

Nitrite Variability in Coastal North Carolina Rainwater and Its Impact on the Nitrogen Cycle in Rain

ROBERT J. KIEBER,*
MATTHEW F. RHINES,
JOAN D. WILLEY, AND
G. BROOKS AVERY, JR.

*Department of Chemistry and Marine Science Program,
University of North Carolina at Wilmington,
Wilmington, North Carolina 28403-3297*

The concentration range for nitrite (NO_2^-) in 115 rain samples collected in Wilmington, NC, from June 1996 through February 1998 was 0.022–0.603 μM . Nitrite concentrations did not correlate with precipitation volume, suggesting a continuous supply of nitrite during rain events possibly by slow scavenging of gas-phase material such as HONO(g) or $\text{NO}_2(\text{g})$ or in-cloud oxidation of other reduced forms of nitrogen. Nitrite levels exhibited no seasonal oscillations, which is in contrast to other rainwater parameters at this site such as pH, nitrate, non-seasalt sulfate (NSS) and ammonium. Concentrations of nitrite did not correlate with concentrations of pollutant indicators (pH, nitrate, and NSS). The concentration of nitrite in both winter El Nino rains and summer tropical rains was less than half its concentration in non-El Nino or non-tropical events, suggesting a possible terrestrial source of nitrite or nitrite precursor. Controlled laboratory studies demonstrated that hydrogen peroxide can oxidize nitrite in rainwater at environmentally relevant H^+ , H_2O_2 , and NO_2^- concentrations. Nitrite oxidation by H_2O_2 in the aqueous phase has important ramifications with respect to N cycling and acid generation within the troposphere.

Introduction

Nitrite is a biologically and chemically labile compound involved in several important processes occurring within the troposphere. It is an intermediate in the formation of nitrate and can act as an oxidant, reductant, or nitrating reagent for organic material. Nitrite also contributes to the oxidizing capacity of the troposphere because its photolysis between 290 and 400 nm results in the formation of hydroxyl radicals (1).

Studies of nitrite concentrations in rain have been limited primarily by the inadequacy of existing analytical methods. Ion chromatography is used extensively in determination of anions in rainwater; however, reliable nitrite analyses are difficult to obtain below 0.5 μM (detection limit of 0.1 μM) (2). A colorimetric technique based on the formation of a diazo dye from reaction of nitrite with *N*-(1-naphthyl)-ethylenediamine and sulfanilamide also exists; however, its detection limit is also too high for rainwater analysis (0.2 μM with a 10-cm cell) (2) and is susceptible to contamination.

Recently, a simple and extremely sensitive aqueous-phase nitrite method capable of detecting 0.1 nM NO_2^- has been developed (3) that is 3 orders of magnitude lower than the methods discussed above. The analysis is based on the reaction of nitrite with 2,4-dinitrophenylhydrazine forming an azide, which is separated from interfering substances and quantified by HPLC. The method is extremely desirable for detecting low concentrations of nitrite encountered in rainwater because it is rapid, has lower process blanks, and samples can be stored up to 1 month prior to analysis once derivatized.

The initial goal of this study was to utilize this advance in analytical methodology to generate one of the first detailed and reliable concentration time series for NO_2^- in rainwater. The data encompassed 21 months of sampling and analysis including several tropical rain events and El Nino rains, which originate in the Pacific, cross over very little land, draw moisture from the Gulf of Mexico, and are maritime in nature similar to tropical systems. This data set also provides information on the influence of these extreme meteorological conditions on commonly monitored rainwater parameters including nitrate, ammonium, non-seasalt sulfate, hydrogen peroxide, and hydrogen ion.

Oxidation of aqueous-phase nitrite is potentially important with respect to nitric acid production within the troposphere. Earlier N(III) to N(V) kinetic studies were conducted using concentrations of nitrite several orders of magnitude higher than rainwater concentrations because of limited analytical capabilities (4–6). The results presented here address the kinetics of aqueous-phase nitrite oxidation in the presence of several important rainwater oxidants including O_2 , H_2O_2 , and iron using environmentally relevant rainwater concentrations.

