



# The role of fossil fuel combustion on the stability of dissolved iron in rainwater



Joan D. Willey<sup>a,\*</sup>, Robert J. Kieber<sup>a</sup>, Joshua J. Humphreys<sup>a</sup>, Briana C. Rice<sup>a</sup>,  
Mark J. Hopwood<sup>b</sup>, G. Brooks Avery<sup>a</sup>, Ralph N. Mead<sup>a</sup>

<sup>a</sup> Department of Chemistry and Biochemistry, University of North Carolina Wilmington, Wilmington, NC 28403-5932, USA

<sup>b</sup> Ocean and Earth Science, University of Southampton, National Oceanographic Centre Southampton, Southampton SO14 3ZH, UK

## HIGHLIGHTS

- Dissolved Fe(II) has decreased in coastal NC rainwater.
- There is less stabilization of Fe(II) (aq) by fossil fuel combustion currently.
- Wet deposition of soluble Fe(II) has decreased to the North Atlantic Ocean.

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## ABSTRACT

The concentration of dissolved Fe(II) has decreased in coastal NC rainwater because of less complexation and stabilization of Fe(II) (aq) by automobile and coal combustion emissions. Better emission control has removed stabilizing organic ligands hence dissolved Fe(II) currently occurs more as inorganic iron, which is not protected against oxidation. Increasing rainwater pH allows oxidation by molecular O<sub>2</sub> in addition to H<sub>2</sub>O<sub>2</sub> and also increases the ratio of the ion pair Fe(OH)<sup>+</sup> to Fe(II) free ion, which increases the oxidation rates by both H<sub>2</sub>O<sub>2</sub> and molecular oxygen. The concentration of H<sub>2</sub>O<sub>2</sub> in rain has increased; hydrogen peroxide is the primary oxidant of inorganic Fe(II) in precipitation. The East Coast of the USA is also receiving less rain of terrestrial origin, which tends to be higher in dissolved iron and organic compounds. All these factors operate in the same direction and contribute to the lower concentrations and lack of stability of Fe(II) in rainwater currently observed. Results of this study suggest that wet deposition of soluble Fe(II) is an episodic, temporally variable factor in the iron cycle in oceanic regions adjacent to developed or developing coastal regions.

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## 1. Introduction

Iron in rainwater is an important part of the dynamic atmospheric redox system and serves as a catalyst for multiple atmospheric reactions. Rainwater iron can act as a phytoplankton nutrient once deposited to surface seawater contributing to regional variation in oceanic primary productivity, as well as variations in phytoplankton community structure (Sunda and Huntsman, 1997). Alterations in the concentration and reactivity of the various dissolved iron species in rainwater therefore affects many different aspects of atmospheric and marine geochemistry. Many of these changes can be tracked using the long-term dataset

on coastal rainwater composition generated by event sampling compiled at the University of North Carolina Wilmington since 1985.

Fe speciation studies conducted approximately a decade ago at this location demonstrated that dissolved iron occurred in approximately equal nM concentrations of Fe(II) and Fe(III) in rainwater (Willey et al., 2000b) even in the presence of more than 20 μM hydrogen peroxide (Kieber et al., 2003a; Willey et al., 2005). Additional studies demonstrated that Fe(II) is protected against rapid peroxide oxidation by complexation with a strong organic ligand(s) (Kieber et al., 2005). The stability of Fe(II) in rainwater was further demonstrated during rainwater-seawater mixing experiments both in Wilmington (Kieber et al., 2001b) and at the Bermuda Atlantic Time Series Station (Kieber et al., 2003b). Fe(II) can be produced photochemically from Fe(III) in rainwater,

\* Corresponding author.

E-mail address: [willeyj@uncw.edu](mailto:willeyj@uncw.edu) (J.D. Willey).

however unlike the stabilized Fe(II) in rainwater (Kieber et al., 2005), the photochemically produced Fe(II) oxidizes within hours of removal from light. Fe(II) therefore occurs in at least two forms in rainwater along with at least two classes of Fe(II) ligands, one extremely strong and one weaker (Willey et al., 2008) similar to that observed for copper in rain at this location (Witt et al., 2007).

The origin and composition of the Fe(II) ligands is unknown. However, previous research indicates that dissolved organic carbon (DOC) and chromophoric dissolved organic matter (CDOM) have both marine and terrestrial sources at this location (Avery et al., 2006; Kieber et al., 2006; Willey et al., 2000a). Terrestrial/continental rain has higher DOC and CDOM compared to marine rain (Kieber et al., 2006; Willey et al., 2000a), as well as higher dissolved Fe(II) and Fe(III) (Kieber et al., 2001a; Willey et al., 2000b). Based on  $^{14}\text{C}$  analysis and FTICR spectroscopy, both marine and terrestrial rain contain a significant fraction of organic carbon of fossil fuel origin (Avery et al., 2006; Mead et al., 2013). The DOC content in Wilmington rainwater has decreased by 48% between 1995 and 2013 due in part to the introduction of reformulated gasoline (RFG) in 1996 (Willey et al., 2006) while VOC (volatile organic carbon) emissions have decreased nationwide by 36% over this same time period (<http://www.epa.gov/airtrends/aqtrends.html>). The presence of less DOC from fossil fuel combustion during the same time period as Fe(II) concentrations have decreased suggests there may be a link between these two rainwater components.

The goal of the present study was to explore why the speciation of iron in rainwater has changed over the last 10 years at this location, with particular emphasis on processes that have impacted the stability of Fe(II) in rainwater, including changes in fossil fuel combustion. Understanding the mechanisms that contribute to the lifetime of Fe(II) both in rainwater and after deposition to surface seawater is critical to understanding the relative importance of rainwater Fe(II) in atmospheric processes as well as in the marine iron cycle.

