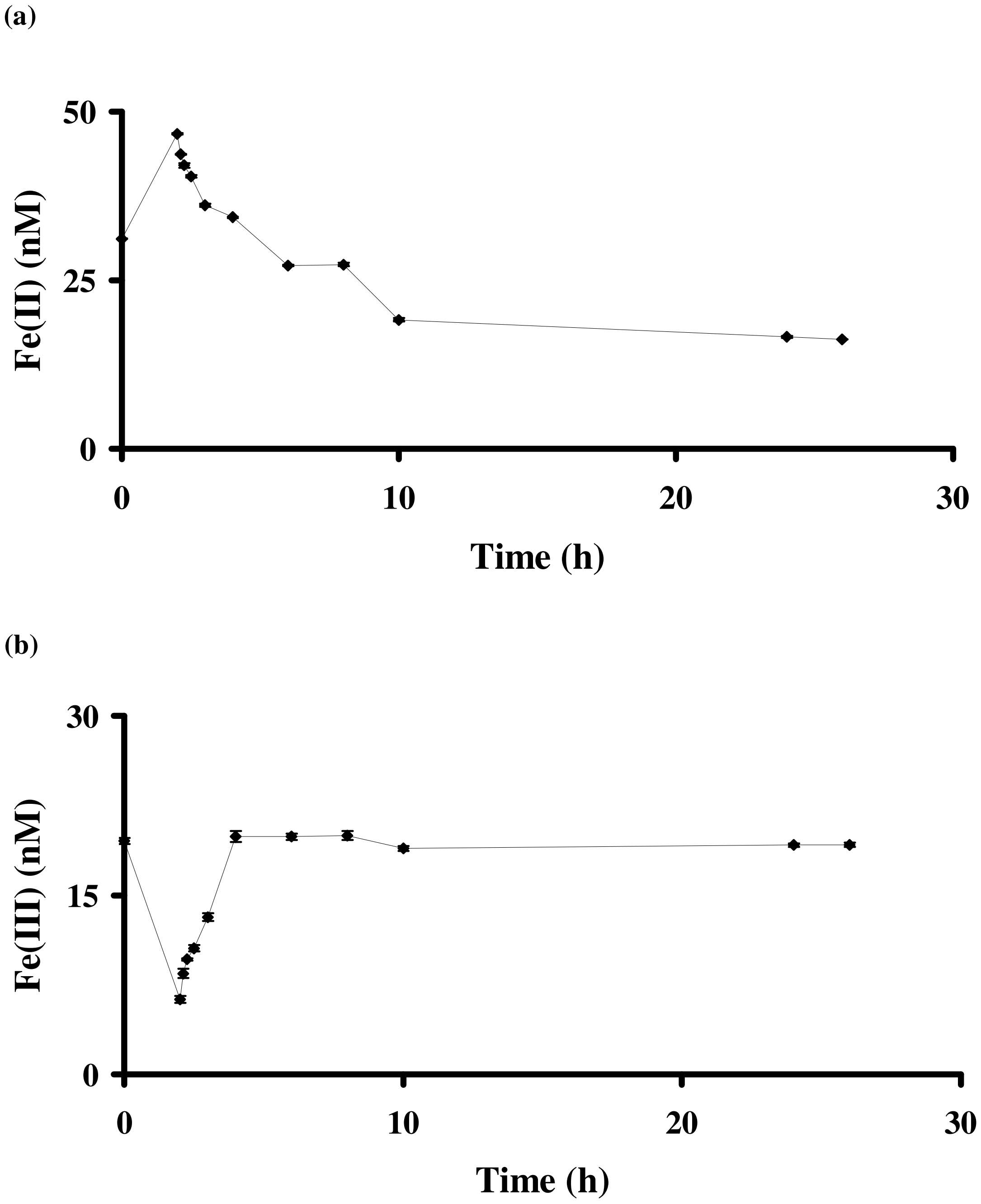

Figure 2-a and b. Concentration of Fe(II) and Fe(III) (nM) as a function of time (h) in an authentic rain sample (Event # 447) irradiated for 2 h and then stored dark for the remainder of the experiment. The initial pH was 4.42 with a hydrogen peroxide concentration of 11.8 μM.

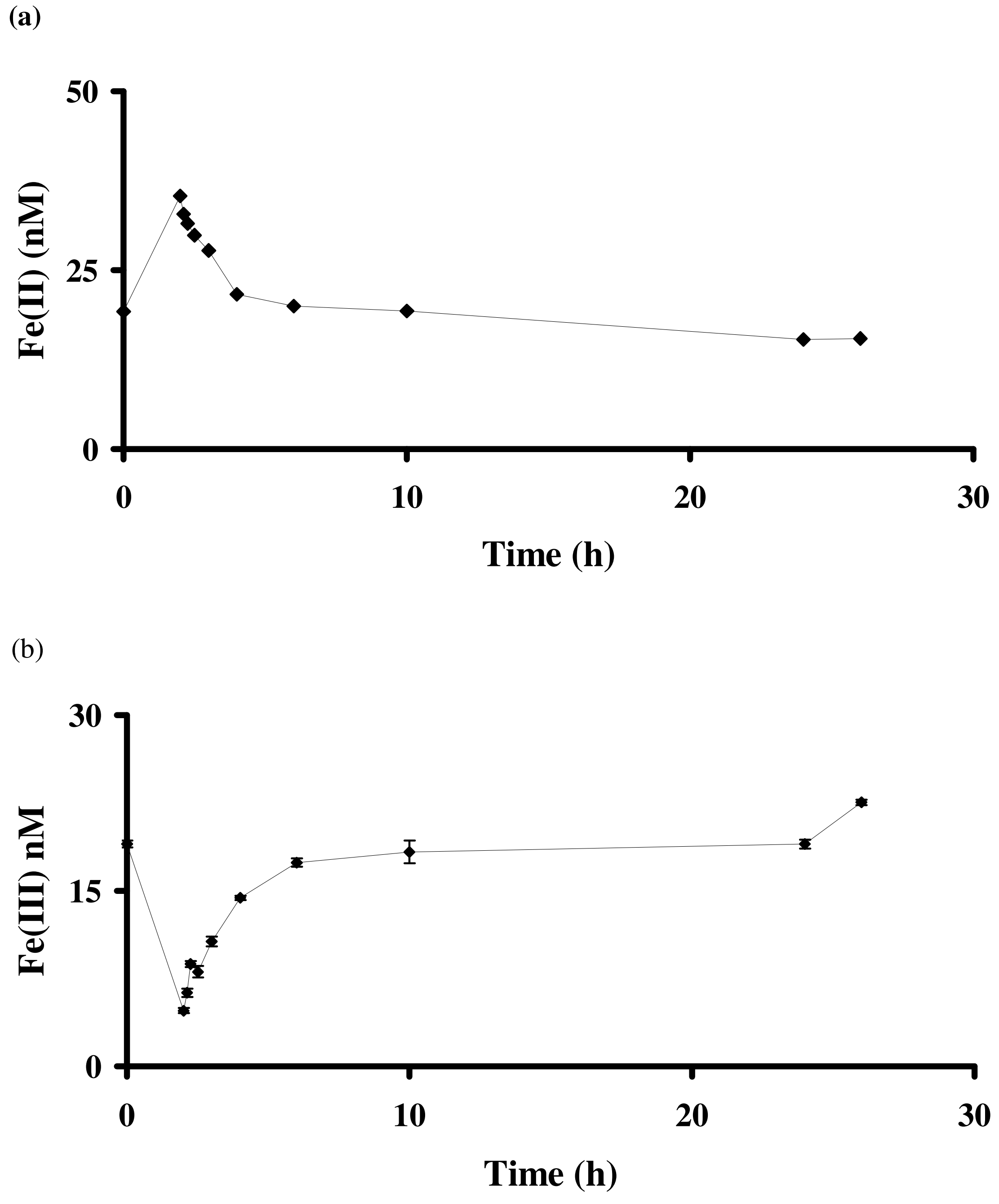

Figure 3-a and b. Concentration of Fe(II) and Fe(III) (nM) as a function of time (h) in an authentic rain sample (Event # 453) irradiated for 2 h and then stored dark for the remainder of the experiment. The initial pH was 4.42 with a hydrogen peroxide concentration of 11.8 µM.

