**Atmospheric
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Dynamics of the chemical composition of rainwater throughout Hurricane Irene

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Abstract

Sequential sampling of rainwater from Hurricane Irene was carried out in Wilmington, NC, USA on 26 and 27 August 2011. Eleven samples were analyzed for pH, major ions (Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+), dissolved organic carbon (DOC) and hydrogen peroxide (H_2O_2). Hurricane Irene contributed 16 % of the total rainwater and 18 % of the total chloride wet deposition received in Wilmington NC during all of 2011. This work highlights the main physical factors influencing the chemical composition of tropical storm rainwater: wind speed, wind direction, air mass back trajectory and vertical mixing, time of day and total rain volume. Samples collected early in the storm, when winds blew out of the east, contained dissolved components indicative of marine sources (salts from sea spray and low DOC). The seasalt components in the samples had two maxima in concentration during the storm the first of which occurred before the volume of rain had sufficiently washed out seasalt from the atmosphere and the second when the air mass dipped to low elevations over the Atlantic Ocean followed by rapid vertical mixing. As the storm progressed and winds shifted to a westerly direction, the chemical composition of the rainwater became characteristic of terrestrial storms (high DOC and NH_4^+ and low seasalt). This work demonstrates that tropical storms are not only responsible for significant wet deposition of marine components to land, but terrestrial components can also become entrained in rainwater, which can then be delivered to coastal waters via wet deposition. This study also underscores why analysis of one composite sample can lead to an incomplete interpretation of the factors that influence the chemically divergent analytes in rainwater during extreme weather events.

1 Introduction

Extreme weather events that include heavy rain and high winds can result in significant depositional fluxes of chemical species over short periods of time, resulting in a significant impact on the biogeochemistry of the receiving watersheds (Avery et al.,

2004). Most notably, tropical storm systems have been shown to be responsible for major depositions of sea salt (Na^+ and Cl^-) to land. Previous work at this site has shown that single tropical weather events contributed over half the annual wet deposition of chloride (Cl^-) in 1984, 1989 (Willey and Kiefer, 1993) and 2006 (Miller et al.,

5   2008). Similarly, the elemental analysis of rainwater collected during typhoon events in Okinawa Island, Japan revealed ion ratios consistent with the composition of sea salt (Sakihama and Tokuyama, 2005). The isotopic analysis of DOC in rainwater collected during two hurricanes revealed it was largely of marine origin (Raymond, 2005).

In addition to the deposition of marine-derived components to land as a result of

10   hurricanes and typhoons, shifting winds during the course of a storm could result in delivery of terrestrial compounds to coastal waters via wet deposition. For example, previous work at this site during Hurricane Isabel in 2003 showed high ammonium (NH_4^+) and amino acid concentrations when the air mass back trajectory coincided with a region with an active animal agricultural industry (Kieber et al., 2005). High fluxes

15   of heavy metals from anthropogenic sources have been reported in precipitation from typhoons in Taiwan (Cheng and You, 2010). Additionally, the DOC in rainwater is more bioavailable than river water (Avery et al., 2003), suggesting hurricanes can contribute significantly to the annual flux of bioavailable DOC (Avery et al., 2004). These large depositional events have significant implications for coastal waters that may be sensi-

20   tive to the deposition of nutrients (Kieber et al., 2005; Avery et al., 2004) and pollutants (Cheng and You, 2010) from terrestrial sources.

The degree to which various meterological factors (wind speed, direction and air mass elevation) control the chemical composition of rainwater throughout a tropical precipitation event remains uncertain. Previous studies were of partial analytical scope

25   (Kieber et al., 2005), had limited shifts in air mass back trajectories (Miller et al., 2008) or did not aim to sample with enough temporal resolution to demonstrate how changes in wind direction influence the chemical composition of rainwater throughout a single tropical event (Cheng and You, 2010). The goal of the present study was to carry out a suite of chemical analyses on analytes coming from different sources on samples

collected with high temporal resolution throughout a single tropical storm event so that the effects of a dynamic weather system could be assessed. Our coastal location is an ideal place to carry out such a study in which it is necessary to delineate marine and terrestrial sources. Additionally, the regular analysis of the chemical composition of rainwater at our location allows for an understanding of the significance of a single extreme weather event in the context of annual wet depositional patterns.

2 Methods

2.1 Sample collection

The 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° 13.9′ N, 77° 52.7′ W, 8.5 km from the Atlantic Ocean). All rainwater event samples were collected using an Aerochem Metrics (ACM) Model 301 Automatic Sensing Wet/Dry Precipitation Collector which housed a 4 l glass beaker placed within a HDPE plastic bucket. All glassware used in this study for sample collection, filtration and storage was combusted at 450 °C in a muffle furnace for a minimum of 4 h to remove organics prior to use.

Hurricane Irene made landfall on the Outer Banks of North Carolina on 27 August, 2011 as a Category 1 hurricane. Rain from the storm began the morning of 26 August in Wilmington, NC, approximately 200 km south of where the storm made landfall. From the time rain started until the storm had passed, rain was collected periodically (every 2 to 5 h) for a total of 11 individual samples and a total of over 200 mm of rain. Early samples (A–C) were collected for three distinct rain bands at the onset of the storm and later samples were collected when rain was continuous. Samples were analyzed immediately upon collection for hydrogen peroxide and pH. Rainwater was filtered (0.2-µm pore size, polysulfone) and 100 µl of 6 M HCl was added to a 40-ml filtered aliquot for DOC analysis. Anion samples were unfiltered and stored at 4 °C until analysis. Sam-

ples for all other analyses were filtered and stored at 4 °C in combusted glass vials until analysis could be carried out.

