

We thank the reviewers for their helpful comments on our manuscript. Please find our line-by-line responses below, summarizing our edits to the main text and supporting information.

Reviewer 1

Ditto et al. present detailed molecular speciation of aerosols sampled during the summer and winter times next to the Long Island Sound. These measurements cover gas and particle phase compounds. In addition, the authors present a novel technique for collecting and detecting polar gases such as alkylamines which are not typically amenable by GCMS techniques. Their results paint a very clear picture that aerosols found in this region have a high fraction of reduced nitrogen compounds. The sources of these compounds are diverse. In addition, winter-time composition reflects more liquid-phase processing compared to summer composition. Overall, the results are very interesting and useful for understanding how the composition of coastal aerosols differ from other regions.

The manuscript is very well written given the sheer amount of data presented. The paper fits well with ACP and should be accepted. Below are minor comments.

Response: We thank the reviewer for their support of our manuscript. Our revisions are summarized below.

Line 81: organic gases and particles.

Response: Revised.

Line 138: what is the mass resolution of the TOF?

Response: The mass resolution ($M/\Delta M$) of the Q-TOF used in this work was approximately 25,000-40,000, with a very high mass accuracy of approximately 1-2 ppm. In our study, we used chromatography to separate compounds prior to their ionization and detection by the mass spectrometer, thus reducing mass spectral interferences from otherwise coincident ions with similar masses. This increases the likelihood of an accurate formula assignment, which effectively extends our identification capabilities well beyond the resolution of the mass spectrometer alone. We added mention of this to the methods section in lines 240-244.

Line 144: would be slightly helpful to define QA/QC

Response: Thanks, we added a definition.

Line 150: Did the authors observe compounds that show up in both positive and negative ion mode? Thus they would be “double-counted” when taking the combined ion signal from both polarities?

Response: We observed a small number of compounds that ionized (and cleared QA/QC for formula assignment) in both positive and negative mode; for these compounds the average abundance was computed and the ion was only counted once. We added a note to the main text to clarify this point for readers (lines 255-257).

Line 167 (and this whole section+ SI section describing the PEEK collection technique): (This is more a comment.) This is a very neat method of collecting these polar gases and seems relatively straight forward for other groups to implement. The details provided in the SI would be enough to be a separate paper for AMT.

Response: We appreciate the reviewer's supportive comment. After some consideration while preparing our initial manuscript, we had decided to keep the discussion of this method together with the presentation of the associated gas-phase data to streamline the dissemination of the method and data. We also wanted to include the method and gas-phase data here for more straight forward comparison with the analogous particle-phase LC-ESI-MS data from the same site. While we agree that the method is interesting and useful for the field on its own, we feel the results from the method are better put into atmospheric context when combined with the aerosol-phase observations and other supporting measurements from the coastal site. We have made sure there are appropriate call-outs in the main text to direct the reviewer to the SI material (e.g., lines 339-340) including in the caption of Figure 1.

Line 276: It was not clear how the authors went from chemical formula to volatility. Did the authors use both the chemical formulae and functionalities in determining this? A few sentences (or a reference) explaining how they did this "conversion" would be helpful.

Response: We used the parameterization discussed in Li et al., Atmos. Chem. Phys., 2016, to go from molecular formula (i.e., without specific structural features) to volatility. We added more details of this method to the text as well as the appropriate reference (lines 459-467).

Figure 3: Are these fractions of total ion signal? It was not clear from the word enhancements. Enhancement over previous studies?

Response: We intended just for this to mean that there was a significant contribution of nitrogen-containing ions at the coastal site relative to other sites we have studied in the past. The pie charts represent fractions of total detected ion signal. We removed the word "enhancement" and clarified the figure caption.

Line 608: What was the range of molecular weights of the gas-phase compounds detected by the LC-MS? It would be interesting to compare the amines/amides (and other reduced nitrogen compounds) observed here with gas-phase CIMS measurements conducted at other coastal areas. Knowing what the actual compounds/chemical formulae are the authors measured here would make the comparison to other studies easier for the reader.

Response: The molecular weight range of the gas-phase I/SVOCs detected by the LC-MS method was 90-280 g/mol, with a few larger LVOCs detected (as shown in Figure 5). We added a figure to the SI showing the range of H/C, O/C, and N/C for all compounds (Figure S14), and included a table with the top 50 most abundant I/SVOCs observed (Table S6).