Experimental Procedures

Reagents and Standards. All chemicals were obtained from Fisher Scientific (Fair Lawn, NJ) or Aldrich Chemical (Milwaukee, WI) and were HPLC grade or certified A.C.S. grade unless otherwise noted. 2,4-Dinitrophenylhydrazine (2,4-DNPH) was recrystallized twice from a 70:30 mixture of acetonitrile and water (vol:vol) followed by a final recrystallization from pure acetonitrile and stored in the dark in air-tight 30-mL Teflon vials. The derivatizing agent was prepared in 30-mL Teflon vials by dissolving 20 mg of recrystallized 2,4-DNPH in 15 mL of concentrated HCl, water, and acetonitrile in a ratio of 2:5:1 (vol:vol:vol). Stock solutions of potassium nitrite (1000 mg/L N, from LabChem, Inc.) were serially diluted to concentrations typically found in rain and were prepared immediately prior to use.

Analyses. Nitrite in rain samples and standards was derivatized with 2,4-dinitrophenylhydrazine for at least 20 min in the dark forming the azide, which was separated from interfering substances by HPLC and quantified by UV detection at 308 nm (3). Derivatized samples and standards were injected into a Rheodyne six-port injector (model 7125, Rheodyne Inc.) with a 2000- μL sample loop and separated isocratically (40% aqueous acetonitrile, 2 mL/min) at ambient temperatures on an 8 mm i.d. \times 20 cm C_{18} reversed-phase Radial PAK cartridge housed in a Radial compression module (Waters Chromatography Division, model 8NVC184, Milford, MA).

Chloride, nitrate, and sulfate concentrations were determined using ion suppressed chromatography and quantified against synthetic rain standards with a precision of better

* E-mail: Kiebert@uncwil.edu; telephone: (910)962-3865; fax: (910)962-3013.

TABLE 1. Simple (sim) and Volume-Weighted (vw) Averages (av), Standard Deviations (σ), and Median Values for Nitrite Concentrations [NO_2^-] in Rainwater Collected in Wilmington, NC, during the Time Periods Indicated^a

	<i>n</i>	amount (mm)	pH	[NO_2^-]					[NO_3^-] vw av (μM)	[NH_4^+] vw av (μM)	% DIN
				sim av (μM)	sim σ	median (μM)	vw av (μM)	vw σ			
all data	116	2152	4.53	0.13	0.09	0.10	0.11	0.01	11.3	6.9	0.56
Jun 1996–Feb 1998 annual	53	855	4.45	0.14	0.08	0.14	0.12	0.01	15.0	4.6	0.61
Oct 1996–Sep 1997 winter	14	209	4.57	0.16	0.07	0.17	0.15	0.02	13.4	5.3	0.80
Dec 1996–Feb 1997 El Nino winter	22	481	4.99	0.12	0.09	0.09	0.07	0.02	4.0	1.4	1.30
Dec 1997–Feb 1998 summer	18	290	4.26	0.13	0.06	0.13	0.13	0.01	22.4	14.5	0.35
Jun–Aug 1997 continental summer	20	403	4.31	0.07	0.07	0.16	0.15	0.02	16.3	7.1	0.64
Jun–Aug 1996 tropical storms	10	327	4.97	0.18	0.13	0.05	0.05	0.02	2.4	1.6	1.02
Jun–Oct 1996											

^a The rain amount is expressed as number of samples (*n*) and mm collected. The vw hydrogen ion converted to pH and vw average nitrate and ammonium concentrations are given. % DIN is the percent nitrite contributes to the total dissolved inorganic nitrogen (DIN) in rain.

than 3% RSD (7, 8). Ammonium was determined using the phenate method (2). Rainwater pH was determined using a Ross model 81-02 electrode calibrated with low ionic strength 4.10/6.97 buffers (Orion Research Incorporated, Boston, MA). pHix ionic strength adjuster (Orion) was added to each sample to match ionic strength of samples to buffers. Duplicate pH analyses agreed within 0.02 pH unit.

Sample Collection and Storage. The primary rain sampling site used in this study was an open area of longleaf pine, wire grass, and turkey oak on the campus of the University of North Carolina at Wilmington (34°13.2' N, 77°51.8' W, 8.5 km from the Atlantic Ocean). This site complies with U.S. EPA specifications for rain gauge and sampler placement (9). All rainwater event samples were collected using an Aerochem Metrics (ACM) model 301 automatic sensing wet/dry precipitation collector housed in a 4-L muffled glass beaker placed within a HDPE plastic bucket. Three separate 5-mL aliquots of rainwater were withdrawn, placed in separate 7-mL Teflon vials, derivatized with 100 μL of DNPH, and refrigerated at 4 °C until analysis within 1 month (3).

