

Author response to reviewer comments on “Dynamics of the chemical composition of rainwater throughout Hurricane Irene”

We thank both reviewers for their careful and thoughtful reviews of our manuscript. Their commentary allowed us to improve the quality and clarity of the manuscript. We have reproduced the reviewer comments below (italicized) with our specific responses to each.

Response to Reviewer #1

Methods. Were any trace elements sampled and analyzed in parallel, as this laboratory is well known for them and their species? Were any components of the carbonic acid cycle analyzed, as with pH well defined anions and insight as to the origin of the Ca excess?
We did analyze some samples for Fe(II/III), but the dataset is incomplete due to availability of personnel to carry out the analysis and loss of power in the lab during the storm that prevented reliable analysis of time-sensitive samples. We did not analyze for any inorganic carbon species so unfortunately we cannot include this in our discussion of the Ca excess.

Page 5, line 6: What is a ration? The constant ion ratio of sea salt chloride to sulfate should be the inverse of 0.0517.

The work “ration” was a typo and has been corrected to be “ratio”. We have reversed Na^+ and Cl^- with SO_4^{2-} in this section so the descriptions are now consistent with the ratios of 0.0601 and 0.0517.

In fact, Fig. 2A suggests there is a small yet resolved excess of Cl relative to Na, as expected during photo oxidation of aerosol chloride. The authors should consult the paper by Keene, et al. on how to best correct for non-sea salt sulfate.

Figure 2A: This is a good point about chloride excess and we have added it to our discussion of Figure 2A in section 3.1 along with the Keene, et al. reference.

Section 2.3: What was the basis for selecting 500 meters for the air mass trajectories; the assumed altitude of rain during such storms?

The elevation of 500 m for air mass back trajectories was used because this is within the well-mixed boundary layer from which precipitation originates. Our group has previously used this elevation for air mass back trajectories in examining the chemistry of hurricane precipitation. A statement has been added to section 2.3 to clarify this: “This elevation was selected as an approximation for the well-mixed boundary layer from which precipitation originated (Walker et al., 2000; Kieber et al., 2005; Miller et al., 2008).” Additional analysis at higher elevations (1000 m) using the HYSPLIT model (not shown) yielded similar results.

Section 3: The annual proportion of the 200 mm (16%) should be reiterated here.

We reiterated the fact that Hurricane Irene was responsible for 16% of the precipitation experienced at our sampling location at the beginning of the results section

In fact the proportion of Cl to Na is not very close to that in sea water, indicating as noted above a small but well resolved excess of Cl for the reasons given.

Yes, we have added a statement pointing out that in fact there is an excess of chloride relative to Na^+ in Section 3.1, indicating some source other than seasalt is contributing to the level of Cl^- detected.

Page 7: Are the CaCO_3 soils local or long range? Again the source might be resolved from solving the carbonic acid system, if the alkalinity were known or assumed conservative in the sea salts.

This is an excellent point regarding the origin of the calcium excess. Unfortunately we were not able to measure inorganic carbon species in our samples to better address it. We do, however, know that local soils contain CaCO_3 and local agriculture uses lime.

Section 3.3: Table 2 should be cited again. The correlation of the acid components should be made with a figure or at least the statistics.

We have added a reference to table 2 in the first sentence of Section 3.3. The statement about acid components has been modified to include the statistics: “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 ($n = 11$, $r > 0.70$, $p < 0.02$ for all correlations, Willey and Kiefer, 1993; Hooper and Peters, 1989).”

Section 3.4: In fact, the hydrogen peroxide shows the same minor peak (Fig. 5) early in the storm as do the acid components. How is this related to the same photo peak or wrap around effect of the storm?

We have added a statement to this section pointing out that the peak H_2O_2 concentration is a consequence of low rain volume and high solar intensity during the preceding time period.

Section 4.1: The vertical movement as shown in Figure 7 is not high, low and then high as described; just a rapid vertical elevation at the end.

The description of the vertical movement of the air mass throughout the storm was clarified in the fourth sentence of the paragraph following the “Discussion” heading: “The vertical movement of the air parcel dipped to lower elevations followed by rapid vertical mixing (Fig. 7C) in the middle of the storm (samples G-H-I) whereas initial and ending samplings had back trajectories that consistently remained over 100 m above sea level in the 24 hours preceding sample collection (Figs 7A, B and D).”