2.2 Chemical analysis

2.2.1 pH

Rainwater pH was measured using a Ross electrode calibrated with low ionic strength 4.10 and 6.97 buffers. Ionic strength adjuster (pHix Orion Research Incorporated, Boston, Massachusetts) was added to each sample to match the ionic strength of samples to that of buffers. Measurements were ±0.01 pH units in the pH 4 range and ±0.03 for samples with pH 5 or above.

2.2.2 Hydrogen peroxide

Hydrogen peroxide (H_2O_2) was analyzed using a fluorescence decay technique involving the peroxidase-mediated oxidation of the fluorophore scopoletin by H_2O_2 in rain buffered at a pH of 7 with a phosphate buffer (Kieber and Helz, 1986). Fluorescence measurements were made on a Turner Designs (Sunnyvale, CA) Model 7200-000 fluorometer equipped with a H_2O_2 module wavelength filter ($\lambda_{ex} = 365 \pm 10$ nm, $\lambda_{em} = 486 \pm 10$ nm). Calibration curves were obtained by preparing standards in ultrapure water (Milli-Q). H_2O_2 standard solutions were prepared fresh from a stock solution of 0.1 M H_2O_2, which had been standardized by titration with phenylarsine oxide. The method has an analytical precision of 2 % relative standard deviation (% RSD) at ambient rainwater concentrations (Kieber and Helz, 1986). All samples were analyzed in triplicate for H_2O_2.

2.2.3 Anions and cations

Anions (Cl^-, NO_3^-, and SO_4^{2-}) were measured with suppressed ion chromatography using a Dionex IC system outfitted with an IonPac® AS14A column and ASRS 300

4-mm suppressor. Standards were prepared from the sodium salts of each anion in ultrapure water (Milli-Q). Anions measurements had a RSD $\leq 5\%$.

Analysis of cations (Na^+, Mg^{2+}, K^+ and Ca^{2+}) was performed under standard Inductively Coupled Plasma (ICP) conditions with a PerkinElmer Model Optima 2100 DV Optical Emission Spectrometer. Samples were acidified to 2% with trace metal grade nitric acid and were allowed to come to room temperature before analysis. A standard curve for each metal was constructed using standards prepared in 2% nitric acid from commercially available ICP stock solutions of Na^+, Mg^{2+}, K^+ and Ca^{2+} (Clåritas). Absorbance was analyzed at 589.592 nm for Na, 285.213 nm for Mg, 766.490 nm for K and 317.933 nm for Ca. All ICP measurements had a RSD $\leq 3\%$.

Nonseasalt sulfate (NSS) was calculated by subtracting sulfate from seasalt (as determined from the constant molar ratio of SO_4^{2-} to Na^+ in seasalt of 0.0601) from the total concentration of sulfate. Sodium data was not available for non-hurricane rain samples in 2011 so NSS was determined assuming a constant ration of Cl^- to SO_4^{2-} of 0.0517. Previous work at our coastal site has demonstrated using either Na^+ or Cl^- as the proxy for sea salt yields results that are within 1% of each other (Willey and Kiefer, 1990), less than the analytical precision of the method.

2.2.4 Ammonium

Ammonium (NH_4^+) analysis was carried out using a modified version of a fluorometric method (Holmes et al., 1999) in which o-phthaldialdehyde (OPA) reacts with ammonia to form a fluorescent chromaphore. The working reagent was prepared by adding 50 ml of an acetonitrile solution containing 2.0 g OPA to 1 l of a 0.1 M borate buffer solution containing 0.3 mM sulfite (to suppress reaction of OPA with free amino acids). The working reagent was stored in the dark for 24 h prior to use. Standards were prepared in ultrapure water (Milli-Q) with NH_4Cl. Analysis was carried out on filtered rainwater samples that had been stored in combusted glass containers at 4 °C for no more than one week at the time of analysis. 1.5 ml of samples and standards were combined with 5 ml of the working reagent in Nalgene HPDE sample vials and allowed to react in the

dark for 3 h. Fluorescence measurements were made on a Turner Designs (Sunnyvale, CA) Model 7200-000 fluorometer equipped with a wavelength filter ($\lambda_{ex} = 365 \pm 10$ nm, $\lambda_{em} = 430 \pm 10$ nm). Each sample and standard was carried out in triplicate. Samples were analyzed without working reagent and with standard additions to correct for background fluorescence and matrix effects, respectively. The detection limit for NH_4^+ in rain by this method is 0.17 µM (Kieber et al., 2005).

2.2.5 Dissolved organic carbon

Dissolved organic carbon (DOC) was determined by high temperature combustion (HTC) using a Shimadzu TOC 5000 total organic carbon analyzer equipped with an ASI 5000 autosampler. Standards were prepared from potassium hydrogen phthalate (KHP) in Milli-Q H_2O. Each sample was injected 4 times with a relative standard deviation (RSD) ≤ 3 %. The detection limit for this instrument is 4 µM DOC.

