

Interactive comment on “Molecular characterization of water soluble organic nitrogen in marine rainwater by ultra-high resolution electrospray ionization mass spectrometry” by K. E. Altieri et al.

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Interactive comment on “Molecular characterization of water soluble organic nitrogen in marine rainwater by ultra-high resolution electrospray ionization mass spectrometry” by K. E. Altieri et al. Anonymous Referee #2 Received and published: 21 December 2011

General comments: This manuscript provides evidence that helps resolve several long-

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standing questions about the biogeochemical cycling of nitrogen. The developments in the analytical technique are outstanding, and really set the agenda for the next stages of research on organic nitrogen in rain and atmospheric aerosol. The manuscript outlines a detailed chemical characterisation of marine rain, and by comparing the results with the data from their previous study of continental samples, along with the trajectory analysis, the authors provide a big step forward towards the goals of identifying the contributory compounds, and their functionality, atmospheric behaviour and sources. They also leave us with several new insights into the enigmas of organic nitrogen: : :

Scientific quality and presentation: The manuscript describes a novel application of the still relatively new ultra-high resolution mass spec technique, and describes the data treatment clearly. The technical challenges of using FT-ICR MS in marine rains are substantial compared with the more concentrated mixtures that the technique is most often used for. The manuscript is also a useful and thoughtful review of related research, bringing together much of the recent literature on characterisation and biogeochemical impact of DON. It sets this analysis in its multiple contexts – rain chemistry, organic matter chemistry, long-range atmospheric transport, and biogeochemical cycling. Another useful feature is the linking of N, S and P in the same 'frame'. Bringing these different biogeochemical components - and indeed research communities – together is an important task for better understanding of natural processes and anthropogenic changes. Overall it is a very nicely written paper - clear, concise while detailed enough to be reproducible, and a pleasure to read. They use well established sampling and analytical methods for the bulk analysis, and provide enough information on the bulk characteristics of the rain to set the context for their detailed characterisation. Seven samples might not sound like much to those outside this field, but the very high resolution chemical characterisation of them is very impressive. A side issue (and pet bugbear!) is that so many papers have “not all data shown”, “data not published”: : : It would be lovely if the organic N research community had a collaborative database where the routinely collected major ions data could be lodged, eventually allowing for more robust statistical and geospatial analysis of the available data to be made (maybe

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my own project for 2012!) In this context, the supplementary materials, although they make rather dry reading: : : are useful to have in the public domain! The paper's findings are well set out, along with clear proposals for follow-on research to close gaps in knowledge.

We thank the reviewer very much for his/her support of this manuscript.

Specific comments: Section 2.3 is really nice – we all use HYSPLIT, but it isn't often that papers have such a clear description. Section 2.4 is where the analytical novelty lies, and it is clearly described, but in some ways slightly uncritical - the approach they use for identifying/allocating chemical formulas to the compound peaks is pragmatic and used elsewhere, but we are left wondering just how robust it is in this new context. In practice, there is comparatively little reliance on specific compound identification in the remainder of the paper, but since this paper is clearly setting out potentially fruitful pathways for future analytical work on rain/aerosol ON, it would be useful at least to propose ways to fine-tune the approach to this context. The community often has to rely on extending techniques that work for marine organic matter to atmospheric OM, even though we know that the compounds and 'assemblages' are likely to be very different.

We agree with the reviewer that the compounds and assemblages in marine organic matter and atmospheric organic matter are likely to be very different. It is true that the compound identification algorithm used was tested against marine organic matter (Kujawinski and Behn, 2006), but the principles are applicable to all organic molecules and are not specific to marine organic matter. Its primary purpose is to assign chemically relevant elemental formulas to each m/z based on set input criteria and chemical relationships. The elements allowed can be controlled by the user, and the chemical relationships should be as applicable to atmospheric organic matter as to marine organic matter (e.g., CH₂, NH, CH₄-O, C₂H₄O, etc.). To highlight this for the reader we've added the following text on page 9, line 8 "The formula finding algorithm does consider functional group relationships in assigning elemental formulas; however, the

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functional group relationships used by CIA are common to refractory dissolved organic matter (e.g., humic acids) as well as to atmospheric organic matter (e.g., CH₂, CH₄-O, C₂H₄O, NH, OH, C₂H₂O; see Table 1 in Kujawinski and Behn, 2006)."

Referencing: Mace et al. also measured rain and aerosol urea in several places around the world (p 31286, line 19).

We thank the reviewer for identifying this oversight. The references were updated on page 4, line 8 to include the three Mace et al., references from 2003 which all measure rain and aerosol urea.

It would be good to see more on the DBE and O:C link to secondary aerosol formation (e.g., beyond 'usually associated with') – since this underpins some of the conclusions, more robust referencing or explanation would be good. This gets some attention in section 3.1, but that is after the link has already been mentioned twice.

The following references were added at the first mention of the relationship between O:C and SOA formation on page 10 line 27: Aiken, A.C. et al., "O/C and OM/OC ratios of primary, secondary, and ambient organic aerosols with high-resolution time-of-flight aerosol mass spectrometry," *Environ. Sci. Technol.*, 2008, 42, 4478-4485. Volkamer, R., et al., "Secondary organic aerosol formation from anthropogenic air pollution: Rapid and higher than expected," *Geophys. Res. Lett.*, 2006, 33 (17), L17811 And on page 12, line 31, we added the following reference which links secondary processing and DBE values:

Bateman, A.P., et al., "Photolytic processing of secondary organic aerosols dissolved in cloud droplets," *Phys. Chem. Chem. Phys.*, 2011, 3, 12199-12212.