Cite non-hurricane sample concentrations for comparison to that of hurricanes, including this and early ones reported by the same group. Is the removal of water soluble aerosols from the troposphere of remote marine origin during the storm transit?

Rainwater components from water soluble aerosols in the early and late time periods of the storm were not totally of marine origin, as discussed in sections 4.1 and 4.4.

Section 4.2: Is it washout or simple dilution of the sea salt?

Yes, we consider this wash-out of seasalt aerosols because the deposition of seasalt during this time period reaches a minimum in sample F even though rain volumes during this time were high and the air mass back trajectories suggested significant marine influence. The second reviewer (below) suggested including deposition plots, which

should further clarify this. In an effort to clarify this section, we removed a statement (“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”) that only distracted from the main point we intended. We also added the word “aerosols” in the following: “We attribute the decrease in seasalt concentrations during this second period of Hurricane Irene to the washing out of seasalt *aerosols* as the total rain volume accumulates and relatively little change in the air mass trajectory is observed.”

Section 4.4: Are the additional inputs of natural and anthropogenic organic material derived as a result of the storm (e.g. high wind stress, resuspension, sea salt photo chemistry?).

Yes, given the high volume of rain, the samples collected at the end of Hurricane Irene had remarkably high levels of DOC. It is likely that this is a direct result of the high winds experienced during a hurricane or tropical storm that may suspend organic material in the air where it can quickly become entrained into rainwater during such an event.

Page 11, lines 11-12: Reword, as the acid components at the end of the storm did exceed that experienced in Phase 1, as did DOC and ammonia. In this case, are these later components redeposited from suspension, or outgassed production in the areas of intensive swine production?

We think it is notable that the levels of ammonium and DOC at the end of the storm exceeded concentrations of these components earlier in the storm by a factor of 5. Yes, we attribute this to the redeposition of DOC from terrestrial material suspended in the high winds of the storm and the deposition of NH_4^+ upon dissolution of NH_3 gas from swine production or other agricultural activities. This is in contrast to NO_3^- and NSS, which occur in rainwater in a form that is chemically distinct (oxidized) from their sources (NO_x and SO_2). We have reworded this paragraph to clarify this point by making the following changes: (1) the word “greatly” was added to the first sentence and (2) the word “replenished” was changed to “regenerated”.

Section 5: Did the high volume of rain in this or other subtropical storms result in an increase in total deposition of all or just the ionic (e.g. sea salt) components?

This question is addressed later in this section. “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.” We attribute this to high rainfall amounts because the volume weighted average concentration of all non-sea salt components was lower during Hurricane Irene than for non-hurricane storms (Table 2).

Response to Reviewer #2

Pt. 1: One of my more important comments is the use of the term “air mass”. This isn’t the appropriate term. What I think you mean to say is “air parcel” mostly. A hurricane isn’t an air mass specifically, but a subtropical low pressure system operating within a maritime tropical air mass. An air parcel is a smaller body of air, which is the term you

should use throughout.

The wording has been changed throughout the manuscript so as to avoid the term “air mass.” We changed it by simply omitting “mass”, occasionally adopting the reviewer’s suggestion of “air parcel,” or sometimes we were able to simply delete it (i.e., “air mass back trajectory” is now “back trajectory.”)

Pt. 2: My second major comment is about the idea of high concentration with low rainfall and suppressed concentrations with high rainfall (dilution). I think some of the conclusions and implications need to be reevaluated based on total mass deposition (by component) during the A-K periods. This will move you farther to the implications, given that you are looking at total deposition and get away from some of the dilution/concentration problems with highly variable rainfall.

This is an excellent point and indeed helps us remove one variable (rain volume) from the study. Therefore we made all figures with concentrations into two-part figures with both concentration and deposition (Figures 3 – 6).

Pt. 3: A few simple things; define the hydrogen peroxide chemical notation Page 4, define RSD, page 4. Only one (or a few) detection limits are reported through section 2, and you might consider listing them all. A table of RSD and detection limits would work very well. The chemical notation for hydrogen peroxide and the definition of RSD were added upon final submission to ACPD. Detection limits were defined for samples with non-detectable concentrations in Table 1 with “<”.