2.3 Air mass back trajectories and supporting meteorological data

Modeled air mass back trajectories (Draxler and Rolph, 2012) were used to track the history of the air mass over Wilmington at the time of sample collection. Trajectories were calculated for the 24 h preceding each sample collection for the air mass at an elevation of 500 m over our sampling location. Supporting meteorological data was obtained from an Automated Surface Observation System (ASOS) at Wilmington International Airport, which is located less than 5 km from our study site. Wind speed and direction data were retrieved from Weather Underground (www.wunderground.com) and are shown in Fig. 1a for the time period of interest. The track of Hurricane Irene was obtained from the National Hurricane Center's GIS archive (www.nhc.noaa.gov/gis).

3 Results

Over 200 mm of rain was sampled throughout Hurricane Irene for a total of 11 samples (Fig. 1b). The results of all chemical analyses for each sample sequentially labeled A–K are presented in Table 1. Rainfall intensity for each sample was calculated by di-
5 viding the rainfall amount by the duration of rain for each sample. The duration of rain was either observed or, when rain was continuous, was the amount of time since the previous sample was collected. Wind direction, wind speed and total rain accumulation throughout the time course of the storm is presented in Fig. 1a and b. Easterly winds predominated early in the storm with a shift towards the west later in the event with
10 sustained winds generally less than $20 \, \text{m s}^{-1}$ throughout the storm. Four different patterns of variation in the concentrations of rainwater components were observed during Hurricane Irene depending upon the origin of the analytes.

3.1 Major ions from seasalt

Concentrations of Cl^-, Mg^{2+}, K^+ and Ca^{2+} were compared to the concentration of Na^+
15 in each sample collected during Hurricane Irene to determine if they originated from seaspray. The molar ratio of Cl^- to Na^+ for these samples (Fig. 2a) was very close to that in seawater (1.165) which has been observed previously at this (Willey and Kiefer, 1993) and other (Sakihama and Tokuyama, 2005) coastal locations. The Mg^{2+} and K^+ to Na^+ ratios indicated a seasalt source of these ions as well (Fig. 2b and d). The
20 data comparing concentrations of Ca^{2+} to Na^+ were less clear as Ca^{2+} levels were higher than would be predicted from a uniquely seasalt source as evidenced by the predominance of data above the line representing the Ca:Na ratio in seasalt (Fig. 2c). The data presented in Fig. 2c suggest that there are significant additional sources of Ca^{2+} to rainwater at this location during tropical events, perhaps suspension of $CaCO_3$
25 containing soils into the air during periods of high wind. Cluster analysis of rainwater composition at this location previously indicated that calcium concentrations were more closely associated with agricultural activities than with seasalt (Willey and Kiefer, 1993).

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The concentrations of seasalt components in rain were highly variable throughout the hurricane with two distinct maxima during the sampling regime (Fig. 3). There was however no correlation between these concentrations rainfall rate or wind speed ($p > 0.1$). A correlation with wind speed was observed in typhoon rain in Okinawa, Japan, by Sakihama and Tokuyama (2005). An initial increase in seasalt deposition through the first maximum at sample C was followed by a decrease to minimum concentration in sample F. Increased seasalt concentrations were again observed in samples G and H with lower concentrations occurring in the last three samples analyzed. The total deposition of chloride during the storm was significant in the context of annual wet deposition with Hurricane Irene accounting for 18 % of the total wet deposition of Cl$^-$ at this location in 2011.

3.2 Dissolved organic carbon and ammonium from terrestrial sources

The patterns of DOC and NH$_4^+$ concentrations throughout the hurricane were similar to each other, but do not resemble the pattern seen for seasalt components (Fig. 4). DOC and NH$_4^+$ concentrations were low ($< 20\,\mu$M DOC and $< 1.5\,\mu$M NH$_4^+$) in the samples collected early and in the middle of the storm while later samples had a marked increase in concentration for both analytes. This pattern suggests DOC and NH$_4^+$ have similar, primarily nonmarine sources (Kieber et al., 2005; Willey et al., 2000).

3.3 Nitrate, nonseasalt sulfate and H$^+$ from anthropogenic sources

The concentrations of nitrate (NO$_3^-$), nonseasalt sulfate (NSS) and the H$^+$ ion were all extremely low compared with more typical Wilmington rainwater (Willey et al., 2006). These concentrations were lowest in mid-storm samples with higher concentrations being detected at the beginning (samples A–C) and end (samples J and/or K) of the storm (Fig. 5). With the exception of sample H for NSS, the similar pattern of changing concentrations for NO$_3^-$, NSS and H$^+$ during Hurricane Irene is consistent with the observation that these analytes are generally positively correlated in rainwater (Willey

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and Kiefer, 1993; Hooper and Peters, 1989). NO_3^- and NSS are both formed as their corresponding acids (HNO_3 and H_2SO_4) upon oxidation of NO_x and SO_2, respectively, that are both emitted from the burning of fossil fuels (Calvert et al., 1985).

3.4 Hydrogen peroxide from photochemical production

5 The highest concentrations of H_2O_2 were detected in samples A–C collected early in the storm during the daylight hours of 26 August (Fig. 6). Concentrations decreased to below 1.5 µM for much of the remaining duration of the storm, which occurred throughout the night and morning of 27 August. The concentration of H_2O_2 did not change until last sample (K) was collected in the afternoon of 27 August; this had a concentration

10 near 5 µM. The higher H_2O_2 concentrations recorded for samples collected during the peak sunlight intensity daylight hours is similar to the pattern observed for hydrogen peroxide in non-tropical events measured at this location during the summer (Avery et al., 2001) and are most likely due to photochemical generation of H_2O_2 in the gas phase from hydroperoxy radicals which are subsequently scavenged into the aqueous

15 phase as rain (Gunz and Hoffmann, 1990; Moller, 2009).