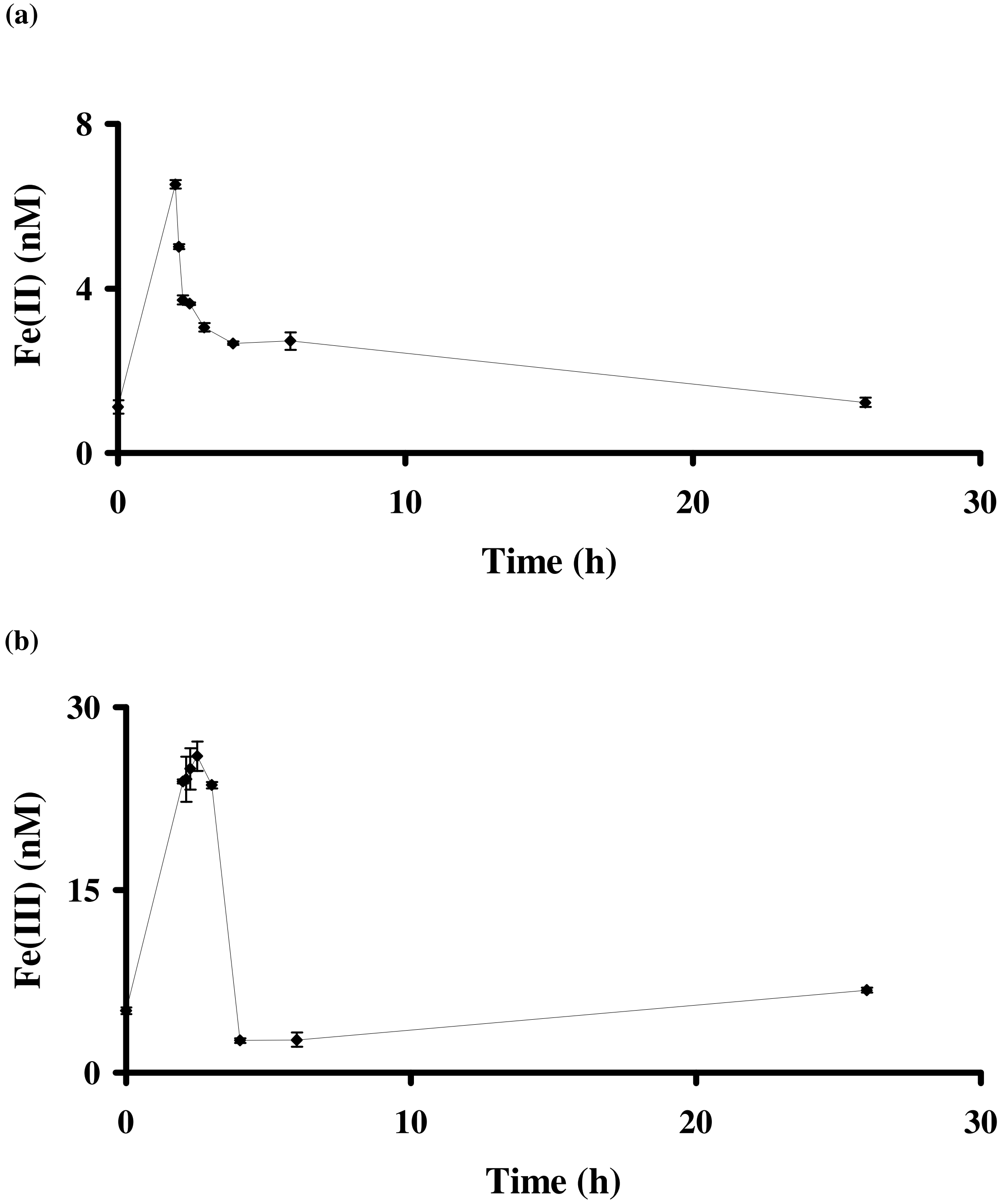

Figure 4-a and b. Concentration of Fe(II) and Fe(III) (nM) as a function of time (h) in an authentic rain sample (Event # 461) irradiated for 2 h and then stored dark for the remainder of the experiment. The initial pH was 4.85 with a hydrogen peroxide concentration of 12.9 µM.

of iron in atmospheric waters (Stumm and Morgan 1996). The inorganic speciation appropriate for pH 4.5 rain is listed in Equations 1-3 below

$$Fe(OH)_2^{+} + H^{+} + H_2O_2 \rightleftharpoons Fe(II) + HO_2^{\bullet} + 2H_2O \qquad \text{(Equation 1)}$$

$$Fe(II) + H_2O_2 + H_2O \rightleftharpoons Fe(OH)_2^{+} + {}^{\bullet}OH + H^{+} \qquad \text{(Equation 2)}$$

$$Fe(OH)_2^{+} + H^{+} + HO_2^{\bullet} \rightleftharpoons Fe(II) + O_2 + 2H_2O \qquad \text{(Equation 3)}$$

In the first set of experiments a series of solutions were spiked with Fe(II) to a final concentration of 100 nM in a SRW (pH 4.5) containing various concentrations of hydrogen peroxide. This experiment was conducted in the dark at room temperature. Iron(II) and Fe(III) concentrations were measured initially and monitored for 6 h (Figure 5). In all three experiments the samples with higher hydrogen peroxide concentrations oxidized at a much faster rate. Samples that did not have a hydrogen peroxide spike did not oxidize as rapidly. The Fe(T) decreased probably because the Fe(III) produced again slowly precipitated out of solution.

In addition to acting as a oxidant of Fe(II), hydrogen peroxide can also act as an oxidant of Fe(II). In order to test the importance of this reaction in rain a second set of experiments was performed where Fe(III) was added to SRW (pH 4.5) with various amounts of hydrogen peroxide. This experiment was conducted in the dark at room temperature. Iron(II) and Fe(III) concentrations were measured initially and monitored for 6 h (Figure 6). In each experiment Fe(II) was rapidly produced by reduction of the added Fe(III). After the initial increase Fe(II) in the sample oxidized back to Fe(III), which slowly precipitated out of solution. The concentration of hydrogen peroxide did was in excess of Fe(T) and did not change.

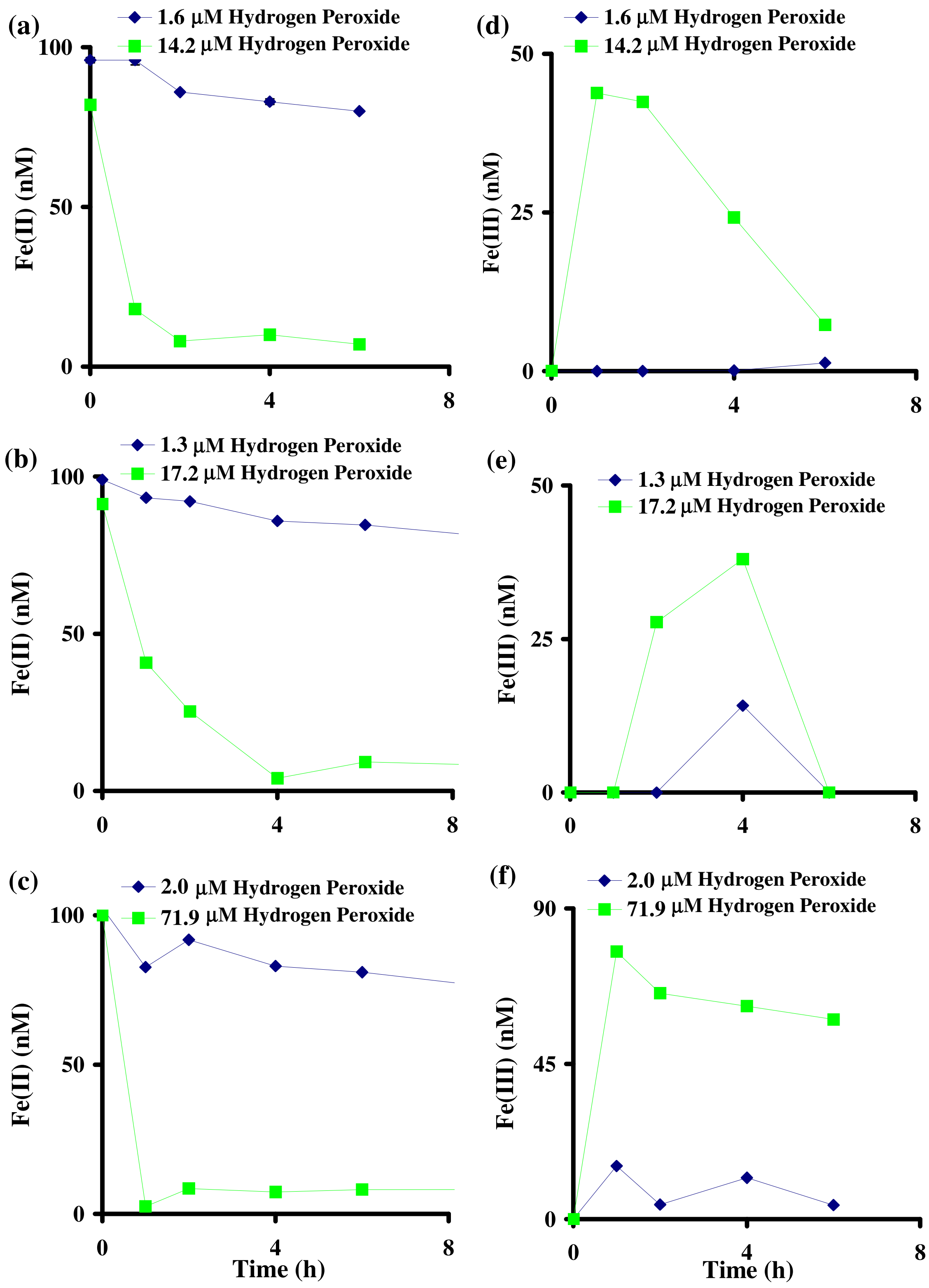

Figure 5-a, b, and c. Concentration of Fe(II) (nM) versus time with various concentrations of hydrogen peroxide. 5-d, e, and f. Concentration of Fe(III) (nM) versus time with various concentrations of hydrogen peroxide. Initial concentration of Fe(II) was 100 nM in synthetic rain.