Reviewer 2

Ditto et al. present a unique dataset on the molecular composition of nitrogen-containing organic compounds in aerosols and the gas-phase. Overall, the methods appear sound, although it requires reading some of their previous papers to establish this. The results presented are interesting and relevant to our understanding of organic aerosol chemical composition. The main concern I have with the manuscript is the lack of engagement with other studies on organic N in rain and aerosols, as well as other high-resolution studies of organic nitrogen chemical

composition. The authors conclusions are similar to what some other studies have found, and it would lend additional credibility to this study to engage with the literature more thoroughly.

Response: We thank the reviewer for their detailed reading of our paper and for their feedback. Please find our line-by-line responses below.

Title – given the small sample set it seems an over-reach to title the paper a “seasonal analysis.” It is more akin to a case study with summer and winter cases. There is not enough information to truly explore seasonality.

Response: We have revised our title to: “Analysis of Reduced and Oxidized Nitrogen-Containing Organic Compounds at a Coastal Site in Summer and Winter” to eliminate the mention of it being a fully seasonal analysis.

Introduction/Discussion – It would be useful to introduce readers to similar studies. This could be done in the introduction or in the discussion. For example, the following seem particularly pertinent to this study and find similar results (with respect to the dominance of reduced N compounds): (Altieri et al., 2009; Podgorski et al., 2012; Spranger et al., 2019; Wozniak et al., 2014). Other related studies include: (LeClair et al., 2012; Mace, Artaxo, et al., 2003; Mace, Kubilay, et al., 2003; Romonosky et al., 2015; G. Zhang et al., 2020; Q. Zhang et al., 2002). This is obviously not an exhaustive list but highlights that the authors have not really gone beyond comparing the results here to their own previous work. This needs to be rectified in order for the manuscript to be publishable in a journal such as ACP.

Response: We thank the reviewer for pointing this out and providing some suggested references to help strengthen our paper’s connections to the literature. We have gone through the suggested references as well as added several others from the literature that demonstrate past observations of water-soluble organic nitrogen in cloud water, rain water, fog water, and in the aerosol-phase. We added paragraphs summarizing this prior work to the introduction section (lines 86-147) because we felt that they would provide better context for the rest of the paper, and have added mention to key results in the results/discussion section where comparisons were appropriate (e.g., lines 678-688, 742-744).

Full citations:

Altieri, K. E., Turpin, B. J., & Seitzinger, S. P. (2009). Composition of Dissolved Organic Nitrogen in Continental Precipitation Investigated by Ultra-High Resolution FT-ICR Mass Spectrometry. *Environmental Science & Technology*, 43(18), 6950–6955. <https://doi.org/10.1021/es9007849>

LeClair, J. P., Collett, J. L., & Mazzoleni, L. R. (2012). Fragmentation Analysis of Water-Soluble Atmospheric Organic Matter Using Ultrahigh-Resolution FT-ICR Mass Spectrometry. *Environmental Science & Technology*, 46(8), 4312–4322. <https://doi.org/10.1021/es203509b>

Mace, K. A., Kubilay, N., & Duce, R. A. (2003). Organic nitrogen in rain and aerosol in the eastern Mediterranean atmosphere: An association with atmospheric dust. *Journal of Geophysical Research: Atmospheres*, 108(D10). <https://doi.org/10.1029/2002JD002997>

Mace, K. A., Artaxo, P., & Duce, R. A. (2003). Water-soluble organic nitrogen in Amazon Basin aerosols during the dry (biomass burning) and wet seasons. *Journal of Geophysical Research: Atmospheres*, 108(D16). <https://doi.org/10.1029/2003JD003557>

Podgorski, D. C., McKenna, A. M., Rodgers, R. P., Marshall, A. G., & Cooper, W. T. (2012). Selective Ionization of Dissolved Organic Nitrogen by Positive Ion Atmospheric Pressure Photoionization Coupled with Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Analytical Chemistry*, 84(11), 5085–5090. <https://doi.org/10.1021/ac300800w>

Romonosky, D. E., Laskin, A., Laskin, J., & Nizkorodov, S. A. (2015). High-Resolution Mass Spectrometry and Molecular Characterization of Aqueous Photochemistry Products of Common Types of Secondary Organic Aerosols. *The Journal of Physical Chemistry A*, 119(11), 2594–2606. <https://doi.org/10.1021/jp509476r>

Spranger, T., Pinxteren, D. van, Reemtsma, T., Lechtenfeld, O. J., & Herrmann, H. (2019). 2D Liquid Chromatographic Fractionation with Ultra-high Resolution MS Analysis Resolves a Vast Molecular Diversity of Tropospheric Particle Organics. *Environmental Science & Technology*, 53(19), 11353–11363. <https://doi.org/10.1021/acs.est.9b03839>