4 Discussion

Changes in air mass origin and elevation as well as wind speed and direction experienced in Wilmington throughout Hurricane Irene allowed for an evaluation of how these physical factors influence the composition of rainwater throughout a single extreme

20 weather event. The 24-h air mass back trajectories for air at an elevation of 500 m over Wilmington at the time of each sample collection are presented in Fig. 7. The air mass origin (Fig. 7e) was marine initially (samples A–H) with an increase in terrestrial influences with shifting wind direction as the storm passed by the region (samples I–K). The vertical movement of the air mass dipped to lower elevations followed by rapid vertical

25 mixing (Fig. 7c) in the middle of the storm (samples G-H-I) relative to the initial and

ending samplings (Fig. 7a, b and d). The air mass and elevation changes of Hurricane Irene presented in Fig. 7 represent four distinct periods which were used to interpret the compositional fluctuations observed in the sequential samples.

4.1 Period I: early rain bands (samples A–C)

The initial samples collected from distinct rain bands early in the storm were characterized by high seasalt (Fig. 3) concentrations, which is consistent with samples collected at this site for non-hurricane rains of marine origin. Non-hurricane marine rains (n = 18) had a volume weighted average Cl^- concentration of 33.3 µM at this location in 2011. The higher seasalt content of the early hurricane samples relative to typical marine storms is likely a result of increasing wind speed and wave action during this time that entrained high levels of seasalt aerosols in the atmosphere (Sakihama and Tokuyama, 2005).

In addition to wind speed, total rain volume is an important factor to consider with regard to the concentration of seasalt in rainwater. The discontinuous rainfall during Period I resulted in a small total volume of rain during this time (Fig. 1b) and contributed to high seasalt concentrations in samples A–C with the highest concentrations recorded for the lowest volume sample C when the rainfall intensity was relatively low (Table 1). All other components (H^+, H_2O_2, DOC, Ca^{2+}, NH_4^+, NO_3^-, and NSS) also had concentration maxima in sample C demonstrating the importance of rain volume in controlling concentrations of all components, regardless of origin.

Concentrations of other components such as NO_3^- and NSS in samples collected during period I were typical of those recorded in other non-hurricane marine storms in 2011. The volume weighted averages of NO_3^- and NSS in non-hurricane marine rain samples (N = 18) at our rain site in 2011 were 6.52 µM and 2.85 µM, respectively. This suggests that levels of NO_3^- and NSS recorded in the first three samples of Hurricane Irene are typical of what is observed at our location during non-hurricane marine rain events and these initial samples likely represent removal of water soluble aerosols from the troposphere by rainfall.

4.2   Period II: wash-out (samples D–F)

Wind speed increased and rainfall became continuous as our sampling campaign continued (Fig. 1a). Despite a previous report of wind speed and seasalt concentration being positively correlated in typhoon rains (Sakihama and Tokuyama, 2005), levels of seasalt (Na^+, Cl^-, Mg^{2+}, K^+) decreased from the maximum observed in sample C to a minimum concentration in sample F even though winds speeds during sampling F were approximately 3 times higher than during sampling C (Fig. 1). The previous study included 2–3 samples for each typhoon, which may not have allowed for an analysis of how additional factors like air mass back trajectory, rain amount and air mass heights influence seasalt concentrations in rainwater. We attribute the decrease in seasalt concentrations during this second period of Hurricane Irene to the washing out of seasalt as the total rain volume accumulates and relatively little change in the air mass trajectory is observed. This interpretation is supported by the decreasing or nondetectable concentrations of all other analytes (DOC, NH_4^+, H^+, H_2O_2, NO_3^-, NSS and Ca^{2+}) during this period as well.

4.3   Period III: low elevation marine air mass (samples G and H)

There was an increase in seasalt concentrations in samples G and H after the period of wash out. This sampling period also corresponds to when the eye of Hurricane Irene was closest to our sampling location (approximately 130 km away when sample H was collected, Fig. 7f). Air mass back trajectories indicate the air masses over Wilmington at the time of these sample collections had previously been at low elevations (< 50 m, Fig. 7c) over the ocean surface. When the air mass dips to elevations close to the sea surface and then is lifted, seasalt again becomes entrained in rainwater. A similar effect was observed at this site during tropical storm Ernesto when Cl^- ion increased mid-storm, eventually reaching a concentration over 1 mM (Miller et al., 2008). Although sample I had a similar air mass elevation (Fig. 7d) to samples G and H, the air mass traveled over significantly more land before reaching Wilmington, so seasalts

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were washed out before reaching the sampling site. The increased turbulence in the atmosphere during this period is also indicated by an apparent decrease in wind speed preceding samples G and H when more vertical mixing likely occurred (Fig. 1a). Components with predominately terrestrial sources (DOC, NH_4^+, NO_3^-, NSS) remained low or nondetectable during Period III as they had been washed out during Period II and the air mass had not yet shifted to over land where their levels could be replenished.