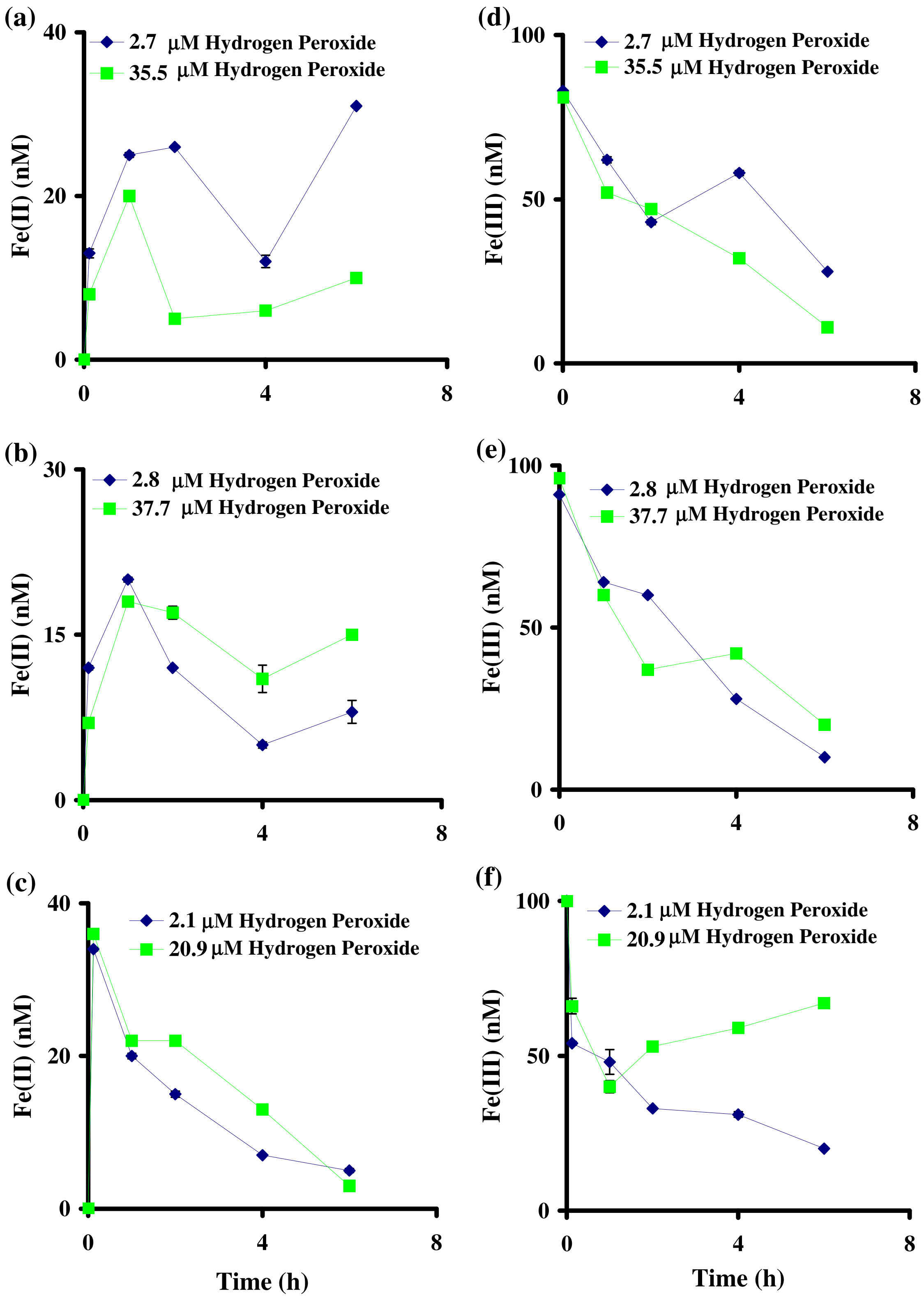

Figure 6-a, b, and c. Concentration of Fe(II) (nM) versus time with various concentrations of hydrogen peroxide. 6-d, e, and f. Concentration of Fe(III) (nM) versus time with various conc of hydrogen peroxide. The initial concentration of Fe(III) was 100 nM in the synthetic rain.

The Fe(II) oxidation rates measured in authentic rain samples varied from 2 to 6 nM/h for samples with low hydrogen peroxide concentrations (less than or equal to 13 µM). Rain samples collected at different times of the day in a previous study at this location (Willey et al. 2000) had an average oxidation rate of 6nM/h with an average hydrogen peroxide concentration of 17 µM. The oxidation rates observed in the photoreduced rain samples were compared to results observed in the field. Earlier studies observed a diurnal oscillation in the concentration of Fe(II) where peak values were observed during the afternoon hours at the time of greatest sunlight intensity (Kieber et al. 2003). After this midday maximum the Fe(II) concentration steadily declined to a minimum during the late evening (12 am to 6 am). The rate of oxidation observed in these field studies was 6nM/h, which is remarkably similar to the oxidation rate observed in the solar simulator studies. This suggests that the rate of oxidation observed in the laboratory studies accurately describes what is occurring in rainwater under natural conditions.

When the concentration of H_2O_2 was much larger (>20 µM) the oxidation rate of Fe(II) was much larger. The rate in a 25 µM H_2O_2 containing rain event was 25nM/h, which is more than 3 times the rate in lower H_2O_2 containing rain events (<14 µM). The impact of higher hydrogen peroxide concentrations was also observed in the oxidation of Fe(II) in field studies. Similar study in rain at BATS gave a higher oxidation rate of ~ 30 nM/h with much higher hydrogen peroxide concentration (37 µM) (Kieber et al. 2003 H_2O_2 at BATS).

Forward stepwise linear regression followed by multiple linear regression of the data in Table 1 yields the following equation ($p < .001$). Plot of predicted versus actual rates yields a slope = 0.7334 and intercept close to zero (Figure 7).

$$\text{Rate Loss} = -16.6 + 1.1(H_2O_2) + 0.28(\text{Fe(II)})$$

The mechanism responsible for the loss of photochemically produced Fe(II) in authentic rain is complex because the synthetic rain experiments discussed above demonstrate that hydrogen peroxide can both oxidize and reduce iron. Using the decrease in Fe(II) concentrations over one to six (depending on rate) hours of dark storage a second order rate constant for the oxidation of Fe(II) was calculated for each rain event and SRW sample (Table 1). This rate constant was based on the oxidation of Fe(II) by hydrogen peroxide presented in Equation 2. Table 2 includes data for pH, H^+ concentration, hydrogen peroxide concentration, DOC, and initial Fe(II) and Fe(III) concentrations for the authentic and synthetic rain samples.

The second order rate constants for Fe(II) oxidation in these experiments given in Table 1 are somewhat lower than those reported for hydrogen peroxide rates in Faust et al. (1994), than for oxidation by $\bullet O_2-$ and $HO_2\bullet/RO_2\bullet$, which are orders of magnitude more rapid. These results strongly suggest hydrogen peroxide is the predominant oxidant for Fe(II) in both authentic and synthetic rain.

Fe(II) Addition

In order to better understand the oxidation kinetics of Fe(II) in rainwater, a variety of iron addition experiments were performed. These experiments involved adding an inorganic Fe(II) spike directly to an authentic rain sample, and following the oxidation of the added Fe(II) with time.

Table 1. Measured and predicited rate of Fe(II) loss in authentic rain generated by solar simulator (event ss) and added as a spike (event-spike). Rate loss of Fe(II) in DI added as a spike is also presented. Second order rate constant with number of data points and correlation coefficient generated from: (ln $[H_2O_2]/[Fe(II)] = ([H_2O_2]_0-[Fe(II)]_0)kt$; where: $[H_2O_2]_0$ = initial hydrogen peroxide concentration, $[Fe(II)]_0$ = initial Fe(II) concentration, k = rate constant, t = time, $[H_2O_2]$ = hydrogen peroxide concentration at (t), [Fe(II)] = Fe(II) concentration at (t).

Event	**Rate Loss Measured (nMh^{-1})**	**Rate Loss Predicted (nMh^{-1})**	**2nd Order Rate Constant (k) ($\mu M^{-1}h^{-1}$)**	**n Rate Constant Calculation**	**r Correlation Coefficient**
432ss	25	24	0.020	6	1.00
447ss	5	10	0.020	5	0.98
453ss	4	9	0.017	6	0.99
461ss	4	2	NA	6	0.84
432t-40	4	8	NA	3	0.74
432t-80	10	14	NA	3	0.75
447t-20	6	5	NA	4	0.76
44t7-40	6	9	NA	4	0.88
453t-20	4	2	0.061	4	0.97
453t-40	7	6	0.075	4	0.98
461t-20	4	0	NA	4	0.92
461t-40	9	5	NA	4	0.91
DI-1	19	15	0.025	3	1.00
DI-2	>44	59	< 0.049	NA	NA
DI-3	14	14	0.018	5	0.96
DI-4	33	23	0.037	3	0.99
DI-5	13	20	NA	4	0.89
DI-6	11	11	0.030	5	0.93
DI-7	>32	42	< 0.04	NA	NA

NA = not analyzed
ss = Solar simulator experiment
t-xx = Fe(II) addition experiment-Fe(II) addition (nM)

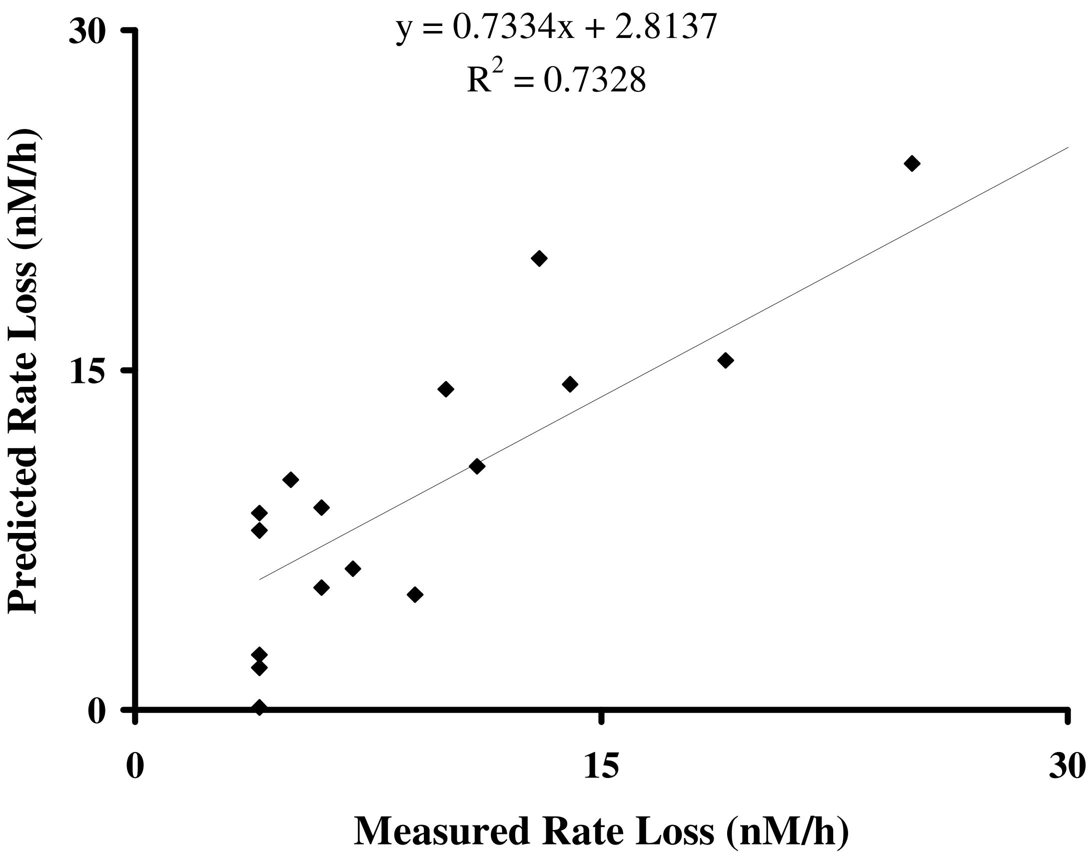

Figure 7. Predicted rate loss versus measured rate loss for irradiated authentic rainwater, Fe addition authentic rainwater, and synthetic rainwater samples.

