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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Molecular characterization of organic aerosol in Himalayas: insight from ultra-high resolution mass spectrometry" *by* Yanqing An et al.

Anonymous Referee #3

Received and published: 20 September 2018

The manuscript presented by Y. An et al. presents the detailed molecular chemistry of two samples collected from the Qomolangma Station in the Himalayas. The detailed molecular chemistry was derived from ultra-high resolution FT-ICR mass spectrometry measurements following electrospray ionization to generate positive ions. The authors discuss the molecular composition of the two samples and compare them carefully to previously published studies using similar approaches. Specifically, they found an increased degree of unsaturation of the prominent species in their study. As the authors suggest, these molecules may contribute to aerosol absorption.

The manuscript is well prepared and the methodology is technically sound. However,

I recommend the authors consider revisions to the manuscript to address method limitations pertaining to the ionization (potential artifacts, differences between + and -, anticipated functional groups, etc.) and discuss more specifically the significance of the results (both with respect to the implications and the limitations).

Specific major comments without any predetermined order:

1. It appears that many assumptions about the ionization method were made in the data interpretation. Those assumptions are not explicitly stated and may be incorrect. (i) For example, NH4+ is a common cation that readily adducts to molecular to assist in forming positive ions (similar to Na+). Please explicitly state your assumptions regarding this possible artifact. (ii) CHON compounds observed in ESI are expected to vary with the ionization mode. For example, reduced N (e.g., amino functional groups) are not expected to be observed in the negative ion mode. Likewise, oxidized N (e.g., nitrate functional groups) are not expected to be observed in the positive ion mode. Please explicitly state your assumptions regarding the ionization method and possible differences between ESI positive ions and ESI negative ions.

2. Due to differences in the ESI ionization process (positive vs negative), the direct comparison of the data can be difficult. Please be sure to check the ionization mode of referenced datasets and discuss the method limitations associated with the datasets and the resulting limitations on the conclusions.

3. How were the molecular formulas and their homologous series formed from biogenic VOCs and biomass burning identified?

4. The phrase "important implications" (line 32) is an empty phrase. Please be more specific with the inferred implications and impacts associated with the studied molecular classes.

5. What do your sample names indicate or represent? Consider changing the samples names to be more descriptive.

6. What is meant by “pristine region”?

7. The literature review describing the significance of light absorbing aerosol is severely out of date.

8. The phrase “Many studies” requires more than just one example reference.

9. The goal of the paper is what exactly?

10. What is the relevance of discussing the tourist season?

11. Ultrasonic baths can introduce reactive oxygen species. What care was taken to avoid extraction artifacts?

12. Please discuss the SPE recovery.

13. Please discuss the steps that were taken to avoid ESI artifacts?

14. The parameters associated with your “custom software” need to be more thoroughly described. How did you eliminate ambiguous formula assignments?

15. What is meant by the “processing error” mentioned in line 161? How did you ensure that the error did not affect the molecular composition?

16. What is the procedure for identifying the NOA compounds with HR-ToF-AMS?

17. How was the influence of potential fresh OA inferred?

18. In the discussion of common ions, the authors assume that the two samples have a similar aerosol source? What if instead, the common compounds are simply not marker compounds. Complex mixtures are expected to have many ions in common.

19. What is the balance of source contribution vs. aerosol aging in these samples.

20. I’m surprised that the long-range transported aerosol reported in Dzepina et al. is similar to the samples reported here. How is that observation justified with respect to the transport pathways?

21. The “distinct group of CHON aromatic compounds” in the lower left of the VK diagram may be incorrect assignments. What are the limits for the DBE range?

22. What is the significance of the difference in the max abundance between H+ and Na+ type ions?

23. The detailed description given over lines 279-298 is quite tedious. Perhaps some of these formulas can be better presented in a figure or table?

24. What is the significance of 1N vs 2N?

25. How do you observe acidic N in the positive ion mode?

26. The statement in lines 330-333 is not convincing. Please rephrase and add more evidence or description.

27. Lines 351- 353: How does the sample matrix effect the observation of ions in ESI?

28. Where are the major products of BVOC as mentioned in lines 359-363?

29. The discussion of the research implications can be enhanced with a deeper discussion of the molecular composition and method limitations. What other observations of absorbing species have been made in the Himalayas?

30. The implications regarding nutrients and biogeochemical cycling are beyond the scope of the current research and seem to be a bit too ambitious. Please revise.

31. Related to the previous comment, did you study deposition?

32. Again, what type of N did you study with your analytical method. Please be clear with the limitations and assumptions that are necessary.

33. How are the measurement sites defined? The listed free troposphere sites do not consistently sample free tropospheric air. In each case, seasonal factors may play a strong role in the height of the boundary layer.

34. Figure 3 appears to contain several high intensity regularly spaced peaks that are

not associated with the sample. Please remove or flag these peaks as contaminants.

35. Please add the specific details regarding your treatment of blank samples to the methods section.

36. How are the FT-ICR MS ions related to the fragment ions from HR-ToF-AMS (as shown in figure 4)?

Additional minor comments:

1. Line 19: DBE = double bond equivalents; DBE is plural not singular

2. Line 31: “high nitrogen containing of aerosol” is unclear. Please rephrase.

3. Line 32: “important implications” (use plural)

4. Line 32: “and the biogeochemical cycle” (insert article)

5. Line 42: “Accompany” is awkward. Please rephrase.

6. Line 43: “to the Himalayas” (insert article)

7. Line 46: “essential” is awkward. Please rephrase

8. Line 172: What is the IA method?

9. Line 181: “transported" (verb tense)

10. Line 185: Fix typo.

11. Lines 247 & 249: “molecular weight” not "molecule weight"

12. Lines 256 & 258: Typo? Did you mean to use Cw or C in these two sentences?

13. Line 261: “carbon oxidation state” (lower case “C”)

14. Line 307: “average O atoms contained in” (plural and verb tense)

15. Line 368: “two compounds” or “two compound groups"

16. Line 373: “believed” (verb tense)

17. Table 1 (and Figure 3): Are the values shown for F30 and F43 for all ions or only unique ions?

18. Figure 1: What is the purpose of the blue shading behind the pie chart?

19. Figure 1 (and elsewhere): Please remember to define all of the acronyms used in the figure within the figure caption.

20. Figure 2: Please include the vertical profile for the back trajectories.

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