Atmos. Chem. Phys. Discuss., 11, C13485–C13488, 2011
www.atmos-chem-phys-discuss.net/11/C13485/2011/

Atmospheric Chemistry and Physics Discussions

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-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 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.

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.

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

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.

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

P31304 – old work (1980s) by e.g. Zafiriou and Zepp and Kieber on photochemistry and the ocean microlayer address this in part – both VOC emission and N reactions.

Technical things: Phosphorus is mis-spelled. Chemical formulae in supp materials don't have subscript numbers. Trajectory figure has 50000 m in caption. 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. 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." ?

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 31283, 2011.