Table 2. pH, H^+, DOC, H_2O_2, Fe(II) at start of oxidation, and Fe(III) initial concentrations for solar simulator and Fe(II) addition to authentic and synthetic rain events.

Event	**pH**	**H^+ (M)**	**DOC (µM)**	**H_2O_2 (µM)**	**Fe(II) (µM) start of oxidation**	**Fe(III) (µM) initial**
432ss	5.63	2.34E-06	469	20.0	89	62
447ss	4.44	3.80E-05	38	11.8	47	20
453ss	4.62	2.40E-05	42	13.4	35	19
461ss	4.85	1.41E-05	112	12.9	6.5	5
432t-40	5.57	2.69E-06	469	4.0	60	61
432t-80	5.57	2.69E-06	469	4.0	90	57
447t-20	4.45	3.55E-05	38	2.0	54	16
44t7-40	4.45	3.55E-05	38	2.0	71	19
453t-20	4.61	2.45E-05	42	2.0	37	19
453t-40	4.61	2.45E-05	42	2.0	58	18
461t-20	4.84	1.45E-05	112	5.1	19	7
461t-40	4.84	1.45E-05	112	5.1	43	6
DI-1	4.44	3.63E-05	NA	2.1	102	ND
DI-2	4.49	3.24E-05	NA	71.9	100	ND
DI-3	4.44	3.63E-05	NA	1.4	99	ND
DI-4	4.48	3.31E-05	NA	17.2	91	ND
DI-5	4.44	3.63E-05	NA	15.7	82	ND
DI-6	4.44	3.63E-05	NA	1.6	81	ND
DI-7	4.49	3.24E-05	NA	53.8	73	ND

NA = Not analyzed
ND = None detected
ss = Solar simulator experiment
t-xx = Fe(II) addition experiment-Fe(II) addition (nM)

Fe(II) addition experiments were conducted using the same rain events used in Figures 1-4. In this experiment, Fe(II) was added as an inorganic spike rather than being generated photochemically. The concentration of Fe(II) and Fe(III) were again measured as a function of time (Figures 8-11) and the behavior of the inorganic iron species was compared to photochemically generated iron speciation. In each experiment, Fe (II) additions oxidized rapidly over the first hour similar to what was observed for photochemically produced Fe(II). After 2 h Fe (II) spikes of 20 nM remained constant and the 40 nM and 80 nM either remained constant or slowly oxidized for the remainder of the 24 h period. This is again similar to what was observed for photochemically produced Fe(II) where the rapid oxidation was followed by a period of relatively stable Fe(II) concentrations. The Fe (II) in samples with no additions of Fe (II) remained stable for the 24 h period.

Organic Iron

The stability of Fe(II) in rainwater was measured in order to assess the importance of organic complexation of iron speciation in rain. The concentration of Fe(II) in several rain events was monitored initially and after 24 h under dark storage and ambient temperature conditions (Figure 12). Iron(II) spikes were added into two synthetic rainwater samples (pH 4.5) to a final concentration of 50 nM and 100 nM and acted as controls. These controls had a H_2O_2 concentration of 3 μM. There was no statistical difference in the Fe(II) concentrations over the 24 h period of dark storage for the authentic rainwater samples (t-testing $p<0.001$). In contrast to authentic rain, the Fe(II) in the synthetic rainwater controls decreased more than 80% in the both samples. The

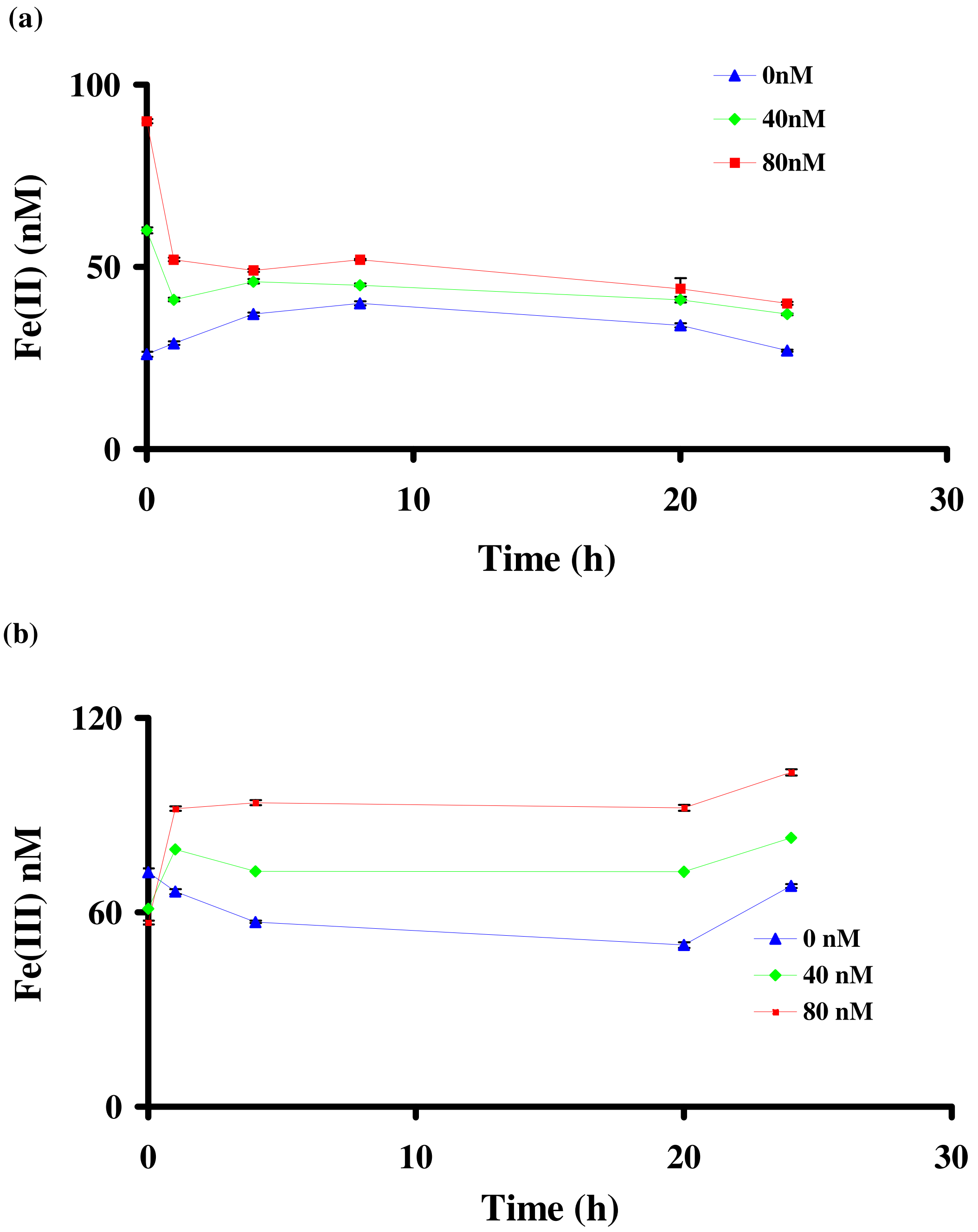

Figure 8-a and b. Concentration of Fe(II) and Fe(III) after addition of 0, 40, or 80 nM Fe(II) as a function of time at a pH of 5.57 and a hydrogen peroxide concentration of 4 µM. Event # 432

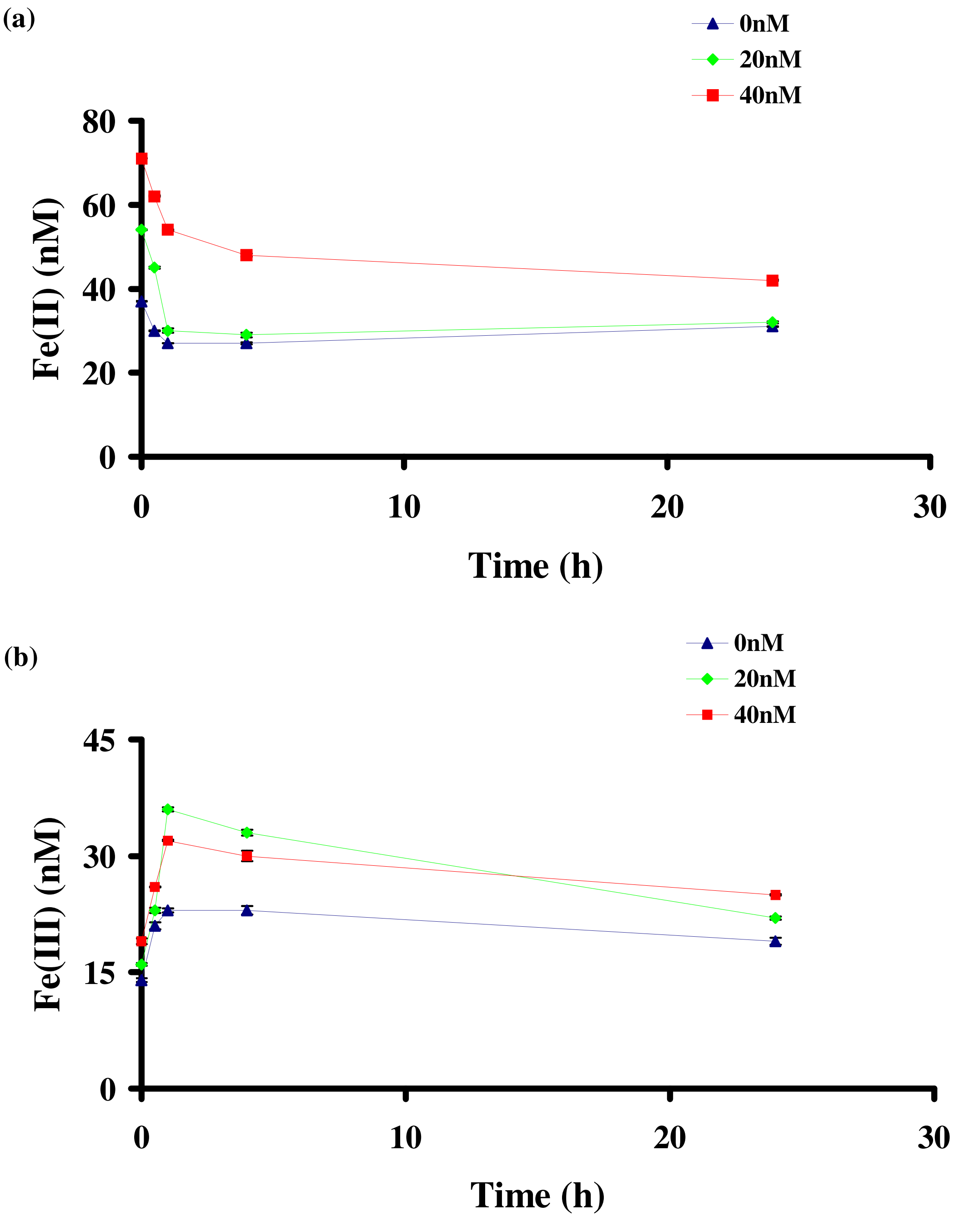

Figure 9-a and b. Concentration of Fe(II) and Fe(III) after addition of 0, 20, or 40 nM Fe(II) as a function of time at a pH of 4.45 and a hydrogen peroxide concentration of 2 µM. Event #447.

