Atmos. Chem. Phys. Discuss., 11, C13346–C13348, 2011
www.atmos-chem-phys-discuss.net/11/C13346/2011/

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 #1

Received and published: 17 December 2011

The paper intends to investigate chemical composition of WSON compound in a number of rainwater samples and assess possible distinctions with respect to geographic location and seasons. Chemical analysis is done by means of ultra high resolution mass spectrometry (UHR-MS) with electrospray ionization (ESI) that enables assignment elemental formulas to individual peaks based on the accurately measured m/z value. The topic of the work and the experimental approach are of substantial importance to the field and therefore have a great potential for publication.

However, in the present submission, the UHR-MS data set is presented in the form that cannot be critically evaluated for its significance and accuracy. Moreover, my brief inspection of the proposed formula assignments reveals major problems with the data processing and interpretation that must be fully resolved before the atmospheric chemistry context of the paper can be reviewed and evaluated. My specific comments are listed below:

1) It is erroneous to assume that sodiation is the only mechanism of ionization in the positive ESI mode. N-containing species (especially with reduced N) often have high proton affinity and are commonly observed as protonated molecules (i.e. [M+H]+ ions). For instance, here I list few examples of m/z values, for which assignments based on protonation give more realistic and chemically meaningful results: e.g. m/z 343.113628 (assigned as C13H26O1N2S1P2-Na+ by the authors) is likely C14 H19N2O8-H+ (343.113592, +0.1 ppm); m/z 236.141111 (assigned as C15H19N1-Na+ by the authors) is likely C10H23N1O3P1-H+ (236.141007, +0.4 ppm). There are numerous examples of this sort and it would not be practical for me to revisit all the assignments presented in the paper. In addition, there is no chemical reason to believe that oxygen-free CxHyNz species can yield sodiated peaks in (+)ESI spectra (i.e. group of peaks assigned as CxHyNz-Na+).

2) Many of the assigned formulas are not chemically legitimate, i.e. they don't obey valence rules. For instance, many of the proposed assignments (e.g. C4H3O2N3P1, C5H7O1N1S1P1, C5H10O1N2S1P1, etc) cannot be associated with even hypothetically drawn molecular structures.

3) Presentation of the UHR-MS results as tabulated data is not sufficient for critical evaluation by both reviewers and general readers. There are numerous tools developed by the HR-MS community that must be applied for data reduction and visualization.

To provide a solid ground for the discussion context of this manuscript, the UHR-MS data must be presented in a reader-friendly, assessable way that should include:

* Presentation of the original UHR-MS spectra (either in the manuscript itself or in the SI file), along with the relevant statistics of assigned vs unassigned peaks.

* Assignments must consider ionization on both sodium and proton, and perhaps on other metal cations too

* The authors should make sure that their peak assignments generate reasonable molecular formulas that conserve valence rules. They also have to explain how they dealt with redundant (multiple possible) assignments.

* Indication of specific fractions of N-containing species out of the total analyzed and identified peaks.

* Data reduction tools such as Kendrick analysis must be used to group and present chemical species in homologous groups. For instance, brief processing of the tabulated data with CH2-kendick analysis places $\sim$50% of the peaks in a number of homologous series containing between 3 to 17 individual peaks. Additional grouping (data reduction) might be obtained using different Kendrick bases and their combinations.

* Also, relative intensities of the individual peaks need to be indicated to ensure that peak assignments covers at least most abundant peaks.

* All items above require graphical presentation that needs to be included at least in the SI file.

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