Wozniak, A. S., Willoughby, A. S., Gurganus, S. C., & Hatcher, P. G. (2014). Distinguishing molecular characteristics of aerosol water soluble organic matter from the 2011 trans-North Atlantic US GEOTRACES cruise. *Atmospheric Chemistry and Physics*, 14(16), 8419–8434. <https://doi.org/10.5194/acp-14-8419-2014>

Zhang, G., Lian, X., Fu, Y., Lin, Q., Li, L., Song, W., et al. (2020). High secondary formation of nitrogen-containing organics (NOCs) and its possible link to oxidized organics and ammonium. *Atmospheric Chemistry and Physics*, 20(3), 1469–1481. <https://doi.org/10.5194/acp-20-1469-2020>

Zhang, Q., Anastasio, C., & JimenezCruz, M. (2002). Water-soluble organic nitrogen in atmospheric fine particles (PM_{2.5}) from northern California. *Journal of Geophysical Research: Atmospheres*, 107(D11), AAC 3-1-AAC 3-9. <https://doi.org/10.1029/2001JD000870>

Methods:

The sampling durations are too short and sporadic to be seasonally representative.

Response: We added a line to the methods section to address the fact that these sampling periods are treated in the text as case studies of summer and winter compositional trends, but longer campaigns would be required for full seasonal analysis (lines 201-203).

Typo page 6 line 130 “loses” should be “losses”.

Response: Revised.

Page 6 paragraph line 133 – what type of air sampler and filter holders were used? What size aerosols were selected for – or was it bulk? More detail is needed.

Response: We used a modified stainless steel Pall filter holder, which we added to the text (line 209). Consistent with our prior published work and the comparison sites in this manuscript, the aerosol size cut was approximately PM₁₀, collected in a custom minimal-inlet combined gas and particle sampler with a fine mesh stainless steel filter upstream of the PTFE filter used for the analysis. This was originally mentioned at line 125 of the text (now line 214), but we added a sentence describing this method in further detail (line 215-218).

More detail is needed on the elemental formula assignments and the handling of blanks. I had to read the entire previous Ditto 2018 and 2020 papers to feel fully satisfied that it was done properly.

Response: We thank the reviewer for diving into our past work to confirm our methods, and we agree that more information should be provided for readers here. We significantly expanded our discussion of these procedures in the Methods section (lines 250-281).

Page 7 line 146 – it’s not clear what the choice of “examined” means here, perhaps “identified” is more appropriate? If this is not correct, then the sentence needs to be re-written for clarity.

Response: We have revised this to say “identified”.

Page 10 line 212 – more information is needed on the typical time scale of hydrolysis for the expected compounds of interest including appropriate references

Response: We added a more detailed discussion expected hydrolysis timescales (lines 370-376).

Page 11 line 237 – more information is needed on the make, model, pump, and size cut-offs of the aerosol sampling system.

Response: We added a few sentences to this paragraph with further details of the system used (lines 410-416).

Page 11 line 243 – why only 48-hour back trajectories? This seems short given the lifetime of PM_{2.5} and some of the gas-phase organics. Some justification is required.

Response: We selected 48 hours to focus on regional influence at the site, and thus constrained our back-trajectory analysis to a regional rather than continental scale. Similarly, we selected 50 m to be high enough to focus on the overall 48-hour dynamics and reduce with the influence of surface topography, as the reviewer mentioned below. Overall, the scope of our HYSPLIT analysis was to look at regional wind patterns beyond just local wind rose data, since local wind rose data could be strongly influenced by localized wind dynamics. We do acknowledge that there could be contributions from air parcels extending beyond 48 hours resulting from the longer lifetime of particulate matter and some gas-phase organic compounds, as noted by the reviewer. We have summarized this with an added a line in the text to justify our choices (lines 421-424).

Page 11 line 246 – Similarly, why was a height of 50m chosen for a ground based sampler? I am assuming it is to get above the errors associated with surface topography, but a description of the choice is required.

Response: See response incorporated above.

Results and Discussion:

3.2.1 – significantly more discussion is needed to explain the determination of IVOC/ULVOC/SVOC/LVOC/ELVOC. The only information presented is in the caption of figure 2 and it is insufficient. The reader must be able to judge if they agree with the classifications.

Response: Thank you for the comment, we expanded our description of how we calculated volatility and classified compounds into volatility bins to the main text (lines 460-468).

Page 13 line 282 – what does the p-value indicate? Is this a t-test to determine of the ozone concentrations are significantly different? Similar questions page 14 lines 290

Response: The p-values listed were indeed from t-tests to determine whether mean values (in this case, ozone concentrations) were statistically significant. As discussed more in response to the comment related to p-values below, we removed all p-values for clarity.