Season Definition and Data Analysis. The three coldest months at this location were defined as winter (December 1–February 28), and the three warmest months were defined as summer (June 1–August 31). Range and median values for nitrite concentrations are reported in Table 1, along with simple averages and standard deviations and volume-weighted averages and standard deviations (both based on *n* – 1). Volume weighting minimizes the effects of small rain events on averages and is the mathematical equivalent to combining all rain samples into one container prior to analysis (9); hence, volume-weighted averages are used primarily in the text. Rainfall amount averages are simple averages. Average pH values were computed from volume-weighted hydrogen ion concentrations. In correlation analysis, *p* ≤ 0.01 was defined as significant. Non-seasalt sulfate (NSS) concentrations were calculated using seawater chloride/sulfate ratios assuming all chloride present was from seasalt, which is appropriate for rain in this coastal location (10).

Controlled Laboratory Studies. Laboratory experiments were conducted to study conversion rates of nitrite to nitric acid by hydrogen peroxide, iron, and oxygen at pH 3.5, 4.5, and 5.5. These hydrogen ion concentrations encompass the pH range typically observed in rain collected at this site (11). Sulfuric acid was used to adjust pH because it is an important acid found in rainwater in eastern North America and because it does not impact N redox cycling. Hydrogen peroxide was

diluted to either 10 or 100 μM , which represent the average and extreme concentrations observed for this area (11). Iron was added as 100 nM Fe(II)Cl₂ or Fe(III)Cl₃ at pH 4.5 which are average concentrations in rainwater collected in Wilmington (12). All experiments were performed at room temperature in the dark to avoid competing light-controlled reactions.

Results and Discussion

Rainwater collected from 115 rain events between June 16, 1996, and February 24, 1998, in Wilmington, NC, had a range of nitrite concentration from 0.022 to 0.603 μM , a simple average concentration and standard deviation of 0.13 ± 0.09 μM , a median value of 0.10 μM , and a volume-weighted average concentration of 0.11 ± 0.01 μM (Table 1). During this 18-month study period, 108 mm of rainfall per month was recorded, which is normal for this region based on the 10-year average from the National Weather Service for Wilmington, NC. In addition, pH, nitrate, and ammonium concentrations were approximately equivalent to the 3-year volume-weighted averages reported earlier for Wilmington of 4.51, 12.8, and 9.0 μM , respectively (13). Nitrite comprised a small (0.56%) but potentially important fraction of the total dissolved inorganic nitrogen (DIN) pool in rainwater at this location.

Annual Data. Data were subdivided into a 1-year time period with samples collected from October 1, 1996, to September 30, 1997, a period chosen as being representative of rain for this region because it excludes extreme weather events including hurricanes, tropical storms, and El Nino (Table 1). The simple average nitrite concentration in rain for this year was 0.14 ± 0.08 μM , the median was 0.14 μM , and the volume-weighted average was 0.12 ± 0.01 μM . These nitrite concentrations are in the same range as reported in ca. 20 samples over the French Atlantic coast (14), although these latter measurements should be viewed with caution because most concentrations were at or near the analytical detection limit of 0.1 μM . Concentrations of hydrogen ion, nitrate, and non-seasalt sulfate were all intercorrelated (*p* < 0.001) in this annual data, which is consistent with earlier studies at this location during 1988–1990 (13) and 1992–1994 (11) and at other locations in the eastern United States (15, 16). The correlation among these ionic species has been interpreted as reflecting their common anthropogenic sources, and hence these are often used as pollution indicators in rain. Nitrite, in contrast, did not correlate with H⁺, NO₃[–], or

NSS during this study. This is consistent with the behavior of nitrite as an intermediate oxidation state of nitrogen in rain, with complex source and sink functions, rather than a single pollutant source. Nitrite also did not correlate with the precipitation amount during this annual event cycle, suggesting that washout is not dominating NO_2^- concentrations in rainwater (17). The lack of correlation with rain amount suggests a continuous supply of nitrite during rain events, possibly by scavenging of gas-phase material such as HONO(g) or $\text{NO}_2(\text{g})$ (14, 18) or oxidation processes involving reduced forms of nitrogen.