The text was modified on page 10 line 25 to explain in more detail the connection between O:C and chemical changes "Changes in elemental ratios can be indicative of atmospheric reactions, for example, O:C ratios increase throughout the day from SOA formation associated with increased photochemistry (Aiken et al., 2008, Volkamer et

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al., 2006).“

P31294 line 25 – This section is interesting. Yes, the long range transport of biomass burning species is possible and yes, the presence of levoglucosan is consistent with that, so more investigation is indeed needed. But the substantial differences (O:C, DBE) between the land and marine CHN+ class complicate the picture. The local marine source option is given a comparatively low-key cursory treatment – what kinds of compounds can we imagine that have such high DBE as well as N:C ratios, and do they correspond at all with what we know about e.g. the chemistry of algal enzymes? You might be able to argue more robustly that the polyheterocyclic kind of compounds you seem to be measuring here are most likely to be created through pyrolytic processes. However Laskin et al 2009's organic N characterisation study (ESI/MS) might be an interesting link – their samples had lower DBE and N:C ratios than you see in the marine samples.

With the change in elemental formula lists described above in response to Reviewer 1, the DBE and N:C of the CHN+ group both decreased, and thus are more comparable to what Laskin et al., 2009 found for ON from biomass burning. Upon further inspection, there are three formulas in the marine rainwater consistent with the dominant CHN-H+ series present in all biomass burning samples in Laskin et al., 2009. As such, we agree with the reviewer that the polyheterocyclic compounds identified are more consistent with pyrolytic processes. The following text has been modified on page 11, line 16 “The DBE and N:C values are consistent with organic N containing biomass burning compounds, and there are three CHN-H+ compounds in the marine rainwater which are components of the dominant Kendrick mass series of CHN-H+ molecules found in all biomass burning samples analyzed by Laskin et al. (2009) (i.e., C₃H₄N₂, C₇H₁₂N₂, C₈H₁₄N₂).”

This section contrasts with the relatively systematic discussion of DMS on p 31299 – and I'm curious about what might the glycine betaine/amine story look like? Can it be traced in this chemical characterisation? Similarly p31297 lines 14 onwards – isn't

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it more likely that peptides would be present in the marine environment degrading to amino acids, rather than amino acids oligomerising in the atmosphere?

We agree with the reviewer that the potential for amino acids and amines to be traced chemically is very exciting. However, the atmospheric reactions of amino acids and amines are poorly characterized and are likely quite complex. We have added some text analyzing the Kendrick mass series in the CHON⁺ compound class as a way to identify series of related compounds that might come from amines/amino acids. Laboratory studies of atmospherically relevant reactions are needed to elucidate the pathways and product formation in reactions of these compounds to truly understand their role. The following text was added on page 14 line 2 “One way to identify these series of related compounds is the Kendrick mass defect (KMD). Compounds with the same KMD have the same number and type of heteroatoms and DBE but differ in the number of CH₂ groups (Hughey et al., 2001). Of all the N containing compounds, 49% of the masses were in a Kendrick series ranging from 3-19 formulas. The longest homologous series was in the N1O5 family which went from C₅H₇O₅N₁ to C₂₃H₄₃O₅N₁. When the Kendrick mass defect is plotted as a function of the nominal Kendrick mass these series of compounds fall on a horizontal line separated by 14 Da (Figure S-5). This makes identifying compounds of different classes visually easier as they are displaced vertically.”

The reviewer raises an interesting point about peptides. It is likely that both types of reactions are happening and the relative importance depends on the conditions present. It would be difficult to identify which type of reaction was contributing to the complexity in the marine rainwater CHON⁺ without knowing more about the reaction products. The following line was added in the discussion of amino acids to introduce this additional possibility on page 13, line 28 “It is possible that the decomposition of protein and pollen could contribute to the reduced N fraction of WSON, and specifically the amino acids and the amino acid like compounds.”

P31304 – old work (1980s) by e.g. Zafiriou and Zepp and Kieber on photochemistry

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and the ocean microlayer address this in part – both VOC emission and N reactions.

The following references were added on page 20 line 2 to properly cite the previous work on VOC emissions from surface ocean photochemistry:

Kieber, D.J., Mopper, K.: Photochemical formation of glyoxylic and pyruvic acids in seawater, *Mar. Chem.*, 21, 135-149, 1987. Zhou, X., Mopper, K.: Photochemical production of low-molecular-weight carbonyl compounds in seawater and surface microlayer and their air-sea exchange, *Mar. Chem.*, 56, 201-213, 1997.

Technical things: Phosphorus is mis-spelled.

We thank the reviewer for noticing this and have corrected this throughout the manuscript.

Chemical formulae in supp materials don't have subscript numbers.

This has been corrected in the supplemental material. Trajectory figure has 50000 m in caption.

This has been corrected in both Figure 1 and Figure 2 captions.

P31299 “One of the only: : :” The only one to your knowledge, perhaps, or the only one of the few P studies that deals with the marine environment.

Text on page 15 line 30 was changed to clarify that we meant one of the few in the marine environment “One of the few compositional studies on aerosol P in the marine environment was conducted by Graham and Duce (1979).”

P 31302 – line 27: Do you mean “The marine biogenic S cycle is well documented, but *P* appears to play an important role in the marine organic aerosol cycle that has not been documented previously.” ?

The text on page 18 line 23 was changed to clarify “There are a large number of organic S containing compounds in the marine rainwater, however, no nitrooxy organosulfates

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or organosulfates. The marine biogenic S cycle involving the conversion of DMS to SO₂ and MSA is well documented, but it appears to play a role in the marine organic aerosol cycle that has not been documented previously leading to the formation of additional organosulfur compounds.”

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