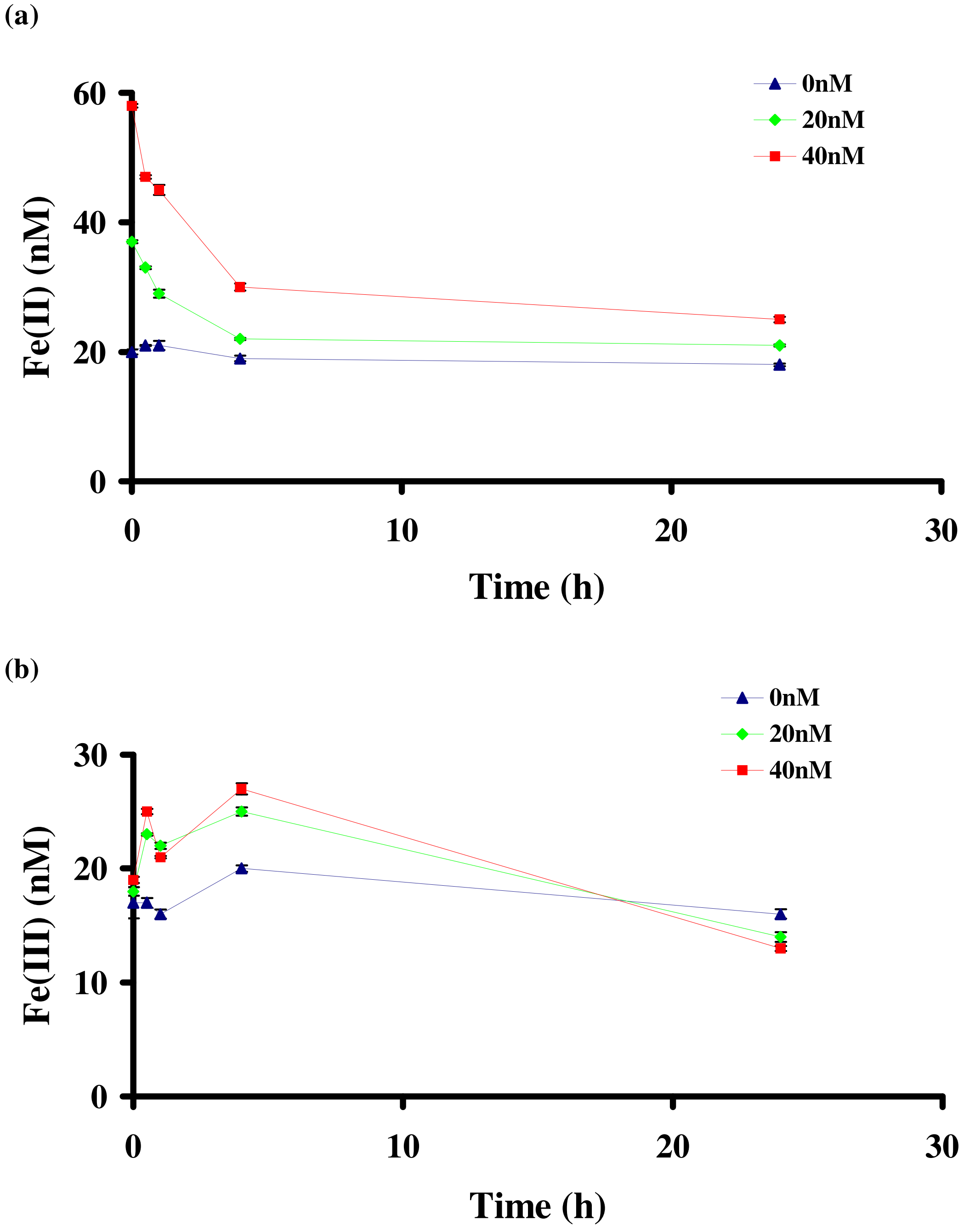

Figure 10-a and b. Concentration of Fe(II) and Fe(III) after addition of 0, 20, or 40 nM Fe(II) as a function of time at a pH of 4.61 and a hydrogen peroxide concentration of 2.0 µM. Event #453.

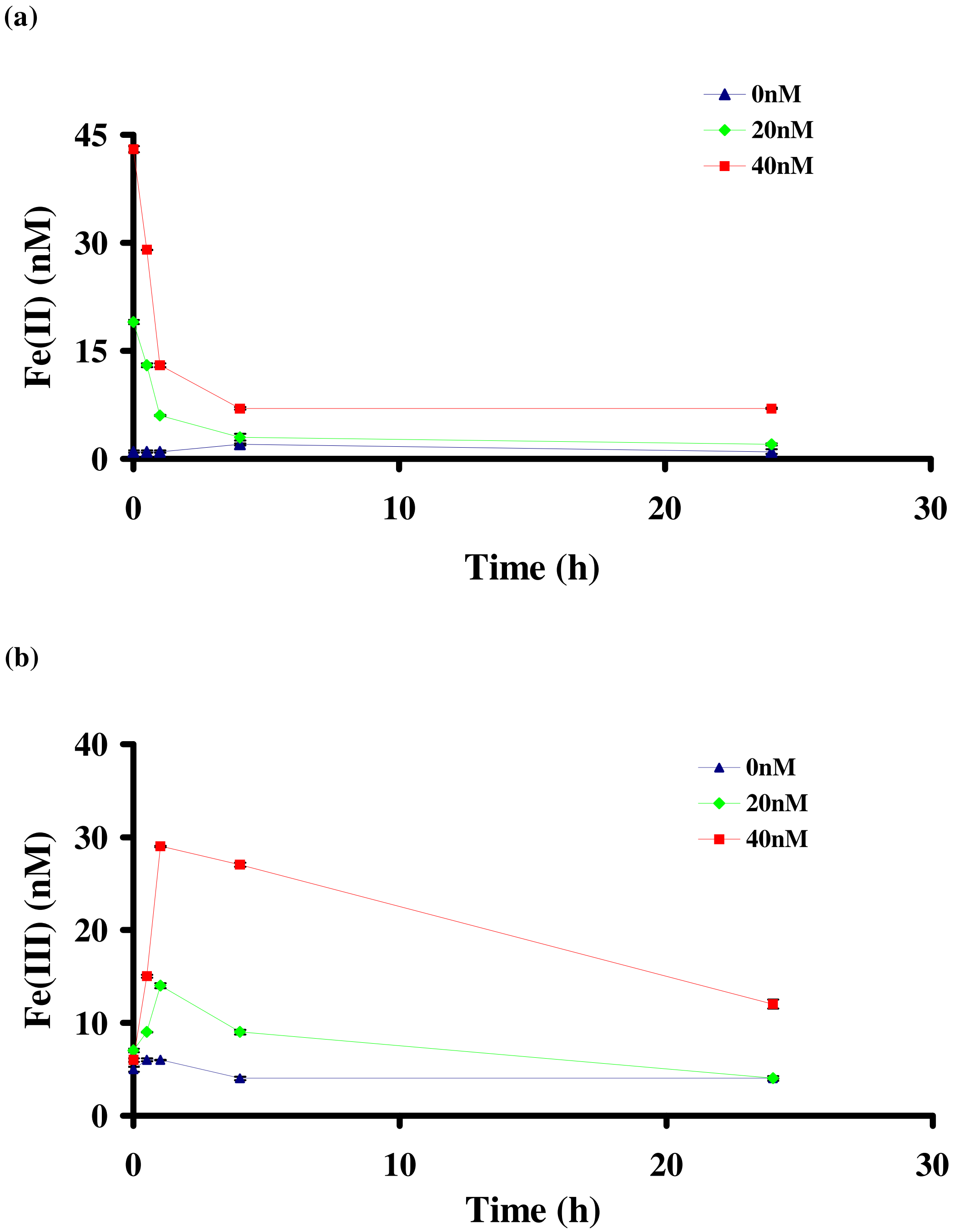

Figure 11-a and b. Concentration of Fe(II) and Fe(III) after addition of 0, 20, or 40 nM Fe(II) as a function of time at a pH of 4.84 and a hydrogen peroxide concentration of 5.1 µM. Event #461.