Seasonal Variations. A winter and summer season without extreme weather events was compared in order to assess seasonal variations in nitrite concentrations. Non-El Nino winter rain from December 1996 through February 1997 was compared to summer rain collected from June 1997 to August 1997 during which time no hurricanes or tropical storms occurred in this region. The volume-weighted average nitrite concentration in non-El Nino winter rain (209 mm) was $0.15 \pm 0.02 \mu\text{M}$ (Table 1). The volume-weighted average nitrite concentration in 1997 summer rain (290 mm) was $0.13 \pm 0.01 \mu\text{M}$ (Table 1). There was no significant difference (*t* test, $p < 0.001$) between nitrite concentration in the 1996–1997 winter season and the 1997 summer season, suggesting that nitrite concentrations in rain are not greatly influenced by seasonal variations. This contrasts with many other rainwater components, such as hydrogen peroxide, hydrogen ion, NSS, and nitrate, that demonstrate marked seasonal oscillations at this location (11, 13) and elsewhere (refs 19 and 20 and references therein). Seasonal variations in these other rainwater components have been attributed to a variety of factors including increased photochemical activity, temperature, and biogenic emissions. The lack of seasonality in nitrite concentration suggests that these seasonally changing physical and chemical characteristics of the troposphere do not dominate nitrite chemistry at this location.

Extreme Weather Events. Winter data from December 1996 through February 1997 (non-El Nino) was compared to El Nino winter rains that occurred December 1997 through February 1998 in order to evaluate the influence of this extreme weather event on nitrite and other rainwater parameters (Table 1). The volume-weighted average nitrite concentration in El Nino winter rain was $0.071 \pm 0.020 \mu\text{M}$, which is approximately half its volume-weighted average in non-El Nino winter rain ($0.15 \pm 0.02 \mu\text{M}$). Other rainwater analytes including nitrate, NSS, pH, and ammonium were also significantly lower in El Nino rains and were approximately equal to background levels found in uncontaminated precipitation in remote regions of the globe (21–24).

The influence of tropical storms and hurricanes was also evaluated and compared to non-tropical rain from June to October 1996, during which Hurricanes Fran and Bertha and two tropical storms, Arthur and Josephine, hit the North Carolina Coast. The volume-weighted average nitrite concentration in tropical storm and hurricane rain was $0.054 \pm 0.020 \mu\text{M}$ (Table 1). The comparable nitrite concentration in non-tropical summer rain during this same time period was higher ($0.15 \pm 0.02 \mu\text{M}$) as it was for the more normal summer of 1997 ($0.13 \pm 0.01 \mu\text{M}$). The concentrations of other analytes (hydrogen ion, NSS, ammonium, and nitrate) were also much higher in non-tropical rain relative to tropical rain, which is consistent with anthropogenic and vegetative sources of these analytes.

The lower concentration of nitrite in tropical and El Nino rains most likely reflects the dominance of maritime influences in these events relative to non-El Nino, non-tropical rains that are a mix of both maritime and continental precipitation at this location. The higher nitrite concentration in non-tropical, non-El Nino rain suggests there is a terrestrial