Pt. 4: Figures: all of the figures are listed with the same problem; e.g. “total rainfall / mm” meaning the units are in millimeters. I think it would be best for all the figures to be listed using parentheses, “total rainfall (mm)”, which I think is more standard for atmospheric journals.

All figures axes are now labeled with units in parentheses.

Pt. 5: Figures again: I would suggest that the authors consider using radial wind direction figures (i.e. like a pollution roses) for figures 3-6 to show the different concentrations with respect to the wind direction. The concentration is defined along the radius, and the angle defines the wind direction. This would be a great addition to the paper, and make understanding by the reader much easier. I would think pairing these with the time graphs would work well. The same might be considered for figure 1 and a wind rose with speed information incorporated into the same graphic.

We considered doing as the reviewer suggests however we found that because there is little variation in wind direction early (samples A-D) and late (samples J and K) in the storm it was hard to distinguish between individual samples.

Pt. 6: Figure 7 F might be best as figure 1. I think the atmospheric scientists would like to see it early. That would define how the hurricane moved, and if you bring all of Figure 7 to the start of the paper, the reader will understand right from the beginning that the early air parcel movement (or “streamlines” if you prefer) came in over the water, and the latter over the land.

We moved figure 7F up in the manuscript so it is now figure 1C.

Pt. 7: Table 1, units and throughout. The air pollution audience will be expecting mg/liter as a unit, to compare it to the numbers they know, rather than micro molar. I think that would be better for understanding, at least from that audience. Again, clarity and understanding. Also, I assume the sulfate column is measured sulfate and not NSS sulfate. If so, I would add in this column here and mark it as a calculated value.

The units in Table 1 have been changed from μM to mg/L for those that may prefer them. However, we decided to keep units in μM in our figures. Although many atmospheric chemists use mg/L, this usually refers to mg per L of air, not mg per L of precipitation. Therefore, keeping units as μM helps avoid confusion.

Pt. 8: Page 1, Line 19. How did you clean the glassware for the basic analytes? Just a short description of the washing method.

Glassware cleaning is described in section 2.1, but we have modified the description of our cleaning procedure to be more detailed: “All glassware used in this study for sample collection, filtration and storage was **rinsed copiously with deionized water to remove salts and then** combusted at 450°C in a muffle furnace for a minimum of 4 hours to remove organics prior to use.”

Pt. 9: Abstract: “the second when: : :”. I don’t think that this statement imparts what happened. I think it should read something like “when the back trajectories showed that large volumes of marine surface air was lifted” or something like that.

The part of the abstract (lines 22-23) that originally read “when the air mass dipped to low elevations over the Atlantic Ocean followed by rapid vertical mixing” now reads “when back trajectories showed large volumes of marine surface air were lifted.”

Pt. 10: Page 5, Line 5: the NADP could provide the 2011 Na values for each week over the year.

Yes, but the most comparable NADP site in Beaufort, NC does not have data for the week of Hurricane Irene. Our analysis shows that NSS calculated with either Na^+ or Cl^- yield results that agree with each other (i.e., are within the analytical precision of the method).

Pt. 11: Page 6, Line 4: you might want to justify your selection of 500m for back-trajectories. This much below the likely cloud bottom, and trajectories are really poor at low altitudes (below 100 m).

As reviewer #1 requested, we clarified our justification of 500 m in our back trajectories in section 2.3.

Pt. 12: Page 6, L 14: I would add in a reference here to Figure 1A also.

The first sentence of the Results section now refers to Figure 1 as a whole rather than just Figure 1A.

Pt. 13: Page 7, L 9: reference to p value. I would put in the range of the correlation coefficients here. I am unclear as to what the p value is referencing.

This statement is meant to indicate there was no correlation found between either seasalt concentration and rainfall rate or seasalt concentration and wind speed. The sentence has been reworded as follows for clarity and the range of p values is included as the reviewer suggested: “There was however no correlation between any seasalt concentration and either rainfall rate or wind speed ($0.124 \leq p \leq 0.450$).”

Pt. 14: Page 7, L 16: versus what? The NADP values? Other? Likely needs a reference.
The last sentence of section 3.1 puts the total deposition of chloride in the context of annual wet deposition at this site. Because this is our dataset (we sample on an event basis and analyze all precipitation at this site), no reference is needed.