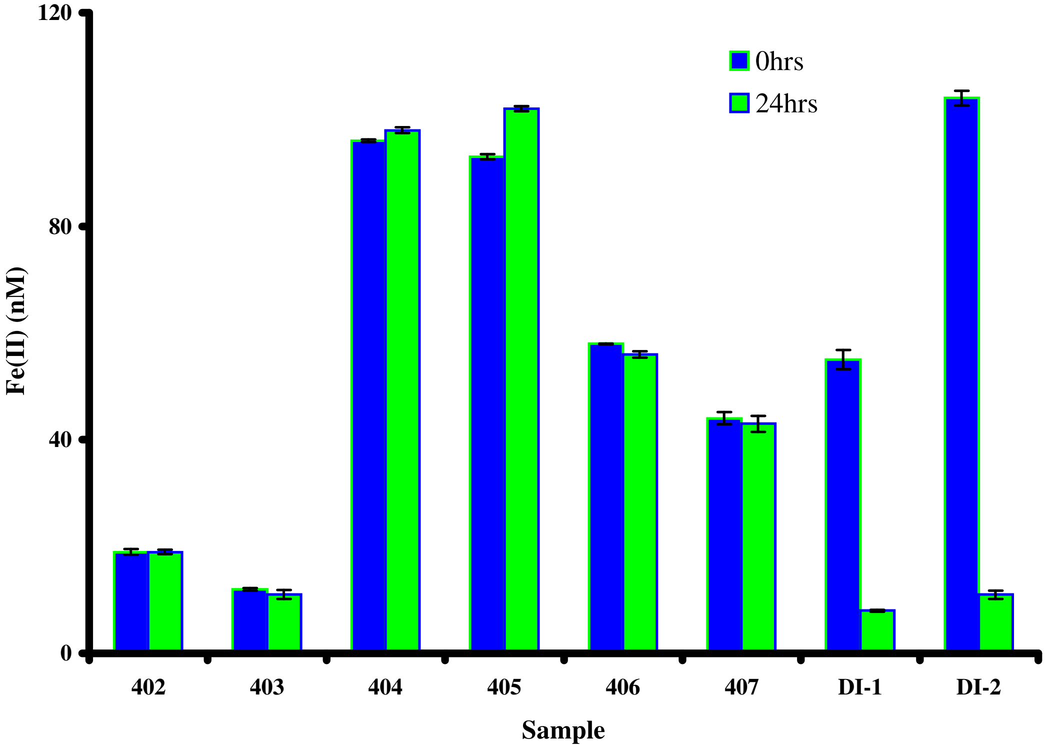

Figure 12. Concentration of Fe(II) (nM) initially and after 24 h dark storage in authentic and synthetic rainwater.

difference in Fe(II) stability in synthetic and authentic rain indicates there is a component of authentic rain that stabilizes Fe(II) against oxidation.

The stability of Fe(II) in authentic rain was also observed during the controlled photolysis experiments presented in Figures 1-4. During these studies Fe(II) was produced by photoreduction of Fe(III) in rainwater samples. The Fe(II) that was produced was quickly oxidized back to Fe(III). Approximately 2 h after irradiation the Fe(II) concentration stabilized at or near the original concentration before irradiation. The results presented in (Figure 12) in combination with the irradiation studies suggests that during the daytime when sunlight is present there is a dynamic interconversion between inorganic Fe(II) and Fe(III) species. Once irradiation ends, there is a stabilized form of Fe(II) which resists oxidation.

To further explore Fe(II) cycling in rainwater, fresh samples of rainwater events used in the photochemical studies were also spiked with inorganic Fe(II) as $FeCl_2$. Iron(II) concentrations were again monitored initially and over a 24h period. The Fe(II) added as an inorganic spike rapidly oxidized, after which the Fe(II) concentrated stabilized at or near the Fe(II) concentration observed in the photochemical experiments. This suggests that the mechanism of oxidation of photoproduced Fe(II) is similar to the mechanism of inorganic Fe(II) oxidation. The similarity of the final Fe(II) concentrations in both cases again indicates that a significant fraction of Fe(II) is complexed and resistant to oxidation.

Fe(II) Stability After UV Oxidation

In order better understand the role of organic ligands on iron speciation in rainwater, a series of UV oxidation experiments were performed using authentic rain events spiked with Fe(II) to a final concentration of 80 nM. Iron(II) and Fe(III) concentrations were measured as a function of time (Figure 13).

In the non-UV oxidized rain event 330 sample the concentration of the Fe(II) spike decreased with time similar to what was observed earlier in titration experiments The Fe(II) concentration stabilized at 27 nM compared to an initial Fe(II), before the Fe(II) spike, was 20nM. When event 330 was UV oxidized to destroy organics prior to addition of the iron spike, Fe(II) concentrations decreased somewhat more rapidly and ended at a much lower concentration (10 nM) than the original sample (20 nM). The initial pH and hydrogen peroxide concentration were 4.41 and 1.6 μM, respectively. The final pH and hydrogen peroxide concentration were 4.43 and 1.6 μM, respectively.

In the non-UV oxidized rain event 346 sample the concentration of the Fe(II) spike decreased more slowly than event 330 and any of the previous Fe(II) addition experiments. The Fe(II) concentration stabilized at a much higher concentration (93 nM) compared to the Fe(II) concentration in the original sample (45 nM). When event 346 was UV oxidized to destroy organics prior to addition of the iron spike, Fe(II) concentrations decreased much more rapidly and ended at a much lower concentration (12nM) than the original sample (45 nM). The initial pH and hydrogen peroxide concentration were 5.81 and 1.2 μM respectively, and the final pH and hydrogen peroxide concentration were 5.84 and 1.1 μM, respectively.

The data presented in Figure 13 provides additional strong evidence of organic complexation of Fe(II). Once authentic rain events were are UV oxidized the samples lost their ability to stabilize Fe(II) at its initial concentration. Event 346 also showed the ability to stabilize Fe(II) concentrations at almost twice the original concentration. This

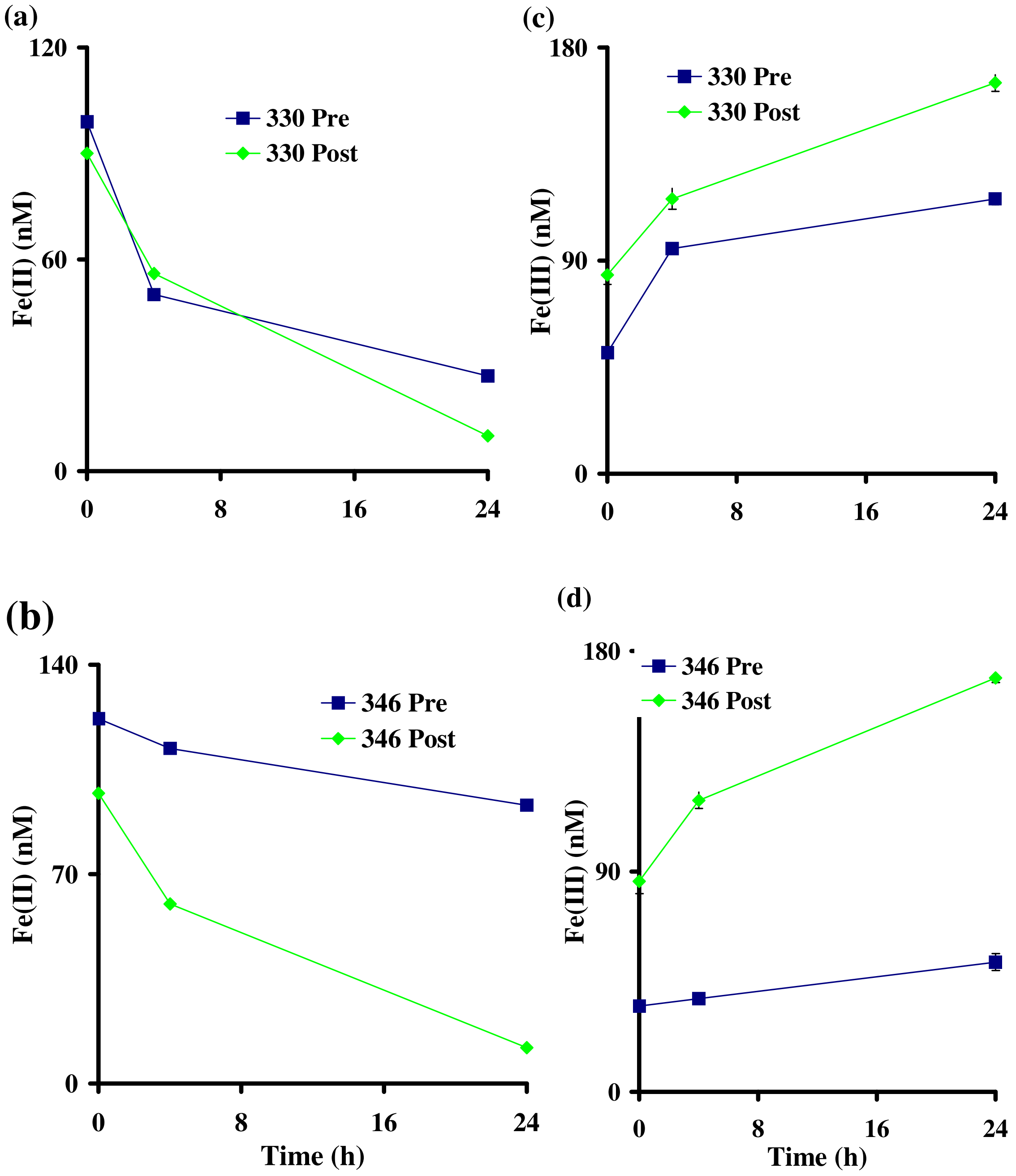

Figure 13-a and b. Concentration of Fe(II) versus time for Pre and Post UV oxidized samples. 13-c and d. Concentration of Fe(III) versus time for pre- and post-UV oxidized samples.

suggests that there was excess organic ligand in this sample, therefore the added Fe(II) was stabilized at a higher concentration. This was not a function of total DOC because both samples had approximately 100 μM DOC. Since the pH and hydrogen peroxide concentrations did not change as a result of UV oxidation, it is unlikely that these parameters are responsible for the different behavior observed between pre- and post-irradiation of authentic rain samples.

These results are similar to previous seawater mixing experiments that showed oxidation of Fe(II) in UV oxidized rain and synthetic rain (Kieber et al. 2000). However, Kieber et al. (2000) showed that Fe(II) concentrations in rainwater remained constant after being deposited into seawater. If free Fe(II) is the only Fe(II) species in rainwater then Fe(II) would rapidly oxidize and precipitate out of solution as $Fe_x(OH)_y$. However, after 4 h Fe(II) concentrations remained stable in the rainwater/seawater sample.