Page 15 lines 317-319 – references are needed here or a more detailed discussion on why aqueous-phase processing leads to the stated shifts.

Response: We originally included a reference to Brege et al., which showed similar results to our observations, but we also included two other references to this section and clarified the text (lines 524-530) to draw connections similar observations in other studies here.

Page 15 line 328 – in this case it seems impossible that the stated p-value is from a t-test suggesting those are different values. Explanation is required.

Response: As stated above, these p-values were indeed from t-tests. We verified that this particular t-test was accurate and did show statistical significance despite the means being similar and standard deviations being large. However, we agree that this p-value could be confusing and misleading due to the large spread of data. To avoid any mis-interpretation, we removed p-values from the discussion. We do not feel this negatively impacts the manuscript because the t-tests were not used to establish statistical significance but were just originally included in case readers were interested in a statistical comparison of the means. Similar to the reviewer, we have decided with this sample set it is better to just provide the means and standard deviations for the reader's own assessment.

Page 16 line 329 – why is in-cloud processing not considered as a contributor to aqueous-phase chemistry throughout the discussion?

Response: We thank the reviewer for this comment and agree that we should be explicitly referring to in-cloud or in-fog processing as part of the discussion. We added a sentence to broaden our definition of aqueous phase processing in the text to make it clear that this could mean in-aerosol, in-cloud, or in-fog processing (lines 511-514). Also, where we discussed our estimates of aerosol liquid water, we also added a comment about observed local weather conditions. During both summer and winter sampling times, local and regional weather conditions were variable over the timescales of the samples, so examining and differentiating the distinct role of clouds, fog, and aerosol liquid water would be challenging. We have made this clear in the text and made sure our mentions of aerosol liquid water were generalized to include other types of atmospheric water.

Figure 2 – Is ion abundance intended to be a proxy for concentration? How was the average volatility determined? How were the volatility classifications assigned (more is needed in the text than the simple statement in the caption). What is the $\log(C_0)$ and how was it determined? The text on lines 358-363 needs to be in the manuscript and not the figure caption. Furthermore the impact of using the same temperature for the summer and winter cases will be significant such that it's not clear what this comparison is actually showing given that the results for winter will be completely different.

Response: The relative distribution of ion abundance in Figure 2 was indeed meant as a proxy for their relative atmospheric abundances, though not explicitly their relative mass concentration. Based on this comment, we realize that this axis label was not clear. We have replaced it with “percent of total ion abundance” to show the distribution of saturation mass concentrations and compound classes as a fraction of all detected compounds. We also added several sentences to the main text to expand on Figure 2's caption and describe how volatility was calculated, how volatility bins were defined, and explicitly defined $\log(C_0)$, as also discussed in response to one of the above comments.

We agree that using the same reference temperature for summer and winter could be unclear if not properly conveyed. We originally included a table in the SI (Table S4) to demonstrate and discuss the expected volatility shift, and presented data in the main text at the same reference temperature for ease of visual comparison between the observed complex mixture of compounds in each season using the same x-axis. However, we recognize that we must make this effect more clear in the main manuscript. To emphasize the effect of temperature, based on this comment we added a dotted black line to Figure 2B to show how the bins would be expected to shift at 270 K in winter (relative to 300 K in summer), and added associated description of the line in the caption. Table S4 is referenced in the figure caption and contains further discussion of the effect of this shift on gas-aerosol partitioning. We also discuss this shift in the text at lines 534-574.

3.2.3 – this is not a comparison to other sites, it is a comparison to the authors previous work. Even if the methods are slightly different, surely some other studies can be compared here?

Response: We thank the reviewer for their comment. Figure 3 and the corresponding text were intended to compare the measurements from this coastal site to those that our group has collected from other sites using identical sampling and analysis methods across all of these sites. This therefore allows us to remove uncertainties that arise from ionization behavior across different instruments or differences in aerosol sampling and analysis methods. To make it the intention of

the section more clear, we changed the title of this section and added a note in the text to describe our rationale for comparing to our own past work (lines 634-638). We also added a note in Figure 3's caption to further emphasize this. Additionally, per the reviewer's earlier comment about adding more references to the literature, we have added more references to other studies to compliment the existing discussion of relevant AMS work in the Long Island region.

Page 19 line 388 – first mention that these are PM10 samples

Response: Thank you for pointing out this was unclear. We had mentioned that we used a mesh screen to limit particle size to approximately PM10 in the methods. To improve clarity, we elaborated on the aerosol sampling approach and size cut in the main text (lines 215-218).

Page 19 lines 389-393 – Some data or figure needs to be presented to justify the statement here.