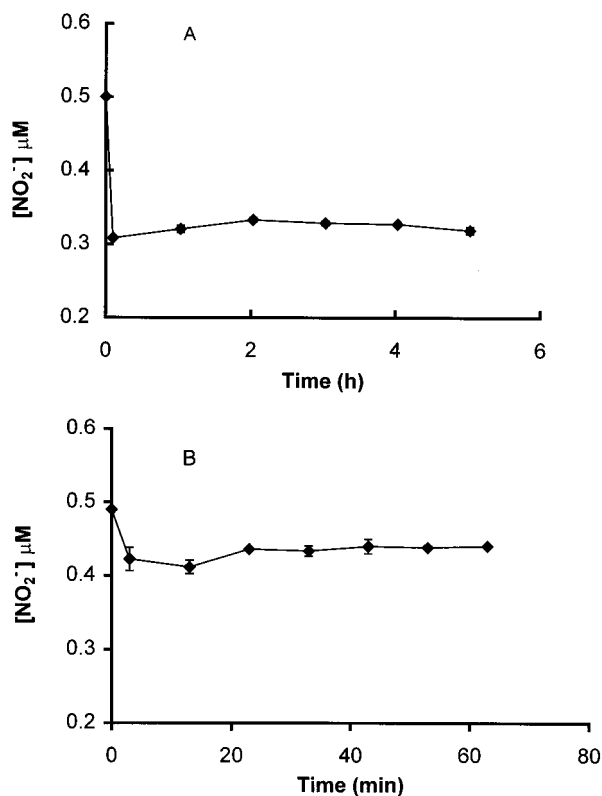


FIGURE 1. (A) Nitrite concentration (μM) as a function of time (h) in pH 4.5 synthetic rain containing $100 \mu\text{M H}_2\text{O}_2$. (B) Nitrite concentration (μM) as a function of time (min) in pH 4.5 synthetic rain containing $10 \mu\text{M H}_2\text{O}_2$.

nitrite source or precursor thereof not found in marine-dominated systems.

An additional impact of extreme weather events on precipitation composition can be seen in the seasonality of nitrate, ammonium, and pH concentrations at this site. Tropical system nitrate, ammonium, and pH levels ($2.4 \mu\text{M}$, $1.6 \mu\text{M}$, and 4.97), respectively, were similar to values determined in El Nino winter rain at this location and are approximately equal to background levels in uncontaminated rain in remote regions (21–24). This is significant because it suggests that the influence of season at this site on rainwater nitrate, ammonium, and pH is removed if the storm is of maritime origin because winter El Nino and summer tropical rains had very similar concentrations.

These results illustrate the importance of extreme weather events on rainwater composition. Annual differences in nitrite concentrations may result primarily from the number of extreme events occurring within a particular year, with maritime influences generally contributing to lower concentrations because of limited contact with terrestrial sources. In addition, the percent contribution of nitrite to DIN is highest in extreme event rain and is determined by the lower nitrate concentration in maritime rain (Table 1).

Kinetic Experiments. A plot of nitrite concentration measured over 5 h at pH 4.5 in the presence of $100 \mu\text{M}$ hydrogen peroxide appears in Figure 1 A. The nitrite concentration decreased from its initial value of $0.5 \mu\text{M}$ to approximately $0.3 \mu\text{M}$ after 5 min in the presence of hydrogen peroxide. After this initial decrease, the NO_2^- concentration remained at $0.3 \mu\text{M}$ during the next 5 h. A similar experiment was conducted with $10 \mu\text{M H}_2\text{O}_2$, which is a concentration more typically observed in rain (Figure 1B). A similar initial nitrite loss was observed after approximately 2 min, after which time the concentration remained at $0.45 \mu\text{M}$ for the duration of the experiment. The net loss in nitrite was smaller