UV Oxidation of Fe(II)-Ligand Complexes in Rainwater

A series of UV oxidation studies were performed to try to elucidate the nature of the organic iron ligands in rainwater. Ultraviolet oxidation was chosen because it destroys all organic iron complexes including those that are so strong that they would not be seen by the ferrozine analysis. Ultraviolet oxidations were performed for 6 h on 17 rain events (Table 3). In each sample there was an increase in total soluble Fe concentration after UV oxidation. This indicates that rainwater contains a very strong organic iron complex which was not detected by ferrozine. When this complex was destroyed by UV oxidation, the total iron signal increased because ferrozine was now able to detect the newly UV oxidized and released iron. No correlation was found between the change in Fe(T) and DOC, hydrogen ion, nitrate, or hydrogen peroxide. In

Table 3. Total Fe concentrations before and after UV oxidation as determined by ferrozine analysis. ΔFe(T) = change in Fe(T) concentration after UV oxidation. DOC, pH, H^+, H_2O_2, and nitrate concentrations are also given for the samples before oxidation.

Event	**Fe(T) Pre (nM)**	**Fe(T) Post (nM)**	**ΔFe(T) (nM)**	**DOC (μM)**	**pH**	**H^+ (M)**	**H_2O_2 (μM)**	**NO_3^- (μM)**
331	118	131	13	105	3.50	3.16E-04	1.5	NA
348	70	85	15	230	3.93	1.17E-04	21.1	NA
366	34	40	6	121	4.00	1.00E-04	13.1	NA
387	7	10	3	18	4.70	2.00E-05	5.7	1.2
388	32	36	4	168	4.69	2.04E-05	8.8	14.0
389	3	5	2	23	5.59	2.57E-06	7.9	1.3
390	6	8	2	62	4.62	2.40E-05	11.8	NA
400	60	71	11	8	5.85	1.41E-06	2.4	3.2
402	28	40	12	64	4.84	1.45E-05	10.5	14.4
403	18	29	11	17	5.94	1.15E-06	4.9	5.2
404	90	116	27	267	4.13	7.41E-05	4.0	54.1
405	130	143	14	114	4.29	5.13E-05	NA	50.1
406	80	88	8	267	4.61	2.45E-05	22.0	31.0
407	44	47	2	41	5.16	6.92E-06	4.5	8.8
409	37	42	5	41	5.12	7.59E-06	5.0	11.2
410	96	112	16	71	4.71	1.95E-05	5.1	30.0
413	108	113	5	31.7	4.62	2.40E-05	14.7	22.1

NA = Not analyzed

addition, samples were 0.05 µm filtered prior to photolysis, therefore the changes observed upon UV oxidation could not be the result of dissolution of colloidal Fe.

Model Ligands

EDTA

In order to further understand organic complexation of Fe(II) in rainwater a series of model ligands were investigated for the iron complexation capacity. Ethylenediaminetetraacetic acid (EDTA) was chosen a first model ligand, to try and mimic the behavior observed in the UV oxidized rainwater samples. A spike of Fe(II) was added to separate synthetic rain solutions to a final concentration of 100 nM. Concentrations of EDTA varied between 0 nM to 400 nM. Increasing the concentration of EDTA caused a correspondingly lower Fe(II) signal up to 200 nM EDTA where there was very little Fe(II) detected by the ferrozine analysis (Figure 14). Increasing the concentration of ferrozine from 250 µM to 2.5 mM did not enhance the signal. Likewise the addition of reducing agent to the samples did not increase the signal. This experiment demonstrates that EDTA is a ligand that is strong enough to out compete the formation of the Fe(II)-ferrozine color complex, and hence avoid detection by ferrozine analysis.

If EDTA is behaving as a model ligand mimicking the behavior of ligands in authentic rain reported in Table 3, UV oxidation should break the EDTA-Fe (II) complex apart, resulting in an increase total the iron signal. Since UV irradiation creates a strong oxidative environment the redox state of Fe was altered so only Fe total analyses were completed on UV oxidized samples rather Fe(II) and Fe(III). Samples that were UV irradiated for 6 h were allowed to sit overnight so that photochemically produced radical species would decompose. Two samples with 100 µM EDTA and 100 nM Fe(II) were

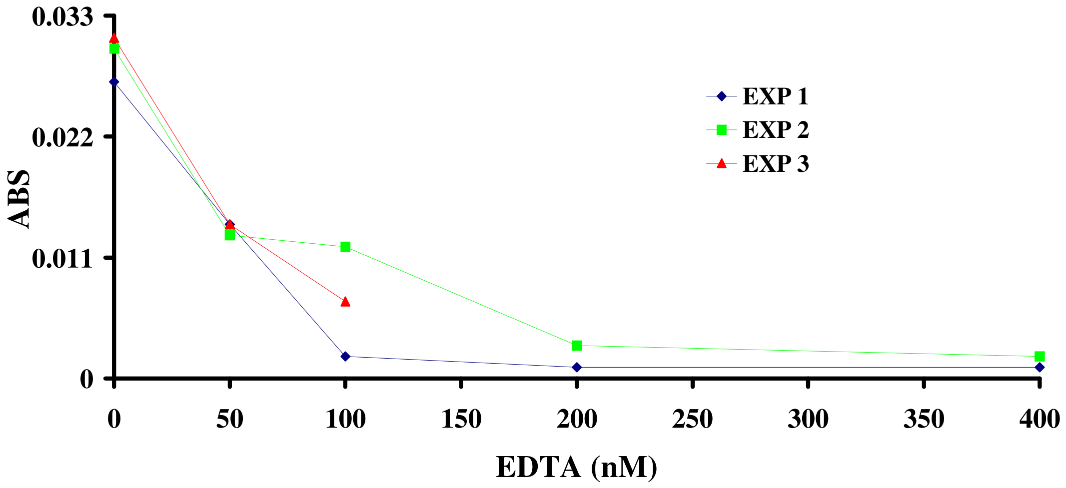

Figure 14. Ferrozine absorbance of a 100 nM Fe(II) synthetic rainwater sample as a function of EDTA concentration (nM)

prepared. As discussed earlier the Fe(II)-EDTA complex was strong enough to out-compete the Fe(II)-ferrozine complex (Figure 14). After samples were UV irradiated for 6 h there was a significant increase in the Fe(T) signal and essentially all of the 100 nM spike of total iron was recovered (Table 4). EDTA was reintroduced to see if the complex would reform in each of the samples that were UV irradiated. EDTA again completely complexed the Fe(II) in the samples, resulting in no iron detected by ferrozine method. These EDTA results are significant because they accurately mimic the behavior observed by the very strong ligand in authentic rain before and after oxidation.

Thiourea and Methanesulfonic Acid as Model Ligands in Synthetic Rain

In order to mimic Fe(II) stabilization by ligand complexation in rain, a series of experiments using synthetic rain and the possible ligands thiourea and methanesulfonic acid were designed. These two ligands are simple sulfur compounds likely to be found in rain, so it is of interest to study their interactions with Fe(II). Synthetic rain samples were spiked with thiourea to final concentrations of 250 μM and 2.5 mM. Iron(II) was spiked into each sample to a final concentration of 80 nM. An 80 nM Fe(II) sample with no added thiourea was also prepared and acted as a control. The concentrations of Fe(II) and Fe(III) were then measured as a function of time (Figure 15). Iron(II) in the samples with no thiourea and 250 μM thiourea oxidized rapidly during the first 2 h of the experiment. This is similar to what was observed during the photochemical and Fe addition experiments. After the first 2 h the rate of oxidation in samples with 0 and 250 μM thiourea slowed down in a manner similar to synthetic rain samples.

These results suggest that 250 μM thiourea is not capable of complexing Fe(II) to an extent which would prevent it from rapidly oxidizing. The synthetic rain sample with

Table 4. Concentration of Fe(T) observed in synthetic rain by ferrozine technique with 100nM Fe(II) and 100μM EDTA before and after UV irradiation for six hours. EDTA was then reintroduced into the sample and Fe(T) was determined again by the ferrozine technique. A = Fe observed before irradiation, B = Fe observed after irradiaion, and C = Fe observed after reintroduction of EDTA

Sample	**Conditions**	**Average**	**Std Dev**
1	A	ND	ND
2	A	ND	ND
1	B	99	3
2	B	107	1
1	C	ND	ND
2	C	ND	ND