4.4 Period IV: terrestrial air mass (I–K)

The final samples collected in our campaign saw increasingly terrestrial influences as winds shifted to out of the north and west (Fig. 1). This was reflected in the composition of samples with increased concentrations of DOC, NH_4^+, NSS, NO_3^- and H^+ (Figs. 4 and 5) as seasalt components were again diminished (Fig. 3). DOC is higher in rainwater events with more terrestrial air mass back trajectories because of additional natural and anthropogenic inputs of organic material into the atmosphere (Willey et al., 2000). Natural terrestrial sources of DOC may become increasingly significant during extreme weather events such as hurricanes when high wind speeds suspend soil or plant material in the air, resulting in DOC levels at the end of the storm that far exceed concentrations measured in earlier samples.

Ammonium concentrations during Hurricane Irene (Fig. 4) had a similar concentration profile as Hurricane Isabel when it passed by this location in 2003. High NH_4^+ samples ($> 4\,\mu M$) in the previous study had air mass back trajectories like those of samples J and K (Fig. 7e). These higher NH_4^+ concentrations during the latter part of the sampling campaign can be attributed to the air mass passing over a region with agricultural activities which is a major source of NH_4^+ to the atmosphere (Kieber et al., 2005). Specifically, the large swine population in North Carolina's Coastal Plain region where trajectories J and K passed directly through is a major local source of ammonium in rainwater (Walker et al., 2000).

Although NSS, NO_3^- and H^+ increased at the end of the storm (Fig. 5), they did not exceed levels experienced in Period I as DOC and NH_4^+ did. We suggest this is

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a result of the differences in the lifetime and source for these groups. After wash out during Period II NO_3^- and NSS most likely have not had time to be replenished in the atmosphere even as the air mass shifted to terrestrial trajectories. Likewise, H_2O_2, which is photochemically generated in the atmosphere, shows only a slight increase in the final sample that was collected in the early afternoon of 27 August (Fig. 6). DOC and NH_4^+, on the other hand, may be redeposited via rain in a state that is not chemically altered or geographically removed from their terrestrial sources.

5 Implications

Examining factors that influence compositional alterations of rainwater during tropical weather events is important because these systems can contribute large, episodically significant wet depositional fluxes of chemically divergent analytes in rainwater over relatively short time scales. Table 2 summarizes the contribution of Hurricane Irene to total annual wet deposition of all components for which annual data is available. Most significant is the contribution by Hurricane Irene of 18 % of the annual wet deposition of Cl^- at this location. The annual contribution of other seasalt components was likely just as considerable, but annual data for these species were not available. Even though this is a large percentage of the total, it is less than other hurricanes which typically contribute approximately half of the annual chloride (Willey and Kiefer, 1993; Miller et al., 2008). The high volume of rainfall experienced during the hurricane resulted in total deposition of other rainwater components that was 1.4–3.9 times that of a typical rain event experienced at this location in 2011. The projected increase in severe storms due to climate change could mean the contribution of these large depositional events to annual wet depositional patterns may become more significant in the future.

The eleven sequential collections reported for Hurricane Irene represent the most detailed temporal analysis of rainwater during a tropical event to date. Hurricane Irene also presented a unique opportunity to understand the factors that drive compositional changes of rainwater throughout an extreme weather event. Parameters such as air

mass origin and elevation as well as wind speed influenced analyte concentrations although the relative importance of these factors was a function of the source of analytes in rainwater. Total rain volume was an important variable for all components measured regardless of source but a simple washing out of rainwater constituents was not observed. This work underscores why analysis of one composite sample cannot capture the complexity of factors that influence compositional changes in rainwater during extreme weather events like Hurricane Irene.

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Table 1. Summary of data for samples collected throughout Hurricane Irene (26–27 August 2011). All concentrations are reported in $mg\,l^{-1}$. (NA = not analyzed).

Sample	Collection time	Amount (mm)	Rainfall intensity $(mm\,h^{-1})$	pH	H_2O_2	DOC	Cl^-	NO_3^-	SO_4^{2-}	Na^+	Mg^{2+}	K^+	Ca^{2+}	NH_4^+
A	9:45	7.1	7.7	5.39	0.40	0.05	2.83	0.17	0.47	1.4	0.15	0.039	0.13	0.0075
B	12:50	9.1	11.0	5.28	0.41	0.11	2.73	0.14	0.44	1.0	0.16	0.037	0.083	0.012
C	15:00	4.1	2.7	4.94	0.65	0.21	9.52	0.28	1.7	5.2	0.64	0.23	0.28	0.026
D	17:35	16.0	8.3	5.30	0.14	< 0.04	4.22	0.037	0.57	1.9	0.26	0.064	0.10	< 0.003
E	19:35	17.2	8.6	5.43	0.038	< 0.04	2.06	0.029	0.29	0.90	0.14	0.024	0.056	< 0.003
F	21:00	23.6	16.6	5.43	0.040	< 0.04	0.087	0.014	0.034	0.088	0.0080	< 0.004	0.010	< 0.003
G	0:05	40.1	13.0	5.66	0.032	0.18	1.36	0.052	0.20	0.70	0.095	0.043	0.13	0.012
H	2:35	27.2	10.9	5.86	0.046	0.19	4.09	0.050	0.63	1.5	0.20	0.068	0.080	0.019
I	5:40	26.7	8.7	5.71	0.040	0.40	0.348	0.056	0.075	0.28	0.026	0.033	0.036	0.051
J	10:45	32.8	6.5	5.28	0.024	NA	0.208	0.048	0.26	0.25	0.011	0.021	0.038	0.083
K	14:15	5.1	1.6	5.25	0.19	1.48	0.262	0.16	0.24	0.21	0.019	0.040	0.052	0.12

Table 2. Contribution of Hurricane Irene to the annual wet deposition of various species at this location. Volume Weighted Average (VWA) concentrations for non-hurricane ($N = 88$) and Hurricane Irene samples are in µM. When concentrations were nondetectable (samples D–F for DOC and NH_4^+), concentrations were assumed to be half the detection limit (Table 1).