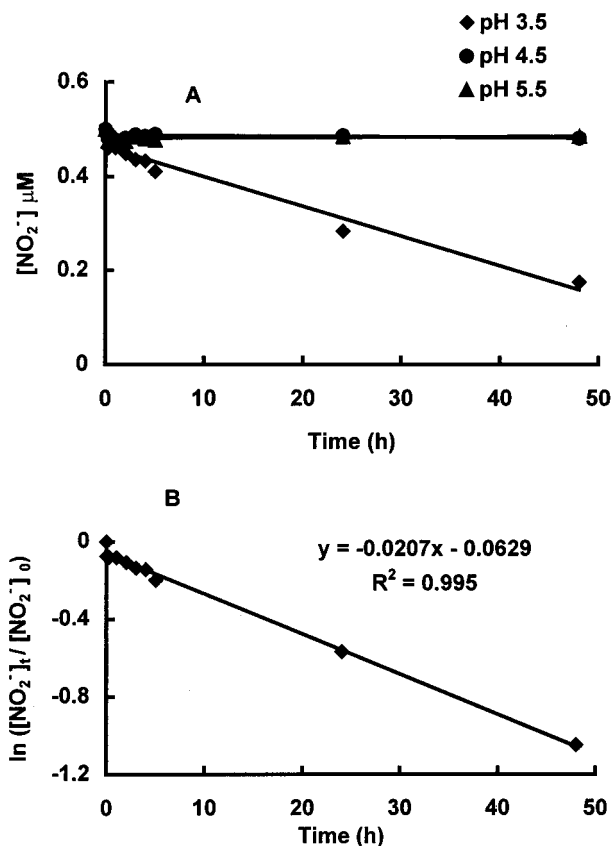


FIGURE 2. (A) Nitrite concentration (μM) as a function of time (h) in pH 3.5, 4.5, or 5.5 synthetic rain containing $10\ \mu\text{M}$ H_2O_2 . (B) $\ln([\text{NO}_2^-]_t/[\text{NO}_2^-]_0)$ versus time in hours for pH 3.5 data from panel A. $[\text{NO}_2^-]_t$ indicates nitrite concentration at time t ; $[\text{NO}_2^-]_0$ indicates an initial concentration of $0.5\ \mu\text{M}$. The slope of this plot yields a first-order rate constant of $5.8 \times 10^{-6}\ \text{s}^{-1}$.

in the presence of less hydrogen peroxide (0.05 vs $0.2\ \mu\text{M}$), suggesting that the reactivity of nitrite toward H_2O_2 is dependent on peroxide concentration present even though in both cases hydrogen peroxide was present in excess of nitrite. The control was $0.50\ \mu\text{M}$ potassium nitrite in oxygenated DI water containing pH 4.5 sulfuric acid with no added hydrogen peroxide. The nitrite concentration in the control showed no change over 48 h in two separate experiments ($n = 15$ measurements, average = $0.50\ \mu\text{M}$, standard deviation = $0.01\ \mu\text{M}$) indicating that nitrite loss reported in Figure 1A,B is due to oxidation by hydrogen peroxide and not molecular oxygen.

Experiments presented in Figure 1 were conducted at pH 4.5, which was the volume-weighted average pH observed in rainwater during this study and previously at this location (13). An additional set of experiments was conducted at pH values of 3.5, 5.5, and 4.5, which encompasses the range of values routinely encountered at this location (Figure 2A). Nitrite was much more reactive in the presence of $10\ \mu\text{M}$ hydrogen peroxide at pH 3.5 as compared with pH 4.5 and pH 5.5. At pH 4.5 and pH 5.5, there was a small rapid initial loss of nitrite (0.02 and $0.015\ \mu\text{M}$, respectively) after which the concentration remained constant, which is consistent with the results presented in Figure 1 at pH 4.5. However, at pH 3.5 nitrite loss occurred over the entire 48 h, suggesting a different pathway of nitrite reactivity toward hydrogen peroxide at this lower pH. The control was $0.50\ \mu\text{M}$ potassium nitrite in oxygenated DI water containing pH 3.5 sulfuric acid with no added hydrogen peroxide. The nitrite concentration in the control showed no change over 48 h in two separate experiments ($n = 17$, average = $0.50\ \mu\text{M}$, standard

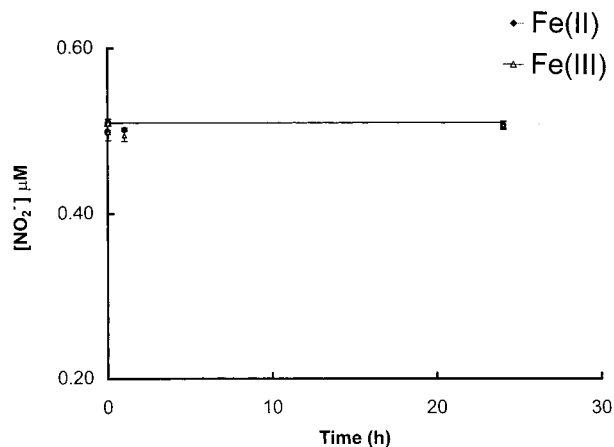
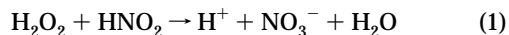


FIGURE 3. Concentration of nitrite (μM) as a function of time (h) in pH 4.5 synthetic rainwater in the presence of $0.1\ \mu\text{M}$ Fe(II) or $0.1\ \mu\text{M}$ Fe(III). Iron added as FeCl_2 or FeCl_3 .

deviation = $0.01\ \mu\text{M}$). The stability of the control indicates that nitrite loss was due to reaction with hydrogen peroxide and not oxygen and that the nitrite concentration change was not caused by degassing of HONO .