Pt. 15/16: Page 7, line 23: space missing in reference list. Page 8, line 1, 15: spaces are missing in two reference lists.
The omitted spaces have been inserted.

Pt. 17: Page 8, L 3: Sulfur is primarily used as a tracer for coal combustion, but NO_x is formed with any combustion, so this is a mixed signal. Perhaps further clarification of the sentence.

The last sentence of section 3.3 has been generalized more; we have changed “emitted from the burning of fossil fuels” to “emitted from combustion processes.”

Pt 18: Page 8, Lines 10-16: This idea is somewhat unclear. Are you arguing that the H₂O₂ that you measured was formed from photochemical reactions during this hurricane? If so, then I do not agree. The conditions during a hurricane would not favor photochemistry due to low radiation levels with cloud cover and high turbulence, both of which are not common during typical SE photochemical episodes. Perhaps I am misunderstanding what your point is? Clarification of the idea is needed.

The reviewer makes a good point that below cloud photochemistry would be very low during a hurricane because of the extensive cloud cover. However, there are several lines of evidence, which suggest that in cloud photochemical production of peroxide occurs. The lack of correlation often observed between peroxide concentration and rain volume has been attributed in part to continuous aqueous phase production which would allow high volume storms such as hurricanes to contain significant peroxide levels even when below cloud gas phase scavenging has been significantly reduced (Moller 2009). Earlier research by our group has also demonstrated that there is a marked diel oscillation in peroxide concentrations at this and other locations in rainwater with the highest concentrations occurring during above cloud peak solar periods. In a more recent paper (2010 Kieber et al. *J. Atmos.Chem.* 64, 149-158) we demonstrated conclusively that small but significant concentrations (a few μM) of hydrogen peroxide could be produced in rainwater exposed to simulated sunlight for 2 hours and that production rates were most significant in low initial peroxide samples ($<20 \mu\text{M}$) as seen in Hurricane Irene.

Pt. 19/20: Page 8, L 19: elevation. Same air mass comment again. What I think you mean to say is that the elevation of the air parcel? Pt. 20. Page 8, Lines 25-28. Same comment again. I think you mean to say that the trajectories show surface air lifting during this period.

See response to Pt. 1. We have reworded this throughout and “air mass” now no longer appears in the manuscript.

Pt. 21: Page 8, beginning discussion. I would suggest adding a sentence or two here that talks about how big the storm was (spatial extend, strength, maximum winds), peak winds experienced at Wilmington, etc. so that the reader has a better idea of how close the station was to the center, high winds and the like.

We have added the following statement to the beginning of the Discussion section: “Hurricane Irene generated tropical force winds extending over a diameter of about 840 km and the eye of the storm was about 130 km away from our sampling location at its closest point. Wilmington, NC experienced peak wind gusts of 30 m/s on the morning of August 27, 2011.”

Pt. 22: Page 9, Lines 13-16: Good discussion of the idea of low volume/high concentrations. The opposite is also likely happening with periods of high rainfall; dilution. You do bring this up later. Therefore, I would recommend adding a figure based on deposition. What I am thinking is a bar chart showing deposition of individual components during the A-K periods. This will integrate this idea and show when the important depositions occurred during these extreme amounts of rain. Total mass deposition by period. This would again be important in Lines 27-29 same page.

See the response to Pt. 2. Unfortunately space does not permit additional figures, but we think the reviewer’s point is demonstrated by the inclusion of deposition figures to compliment all plots of concentration.

Pt. 23: Page 9, L 24: Title. I am not comfortable with the Washout label. Much of the deposition is washout rather than rainout. Therefore, I am not sure what you mean with this label.

Rather than use the term “wash-out” we revised our heading so it is now “Dilution.” We also changed to following statement so as to avoid the term “wash-out” (change emphasized): “We attribute the decrease in seasalt concentrations during this second period of Hurricane Irene to the **removal** of seasalt aerosols from the atmosphere...”

Pt. 24: Figure 1. I would convert the axis to mile per hour (or a second Y axis), for the understanding of the reader. Most still use miles per hour, and are more comfortable with it. In the same vein, mm to inches in Figure 1 b. I would also suggest that you add in mm/sample bar graph under the integrated cumulative rainfall, so the reader has a better idea of when high and low volumes occurred. I would also label F1a as “surface wind direction” for reader clarity. I would also mark in the time axis of F1a when landfall occurred.