	% annual wet deposition from Hurricane Irene	VWA in Hurricane Irene rainwater	VWA for non-hurricane 2011 rainwater
H^+	3.4 %	3.5	19
H_2O_2	2.3 %	2.6	22
DOC	3.1 %	16	95
Cl^-	18 %	50	31
NO_3^-	1.5 %	0.96	12
NSS	3.0 %	1.1	7.0
NH_4^+	2.6 %	1.6	10.1[a]
volume	16 %	210 mm	8.5 mm

[a] Annual data were not available for NH_4^+ in 2011 so the value reported is from annual VWA reported for this location in Kieber et al. (2005).
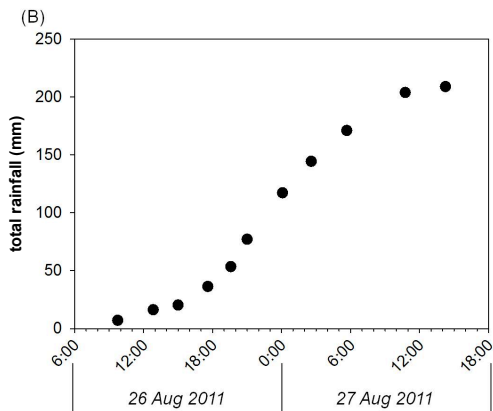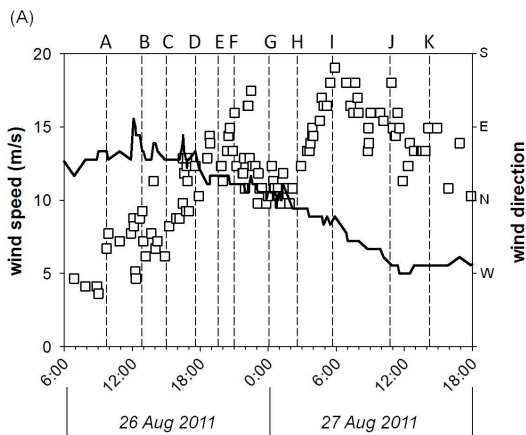
Fig. 1. (A) Plot of wind speed (open symbols) and direction (solid line) throughout Hurricane Irene. Vertical dashed lines indicate when rainwater was collected. **(B)** Cumulative volume of rain collected (mm) versus time.
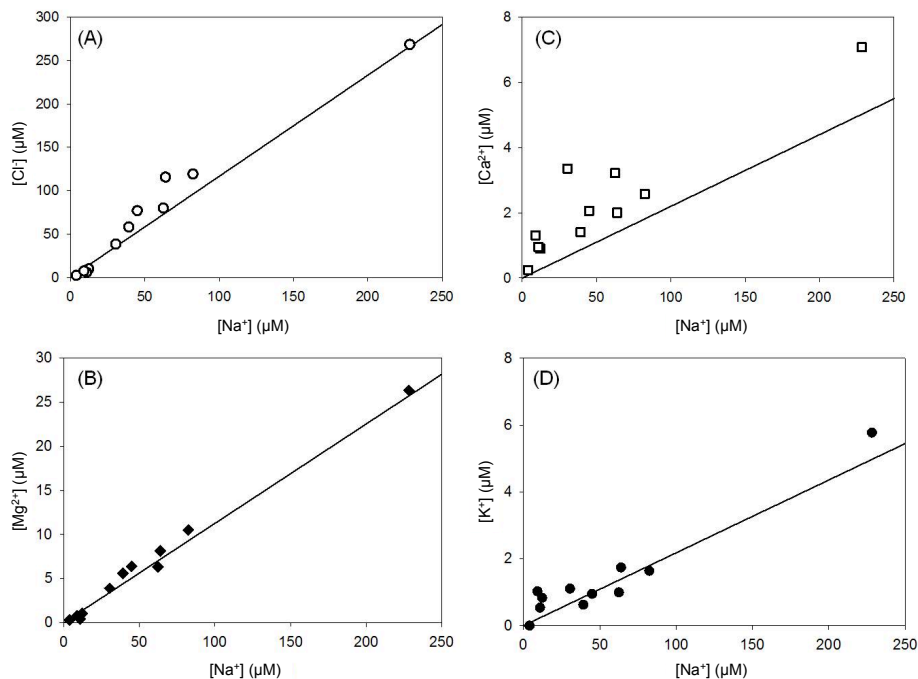
Fig. 2. Correlations of **(A)** Cl$^-$, **(B)** Mg^{2+}, **(C)** Ca^{2+} and **(D)** K$^+$ with Na$^+$. Solid lines represent molar ratios in sea salt.