The reactivity of nitrite with hydrogen peroxide at pH 3.5, which is approximately the pK of HNO_2 of 3.3 (25), suggests that the protonated form of N(III) is the reacting species. This is consistent with earlier mechanistic and kinetic studies (refs 6 and 19 and references therein), which suggest that the overall reaction proceeds via eq 1



with an experimentally derived rate law of

$$\text{rate} = k[\text{H}^+][\text{HNO}_2][\text{H}_2\text{O}_2]$$

It was suggested that although rate changes, the mechanism of N(III) oxidation is not dependent on reagent concentrations (6), which is consistent with our results obtained using realistic concentrations of nitrite in rain. The dependence of nitrite oxidation on the concentration of both hydrogen ions and H_2O_2 in our experiments is consistent with this mechanism. Nitrite loss in the presence of hydrogen peroxide at pH 3.5 followed pseudo-first-order kinetics with a rate constant of $5.8 \times 10^{-6}\ \text{s}^{-1}$ (Figure 2B).

This study demonstrates that hydrogen peroxide is an important oxidant in direct conversion of N(III) species to nitric acid in rainwater at environmentally relevant concentrations. Data presented in Figures 1 and 2 are therefore important in understanding both atmospheric N and hydrogen peroxide cycles. Nitrite oxidation by H_2O_2 may be a source of nitrate in atmospheric waters, especially in cloud-waters and urban environments where concentrations of hydrogen peroxide and hydrogen ions are relatively high.

Other oxidants in rainwater, in addition to hydrogen peroxide, include molecular oxygen and dissolved iron(III). Oxidation by ozone was not considered in these experiments because of its relatively low water solubility at these pH values. A total of $0.1\ \mu\text{M}$ Fe(II) or $0.1\ \mu\text{M}$ Fe(III) was added to synthetic pH 4.5 rainwater containing $0.5\ \mu\text{M}$ nitrite in contact with air in order to evaluate the reactivity of nitrite toward iron and oxygen. No loss of nitrite was observed over 24 h with either $0.1\ \mu\text{M}$ Fe(II) or $0.1\ \mu\text{M}$ Fe(III) at pH 4.5 (Figure 3). Laboratory experiments conducted to evaluate reactivity of nitrite toward Fe(II) with hydrogen peroxide showed that the loss of nitrite did not increase significantly when synthetic rainwater containing $100\ \mu\text{M}$ hydrogen peroxide was compared to synthetic rain containing the same hydrogen

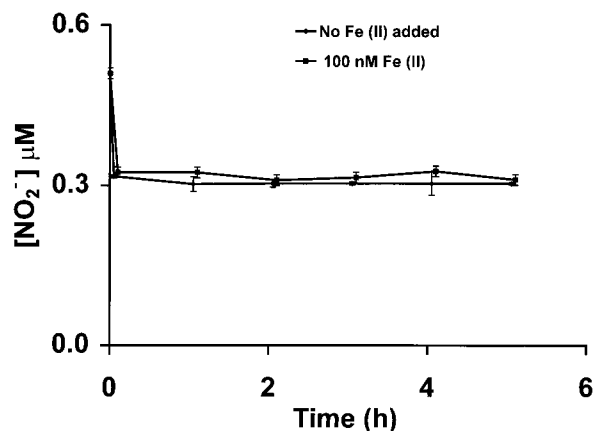


FIGURE 4. Concentration of nitrite (μM) as a function of time (h) in pH 4.5 synthetic rainwater with $100 \mu\text{M}$ H_2O_2 with and without added $0.1 \mu\text{M}$ Fe(II) . Fe(II) added as FeCl_2 .

peroxide concentration and also containing $0.1 \mu\text{M}$ Fe(II) at pH 4.5 (Figure 4). Net loss of nitrite was $0.2 \mu\text{M}$ with hydrogen peroxide alone or with hydrogen peroxide in the presence of $0.1 \mu\text{M}$ Fe(II) , suggesting that iron does not play a significant role in nitrite oxidation at this pH.

These results indicate that $0.50 \mu\text{M}$ nitrite is resistant to oxidation by 10 or $100 \mu\text{M}$ hydrogen peroxide at pH 4.5 or pH 5.5, with or without added $0.10 \mu\text{M}$ Fe(II) or Fe(III) . At pH 3.5, which is found in some rains and many cloudwaters, nitrite, probably as HNO_2 , is rapidly oxidized by $10 \mu\text{M}$ hydrogen peroxide alone. This suggests that maritime rain nitrite, because of its higher pH (4.9), should be stable longer than continental rain nitrite (pH 4.3) even though both have similar concentrations of hydrogen peroxide (11).