We added bars to Figure 1B to represent the size of individual samples, as the reviewer suggested. We did not change the units on Figure 1, however, because we feel that given the international audience of ACP, it would be most appropriate to use metric units throughout the paper.

Pt. 25: Table 2: reference where the annual values are from. Again, the ammonia values are available for the area from NADP (Beaufort, I believe).

Table 2 summarizes the contribution of Irene to annual wet deposition at this site. Because the data that are available from Beaufort are incomplete (several missing weeks throughout the year) and at a different location, we feel it is best to use our own dataset in this discussion. In fact, the Beaufort site may have been damaged during Irene because data from the week of the storm and the seven weeks following are missing even though they report receiving almost 12 cm of rain during the Irene week. The next nearest site is more inland (Hofmann Forest) and it also does not have data for the Irene week. Hence our data for this storm are unique for this region.

Pt. 26: Page 10, lines 10-12: again, the air mass comment. “the back trajectories indicate that the air over Wilm. At the time was originally at the surface and was lifted” or something like that.

See response to Pt. 1. We have reworded this throughout and “air mass” now no longer appears in the manuscript.

Pt. 27: Page 10, Lines 18-20. The sentence “the increased...” needs some clarification. The sentence in question (“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.”) did not add much to our discussion here so based on the reviewer’s comment we decided to remove it completely.

Pt. 28: Figure 5, Page 10 lines 26-27. This seems a bit problematic to me. NSS was high during the low volume early rainfalls with maritime air. Then you argue that it goes back up due to air moving over land. This point can be clarified by a deposition plot rather than concentration plots (you stay away from the dilution/concentration problems mentioned earlier). I again would argue for addition of a total deposition plot for A-K for the ions (or major ions if space is an issue). I would expect to see little deposition early of continental ions and heavy depositions later. This point is again shown in Page 11, lines 1-2. Your concentration plots do not show this for NSS. Deposition plots would likely show your point very clearly. This would also (likely) clarify your argument in lines 11-18.

See response to Pt. 2. The addition of deposition plots should make this more clear.

Pt. 29: Table 2: I would add “Concentration” to the column labels.

We have added “concentration” to the two column headings on the right of Table 2.

Pt. 30: Page 11: I would bring in data from a nearby NADP site for comparison. You would then be able to show in table 2 (hopefully) high deposition rates of the other components. As it reads, only the Cl value is high.

Unfortunately the weekly data that is available from the NADP site in Beaufort is incomplete and does not include the week of Hurricane Irene (see response to Pt. 25). We feel that other NADP sites in our region are too far inland to be comparable to this our dataset and therefore we prefer to limit our discussion to our data.

Pt. 31: Page 12, Lines 3-5: I would say that this increase is only theorized at this point. Some are projecting this, but it is still speculative.

We have corrected the statement to reflect that increased occurrence of hurricanes with climate change is only speculative. The statement, “the projected increase in severe storms” has now been changed to “the possible increase in severe storms”.

Pt. 32: Page 12, Lines 9-12; same air mass and elevation point as before.

See response to Pt. 1. We have reworded this throughout and “air mass” now no longer appears in the manuscript.

Pt. 33: Page 12, lines 11-12. “but a simple..” again this washing out is unclear. Most of the components were washed out, and you have no way to tell if they were washed out or rained out (in cloud). I think you are arguing for not simple dilution? If this is the case, I do agree with this either. All of the concentrations are depressed during high rainfall. Total mass deposition plots will clear this up, I believe.

See response to Pt. 2.

Pt. 34: Figure 7. I would identify, somehow, along the track, when the samples were taken. This will relate to the reader when the samples were taken to the hurricane position.

This is a good idea to help the reader relate the track to our sampling campaign. However, we found that labeling all the sampling times along the hurricane track resulted in the hurricane track figure (now Fig. 1C) being too crowded. Instead we indicated when the first and last samples were collected. We collected and analyzed all precipitation that resulted from Hurricane Irene at our sampling location.

Pt. 35: Figures: some points have error bars and some do not. If you have multiple samples per point, then they should all have error bars. Error bar definition should be stated in the captions.

We have explained the error bars in figure captions when they occur (Figures 4 and 6 for NH_4^+ and H_2O_2 , respectively). RSD is reported in the experimental for all our measurements in section 2.