Chemical composition of rainwater throughout Hurricane Irene

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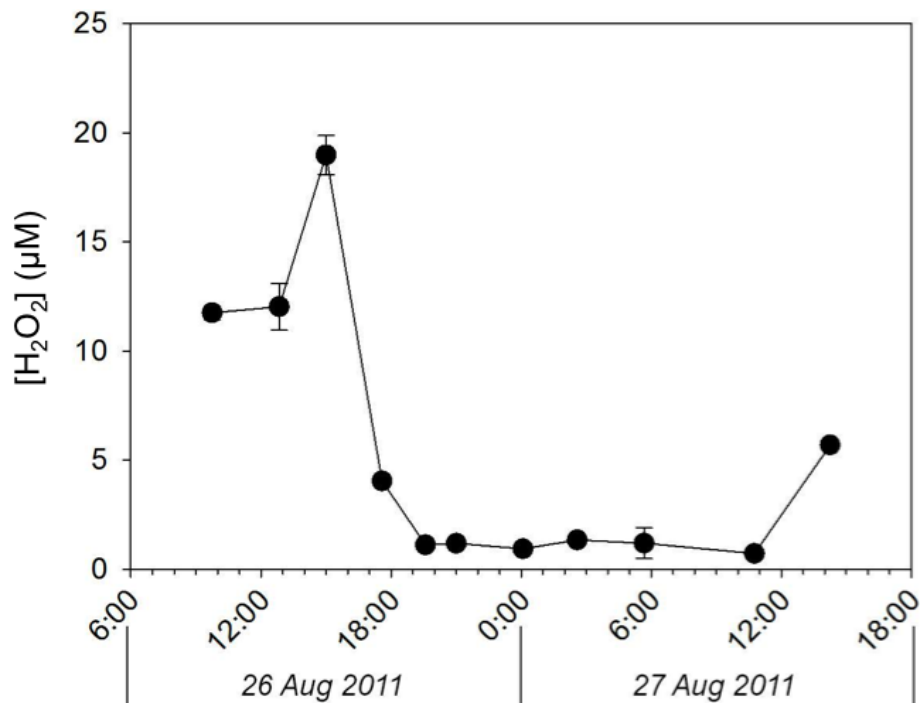| Abstract | Introduction |
| Conclusions | References |
| Tables | Figures |

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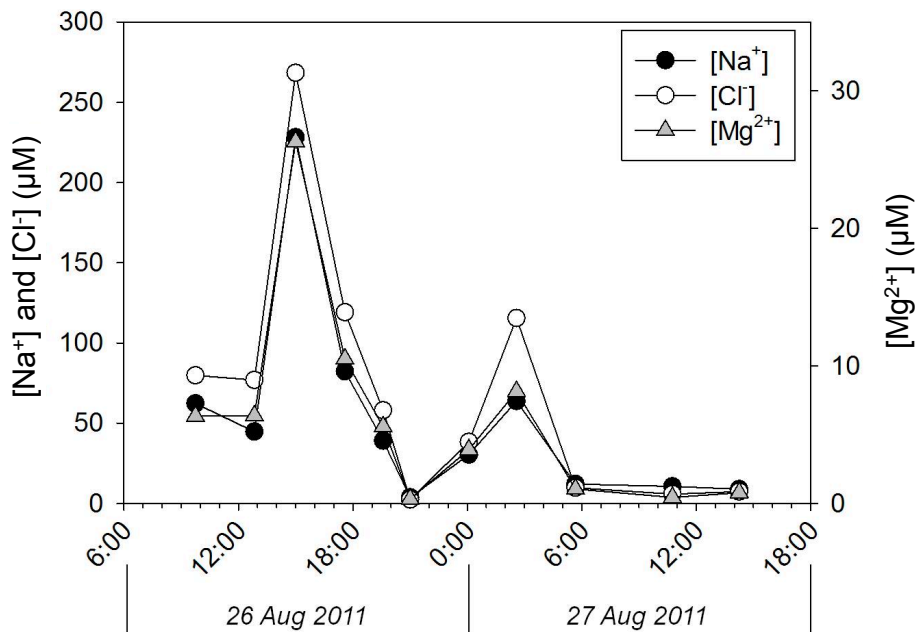
Fig. 3. Concentrations of seasalt components Na^+, Cl^- and Mg^{2+} throughout Hurricane Irene.
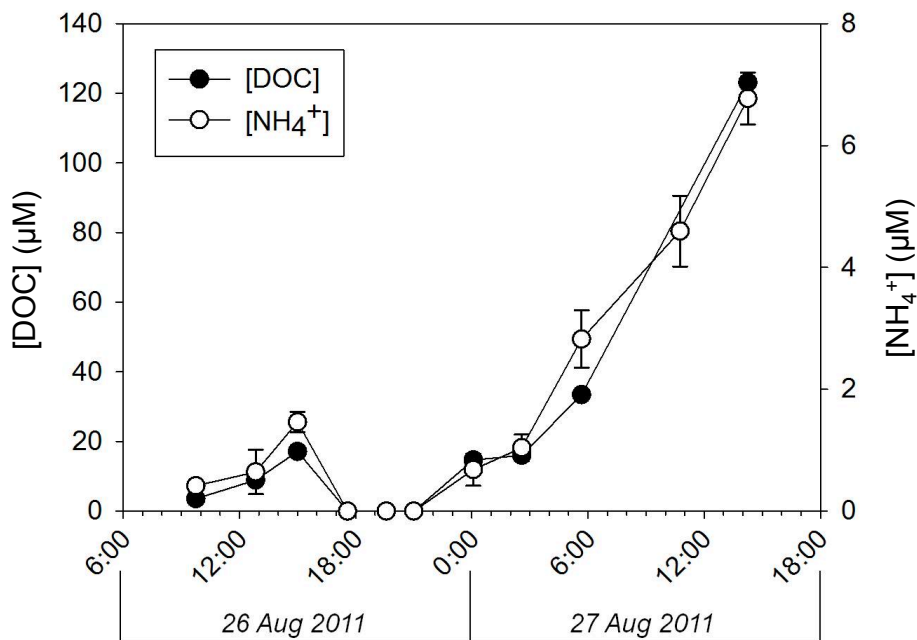
Fig. 4. Concentrations of DOC and NH_4^+ in rainwater collected throughout Hurricane Irene.
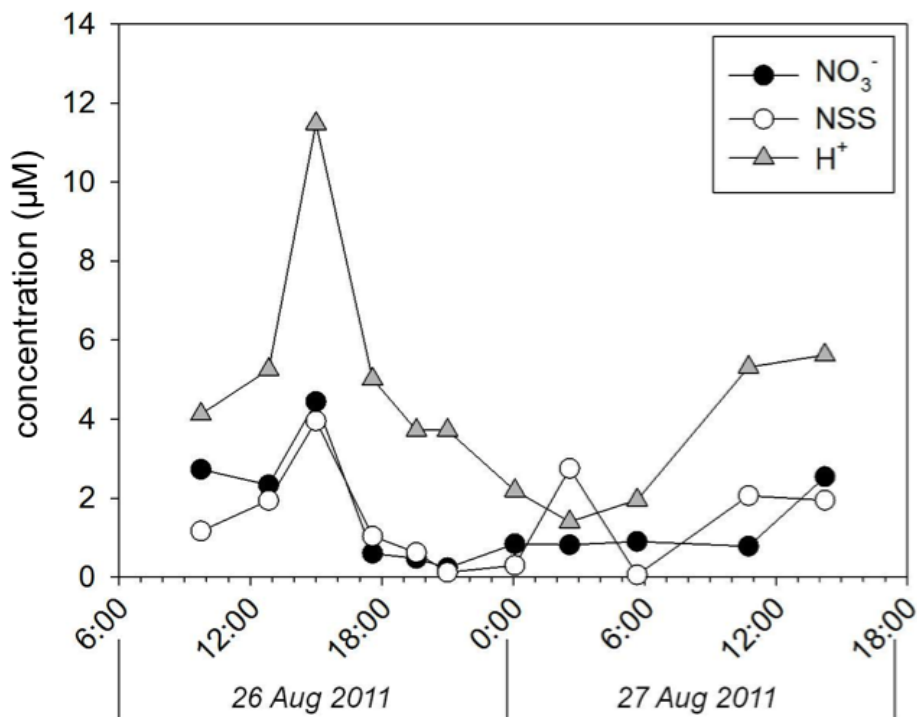
Fig. 5. Concentrations of NO_3^-, NSS and H^+ ion throughout Hurricane Irene.