Response: We agree with the reviewer and have added a table to the SI with the data to show this (Table S5). This was intended to be a concise point on the unlikely bias in the data. We summed up the total nitrogen content across each particle size and compared it across particle sizes. There was no significant difference in the prevalence of nitrogen containing compounds, with 69%-71% of ion abundance for $PM \leq 2.2 \mu m$ and 69%-73% of ion abundance for PM ranging 2.2-10 μm representing compounds containing at least 1 nitrogen atom. We added this statement to the main text (lines 663-665). We also performed a t-test across the collected samples to compare the mean contribution of N-containing ions for each particle size to the N-contribution for the largest particle size measured (PM_{9-10}). We did not observe any statistically significant enhancements in the contribution of nitrogen-containing species in larger particles relative to smaller ones (i.e., for all t-tests, $p > 0.05$). This is shown in Table S5.

Figure 3 – Given that it is known that ionization efficiencies vary for the different groups of compounds, it seems to make more sense to use the number of compounds not weighted by compound abundance. The weighting is related to both the concentration and ionization efficiency in an unknown manner so it is not clear what the weighting actually means for the results.

Response: We acknowledge that there is variability in ESI response factors across compound classes. Because we are dealing with a complex mixture of multifunctional species, determining exact relationships between compound classes and their ESI response factor is indeed very challenging. Despite these expected variations, we feel that ion abundance is still a useful way to compare the summer and wintertime compound distributions. During our prior testing of ionization efficiency in our ESI source with a range of authentic standards, when we observed very large differences in response compared to the average response of our set of functionalized compounds tested (e.g., CH, CHS species), we excluded those compound classes from subsequent analyses to reduce potential bias due to very large differences in ESI response factors.

Still, we think that showing data presented in terms of both ion abundance and by occurrence are useful, so we have added the figures by compound occurrence that the reviewer requests. However, to avoid excessive duplication of all figures in the main text, we created versions of each figure shown by compound occurrence (i.e., not weighted by abundance) and added them to the SI, with references to these figures in their main text counterparts. We note that in general, figures look similar weighted by abundance or unweighted, so our conclusions in the manuscript

are not impacted by the figures we used for data interpretation. We have also added a note to the methods section to discuss this (lines 296-299).

Page 21 paragraph starting on line 424 – given the discussion of possibilities, it would be useful if the authors proposed what they think is the most likely driver in winter. For example, it is probably not the marine source given that surface ocean productivity should be at a minimum in winter. But what is most likely?

Response: We agree with the reviewer's thought that in the summer, the natural amine sources (particularly the marine source) likely play a more important role than in winter. Based on the available data, we are unable to infer and justify a single source in the winter. One possibility is that a collection of anthropogenic sources including residential biomass burning likely drives the distributions we observe. We added a note to the text to mention this (lines 733-734), but we also want to reiterate that the CHN aerosol phase fraction makes up just 1-3% of identified aerosol species in the winter (1% in the summer).

The reference on page 22 line 460 seems out of place – the sentence reads as if these assignments are for the current dataset but then refers to previous work. This needs to be clarified. Were some of these samples published in the previous study?

Response: Ditto et al. 2020 was a short communication in *ES&T Letters* that included a broader survey of functional groups across the complex aerosol mixture via MS/MS using 3 different sites. Based on the results of that study, where one of the sites was the YCFS, we decided to pursue a more in-depth analysis specifically of the nitrogen-containing aerosols and gases observed at the YCFS site. Thank you for pointing out this potential source of confusion. We have moved the reference to a more appropriate location (line 761). We emphasize that in Ditto et al. (2020), we did not examine the functional groups contributing to CHN and CHON species, as is being discussed in this section of the manuscript, nor did we perform any other in-depth analyses of the nitrogen-containing species. These analyses are completely unique to this work and are not duplicated from our past overview study.

Page 25 line 519-520 – this seems indicative of a marine signal?

Response: We agree, and we have added mention of this in the text.

Page 33/31 lines 632-633 – but this was significantly less so in winter, correct? So what is the connection?

Response: Thank you for pointing out the need for clarification here. At lines 632-633, we were comparing the gas-phase CHON O/N < 3 species to the particle-phase CHON O/N < 3 species. In the summer and winter particle-phase data, we observed similar contributions from CHON (O/N < 3)—roughly 20% of total ion abundance in summer and 19% in winter. The larger difference between summer and winter was for the CHON (O/N > 3) compound class, which was greatly enhanced in summer. Since the gas-phase measurements for LC analysis were made in the winter, we clarified that this comparison should be made for the wintertime particle-phase data (line 949).