Acknowledgments

This work was supported by NSF Grant ATM-9530069. The Marine and Atmospheric Chemistry Research Laboratory group at UNC-Wilmington assisted with sampling and analyses.

Literature Cited

- (1) Deng, Y.; Zuo Y. *Chemosphere* **1998**, *36*, 181–188.
- (2) Eaton, A. D.; Clesceri, L. S.; Greenberg, A. E., Eds. *Standard Methods for the Examination of Water and Wastewater*, 19th

- ed.; American Public Health Association: Washington, DC, 1995; pp 4-1–4-5 and 4-81–4-84.
- (3) Kieber, R. J.; Seaton, P. J. *Anal. Chem.* **1995**, *34*, 3261–3264.
- (4) Bhattacharyya, P. K.; Veeraraghavan, R. *Int. J. Chem. Kinet.* **1977**, *9*, 629.
- (5) Damschen, D. E.; Martin, L. R. *Atmos. Environ.* **1983**, *17*, 2005.
- (6) Lee, Y. N.; Lind, J. A. *J. Geophys. Res.* **1986**, *91*, 2793–2800.
- (7) U.S. EPA. *Operations and Maintenance Manual for Precipitation Measurement Systems*. EPA-600/4-82-042b; U.S. Environmental Protection Agency: Research Triangle Park, NC, 1981.
- (8) Fitchett, A. W. In *Sampling and Analysis of Rain*; Campbell, S. A., Ed.; ASTM Special Technique Publication 823; ASTM: Philadelphia, PA, 1983; pp 50–60.
- (9) Topol, L. E.; Levon, M.; Flanagan, J.; Schwall, R. J.; Jackson, A. E. *Quality Assurance Manual for Precipitation Systems*; EPA/600/4-82-042a; Environmental Protection Agency: Research Triangle Park, NC, 1985.
- (10) Willey, J. D.; Kiefer, R. H. *Mon. Weather Rev.* **1990**, *118* (2), 488–494.
- (11) Willey, J. D.; Kieber, R. J.; Lancaster, R. D. *J. Atmos. Chem.* **1996**, *25*, 149–165.
- (12) Williams, K. University of North Carolina at Wilmington, Unpublished M.S. thesis results, 1998.
- (13) Willey, J. D.; Kiefer, R. H. *J. Elisha Mitchell Sci. Soc.* **1993**, *109* (1), 1–19.
- (14) Collis, Y.; Souchu, P.; Treguer, P. *Atmos. Res.* **1989**, *23*, 97–104.
- (15) Gorham, E.; Martin, F. B.; Litzau, J. T. *Science* **1984**, *225*, 407–409.
- (16) Hooper, R. P.; Peters, N. E. *Environ. Sci. Technol.* **1989**, *23*, 1263–1268.
- (17) Sakugawa, H.; Kaplan, I. R.; Shepard, L. S. *Atmos. Environ.* **1993**, *27B*, 203–219.
- (18) Sjodin, A. *Environ. Sci. Technol.* **1988**, *22*, 1086–1089.
- (19) Gunz, W. G.; Hoffmann, M. R. *Atmos. Environ.* **1990**, *24A* (7), 1601–1633.
- (20) Sakugawa, H.; Kaplan, I. R.; Tsai, W.; Cohen, Y. *Environ. Sci. Technol.* **1990**, *24* (10), 1452–1462.
- (21) Galloway, J. N.; Likens, G. E.; Keene, W. C.; Miller, J. M. *J. Geophys. Res.* **1982**, *87* (11), 8771–8786.
- (22) Likens, G. E.; Keene, W. C.; Miller, J. M.; Galloway, J. N. *J. Geophys. Res.* **1987**, *92* (D11), 13,299–13,314.
- (23) Eklund, T. J.; McDowell, W. H.; Pringle, C. M. *Atmos. Environ.* **1997**, *31* (23), 3903–3910.
- (24) Williams, M. R.; Fisher, T. R.; Melack, J. M. *Atmos. Environ.* **1997**, *31* (2), 207–217.

Received for review June 29, 1998. Revised manuscript received November 2, 1998. Accepted November 4, 1998.

ES980655O