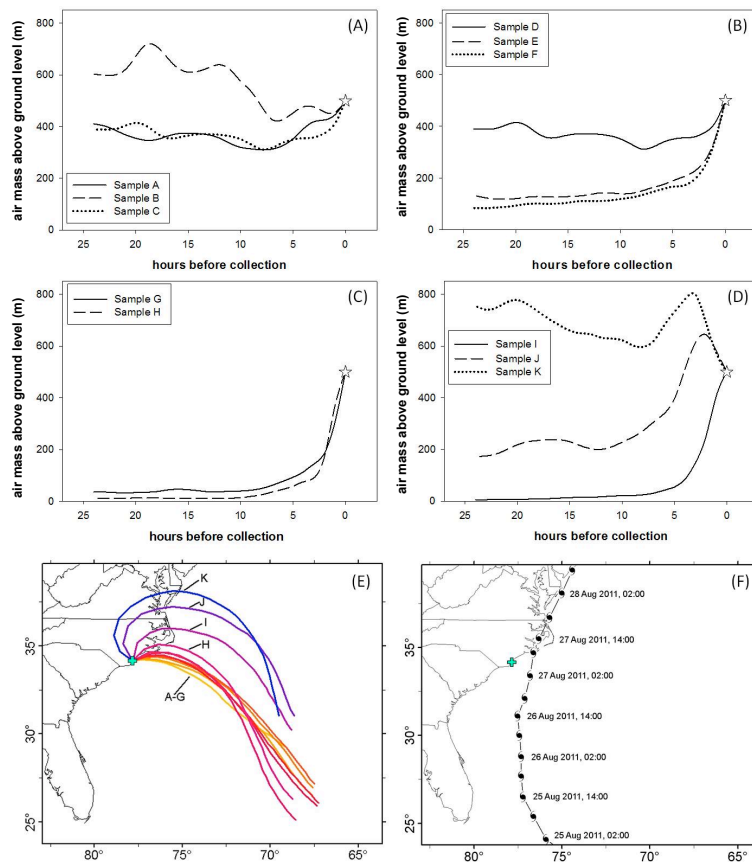**Fig. 6.** Concentrations of H_2O_2 throughout Hurricane Irene.

Fig. 7. Vertical movement of 500-m air mass during the 24 h preceding sample collection for samples during **(A)** period I, **(B)** period II, **(C)** period III and **(D)** period IV. **(E)** Air mass back trajectories at an elevation of 500 m for 24 h preceding each sample collection. **(F)** Track of Hurricane Irene. The sampling location is indicated by "+" symbol.

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