## 2. Methods

### 2.1. Rainwater collection

Rainwater was collected on the University of North Carolina Wilmington campus ( $34^{\circ}13.9'\text{N}$ ,  $77^{\circ}52.7'\text{W}$ , 8.5 km from the Atlantic Ocean) on an event basis, which allows analyses or storage procedures to be initiated within minutes of collection, reducing the possibility of compositional changes between the time of rainfall and analysis. Rainwater samples were collected using Aerochem-Metrics Automatic Wet-Dry Precipitation Collectors. Trace metal clean procedures were used for all rain samples for iron analysis (Bruland, 1980; Bruland et al., 1979; Tramontano et al., 1987); samplers for trace metal analyses were modified to be trace metal clean (Kieber et al., 2001b; Tramontano et al., 1987). Samples for other analytes were collected in an automatic collector with a glass beaker that had been thoroughly rinsed with deionized water and combusted at  $400^{\circ}\text{C}$  for at least 4 h. A portion of each rain sample was filtered under low vacuum immediately upon collection through a  $0.4\ \mu\text{m}$  Millipore polycarbonate filter throughout 2002, and beginning in 2003 with a trace metal grade acid-washed  $0.2\ \mu\text{m}$  Gelman Supor<sup>®</sup> polyethersulfone filter for iron analysis. This change in filter pore size may have removed some Fe(III) but did not affect Fe(II) (Table 1) (Hopwood, 2015; Kieber et al., 2001b).

### 2.2. Automobile exhaust collection

Vehicle exhaust was collected from 13 model year 1998–2012 cars/light duty trucks including one diesel vehicle to look for Fe(II)

**Table 1**

Volume weighted average concentrations and standard deviations of the iron species indicated (nM) compiled on an annual basis or as summer quarters (July, August, September).  $N_1$  = number of samples for Fe(II) and Fe(III),  $N_2$  = number of samples for total Fe, na = not analyzed, and \* = July only.

Year	$N_1$	Fe(II)	Std dev	Fe(III)	Std dev	Fe <sub>Tot</sub>	Std dev	$N_2$	Fe(II)/Fe(III)
<b>Annual</b>									
1998–99	48	42	6	33	5	298	50	62	1.27
2001	54	31	6	48	8	231	49	44	0.65
2003	13	28	7	25	7	na	na	na	1.12
2008	53	10	2	11	2	121	25	36	0.91
2011–12	26	3.8	0.9	12	4	na	na	na	0.32
<b>Summer</b>									
1997	11	36	7	31	9	358	104	11	1.16
1998	16	44	12	31	10	306	50	16	1.42
2000	17	52	13	46	13	na	na	na	1.13
2001	17	30	7	28	7	183	37	16	1.07
2002	17	7.2	3.0	11	5	na	na	na	0.65
2008	23	10	3	13	4	225	28	6	0.77
2011	11	5.3	1.7	15	4	na	na	na	0.35
2013*	7	3.0	0.2	11	2	762	150	8	0.27

complexing capability (Table S1). Only single exhaust systems were measured. Exhaust was collected by placing a 500 mL FEP (fluorinated ethylene propylene resin) wash bottle with the end cut off attached to the tailpipe of a car secured with a pipe clamp. Before ignition of the vehicle the bottle was attached to the tailpipe and the opposite end of the apparatus was attached to a 250 mL low-density polyethylene (LDPE) bottle containing 250 mL of synthetic rainwater (SRW, pH 4.5 sulfuric acid). The sample was collected by bubbling exhaust through 250 mL of SRW for 10 min. Ten minutes was chosen because fluorescence and DOC concentrations fell in the range of previous published rain values after that sampling time (Kieber et al., 2006; Willey et al., 2000a). All exhaust was filtered ( $0.2\ \mu\text{m}$ ) prior to analysis and experiments.

### 2.3. Coal exhaust collection

Pittsburgh bituminous coal from the Pittsburgh formation in western Pennsylvania USA was combusted (coal sample 4.6 g, 8.1 g, 6.6 g, or 13.5 g) using a Bunsen burner. After 2–5 min of combustion the ignited coal was put into a 500 mL side-arm flask connected to the lab air system. The top was closed and a 250 mL low-density polyethylene (LDPE) bottle containing 250 mL of SRW was attached to allow the exhaust to bubble through the SRW. The collection lasted until the coal extinguished (up to 5 min), after which the SRW was filtered ( $0.2\ \mu\text{m}$ ). This combustion process was sufficient to reveal the possibility of reaction.

### 2.4. Analytical methods

#### 2.4.1. Fe analysis

All samples for trace metal analysis were processed in a class 100 laminar flow clean hood, stored in Teflon containers and analyzed in triplicate using trace metal grade reagents. Milli-Q Ultra Plus ( $\geq 18\ \text{M}\Omega\ \text{cm}^{-1}$ ) deionized water was employed to prepare pH 4.5  $\text{H}_2\text{SO}_4$  (synthetic rainwater, SRW) used to prepare standards and blanks. Fe(II) and Fe(III) were determined spectrophotometrically using a modification of the ferrozine method (Stookey, 1970). Fe(II) was measured minutes after addition of ferrozine while the sum of Fe(III) and Fe(II) was measured after reduction by hydroxylamine hydrochloride for 1 h followed by complexation with ferrozine. The resulting difference provided the concentration of Fe(III). Addition of ferrozine to Fe(III) standards without prior reduction resulted in no measureable Fe(II) after 1 h storage indicating that no Fe(II) was produced from Fe(III)

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