ND = None detected

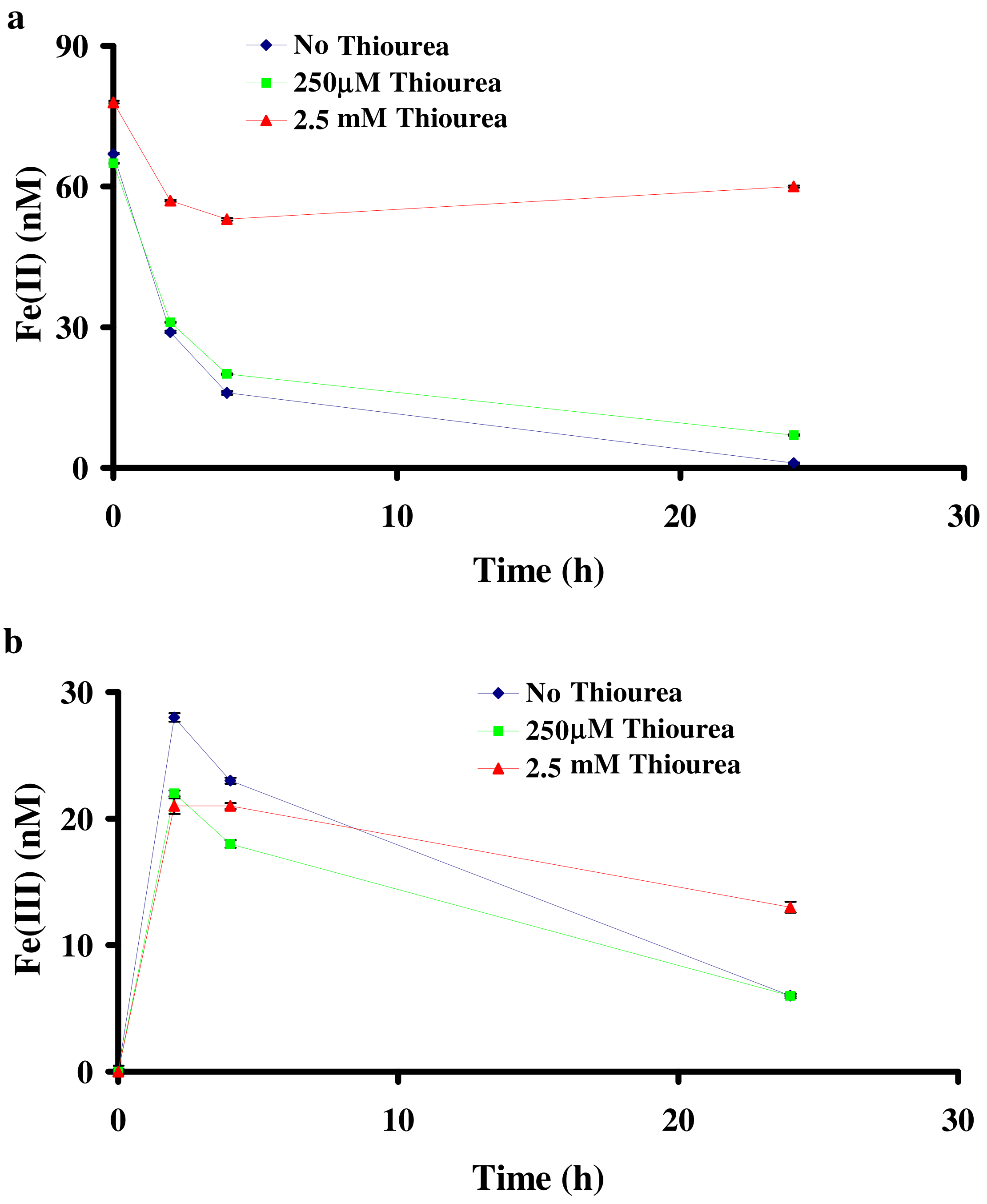

Figure 15. Concentration of Fe(II) and Fe(III) as a function of time for 0, 250 µM, and 2.5 mM additions of thiourea to sample.

2.5 mM thiourea oxidized more slowly during the first 2 h compared to the 0 and 250 μM thiourea samples. In contrast to the 0 and 250 μM thiourea samples the concentration of Fe(II) in the high thiourea sample remained stable after 4 h dark storage. Although this concentration of thiourea is environmentally unrealistic, these results do demonstrate that naturally occurring ligands are capable of mimicking the stabilization of Fe(II) observed in authentic rainwater.

A second experiment using methanesulfonic acid as a possible rainwater ligand was also designed to mimic the Fe(II) stabilization in rainwater. Synthetic rainwater samples were spiked with methanesulfonic acid to final concentrations of 250 μM, 2.5, and 25 mM. Iron(II) was again spiked into all samples to a final concentration of 80nM. A control sample with no added methanesulfonic acid and 80 nM Fe(II) was prepared. Iron(II) and Fe(III) concentrations were analyzed as a function of time. Iron(II) concentrations in samples with added methanesulfonic acid were stable for approximately 2 h. The control rapidly oxidized as in previous experiments. After the first 2 h, Fe(II) in the samples with methanesulfonic acid rapidly oxidized to very low concentrations in a manner similar to what was observed in synthetic rain with no added ligand. The behavior of the samples with added methanesulfonic acid are in contrast to what was observed in the photochemical and Fe titration experiments, where Fe(II) rapidly oxidized over the first two hours and then stabilized for the remainder of the experiment. Since rainwater samples exhibit Fe(II) stability for 24 h it is unlikely that methanesulfonic acid is responsible for the stability that was seen in previous experiments.

Organic Fe(III)

The photochemical experiment presented in Figures 1-4 can provide information on the amount of organically complexed Fe(III) in rainwater. A key assumption in this interpretation is that the Fe(III) produced photochemically is generated from organically complexed Fe(III) (Equation 4). In this scenario there is a ligand to metal electron transfer resulting in production of reduced metal and oxidized ligand. Kieber et al. (2003) have demonstrated that this is the most likely photochemical production mechanism of Fe(II) in rainwater. During the 2 h of irradiation in the solar simulator, over 50% of the Fe(III) present in the sample was photoreduced to Fe(II). The concentration of Fe(III) that was reduced during the photochemical experiments was organically complexed (Table 5). This is based on the hypothesis that the electron gained came from the ligand that was complexing the Fe(III) (Kieber et al. 2003).

$$\mathrm{Fe(III)\text{-}Org} + h\nu \rightarrow \mathrm{Fe(II)} + \mathrm{Org}^{+} \qquad \text{(Equation 4)}$$

Fe(II) Stability in Seawater

Previous experiments has shown that authentic rainwater Fe(II) concentrations are stable for up to approximately 4 h when added to ogliotrophic seawater (Kieber et al. 2001). These authors suggested that organic complexation is responsible for this Fe(II) stability in seawater. Inorganic Fe(II) in synthetic rainwater was very rapidly oxidized (< 2min) to Fe(III) once added to seawater at a pH of 8.1 (Kieber et al. 2001).

In order to mimic rainwater Fe(II) stability once added to seawater, a ferrozine experiment was designed. Synthetic rainwater samples were spiked with Fe(II) to a final concentration of 100 nM. The synthetic rainwater samples were then mixed with ogliotrophic seawater similar to what was done by Kieber et al (2000). Ferrozine was then immediately added to the sample once the mixing was complete. Iron(II)

Table 5. Fe(III) concentrations in rain before and after photochemical reduction. Change in Fe(III) concentration and percent of Fe(III) reduced are also displayed along with pH, hydrogen ion, hydrogen peroxide, and DOC concentrations.

Event	Fe(III) (nM) Pre	Fe(III) (nM) Post	ΔFe(III)	% Reduced	pH	H^+ (M)	H_20_2 (μM)	DOC (μM)
248	17	4	13	75	4.33	4.68E-05	13.6	28.7
271	9	0	9	100	4.35	4.47E-05	25.1	26.3
274	15	6	9	59	4.32	4.79E-05	13.6	15.5
432	62	8	54	87	5.63	2.34E-06	20.0	469
447	20	6	14	70	4.42	3.80E-05	11.8	37.2
453	19	5	14	74	4.62	2.40E-05	13.4	41.8

concentrations were monitored for 4 h (Figure 16). In all three experiments, ferrozine was able to complex a concentration of Fe(II) and stabilize it for 4 h. The significance in these experiments were that the stability of Fe(II) in authentic rainwater/seawater mixing experiments was mimicked using a synthetic rain sample. This provides evidence that ligands found in rainwater could complex Fe(II) strongly enough to stabilize that Fe(II) once deposited into the oceans, thus making Fe(II) potentially available to phytoplankton in the open ocean.

A second series of rainwater/seawater mixing experiments were performed with thiourea and methanesulfonic acid as potential Fe(II) complexing ligands. Thiourea was spiked into synthetic rainwater samples to a final concentration of 1 μM. These samples were then spiked with Fe(II) to final concentrations of 20 and 40 nM. Iron(II) concentrations were monitored as a function of time after addition to ogliotrophic seawater. Iron(II) in the synthetic rainwater sample completely oxidized before 1 h; similar results were observed for methanesulfonic acid. Because thiourea and methanesulfonic acid could not stabilize Fe(II) when mixed with seawater, it is unlikely that these ligands are responsible for Fe(II) stability observed during rainwater/seawater mixing experiments.

Amino acids were also used as possible organic ligands in synthetic rainwater. Synthetic samples were spike with the amino acids cysteine, glycine, histidine, and serine to a final concentration of 1μM each. Samples were spiked with Fe(II) to a final concentration of 80 nM. Iron(II) concentrations were monitored as a function of time. Iron(II) completely oxidized within 2 h, suggesting that these amino acids are not

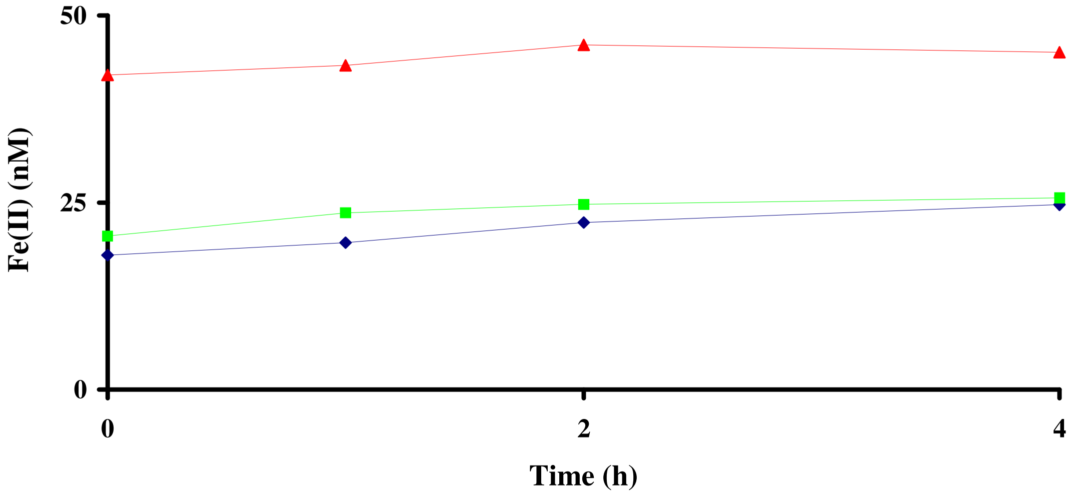

Figure 16. Concentration of Fe(II) as a function of time for ferrozine-Fe(II) complex in the presence of seawater.

responsible for the organic complexation seen when authentic rainwater is mixed with seawater.

CONCLUSIONS

1. Inorganic Fe(II) oxidation displays the same behavior whether Fe(II) is photoproduced added as an inorganic spike.
2. Fe(II) oxidation follows second order kinetics with hydrogen peroxide acting as the oxidant. The average rate constant for these reaction is $0.02\ \mu M^{-1}h^{-1}$ with average Fe(II) rate loss was 6 nM/h in samples with low H_2O_2 concentrations ($<15\ \mu M$) and >20 nM/h in samples with high H_2O_2 ($20 \mu M$).
3. During daytime hours there is a dynamic interconversion between Fe(II) and Fe(III) species in rainwater. During dark hours the Fe(II) is oxidized back to Fe(III). Eventually, Fe(II) concentrations stabilize because, the organic complexation of Fe(II) is resisting oxidation. However, in the presence of sunlight or UV oxidation organic-Fe complexes can break down reforming inorganic Fe species

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