

Interactive comment on “Seasonal and diurnal variations of particulate nitrate and organic matter in the Central European atmospheric aerosol” by L. Poulain et al.

Anonymous Referee #3

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This manuscript investigates the seasonal and diurnal variations of organics and nitrate from 3 campaigns in central Europe during 3 different seasons, summer, autumn, and winter. While it is of no doubt that a lot of data have been collected, the data included in this manuscript seem inadequate to support many of the conclusions the authors intended to make. The discussions of the organics seem to be focused only on two m/z s, m/z 43 and m/z 44. I understand that these two m/z s are important markers for oxygenated OA (OOA), however, the authors did not perform any factor analysis in this work and so it did not provide any context why they only focused on these two m/z s. It appears that most of the discussions are based on the assumption that secondary organic aerosols dominate the total OA. However, no data are provided in the manuscript

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to support this. Instead of focusing the work on these two m/z s, when discussing the “aerosol composition”, they should at least show some mass spectra and also discuss other m/z s, such as m/z 55 and 57. The section regarding the partitioning of nitrates is highly speculative owing to the lack of many gas-phase measurements. Since the authors cannot provide the data to support their hypothesis, the arguments in that section are weak and require more work.

Based on the above reasons, I do not recommend the manuscript to be published in its current form.

Specific comments:

1. Abstract, first sentence. The sentence is unclear. Are the authors referring to the uptake of PAHs and n-alkanes onto aerosol surface? As far as I understand, under most cases, these compounds do not exist in particle phase, on the other hand, the oxidation of such compounds can form products of low volatility that then partition into the aerosol phase (SOA formation).
2. Abstract, line 15. What “discrepancy” are the authors referring to here?
3. Page 11613, lines 18 and 19. “depending” should be “dependent”.
4. Page 11614, line 3. “depending” should be “dependent”.
5. Page 11615, line 22. Delete “to”.
6. Page 11616, lines 9 and 10. Awkward sentence. The aerodynamic lens does not “remove” the gas phase. It simply increases the particle concentration relative to the gas-phase species.
7. Section 2.2 in general. The authors can simplify the instrument description and operations of the HR-AMS and cite DeCarlo et al., 2006.
8. Page 11616, line 17. “gas phase” should be “gas-phase species”.

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9. Page 11618, line 25. “considers” should be “taken into consideration”.
10. Page 11618, line 28. “intake” – do the authors mean “inlet”?
11. Page 11620. I think it would be better if the authors present the data in Table 2 as pie charts.
12. Section 4.2. The title of this section is “Changes in organic particulate composition.”, however, the authors pretty much only discussed two m/zs in all of the AMS data, i.e., m/zs 43 and 44. After reading this section I did not get a very good idea regarding the organic particulate composition, other than the variations of these two m/zs and the OM/OC ratio. With respect to the amount of information one can obtain from HR-AMS data, the results presented in this section seem extremely inadequate.
- a. The authors did not even show a single mass spectrum in this manuscript. How does the organic mass spectrum look like? Do they vary in different seasons? Such information should be included (The authors should at least present an average mass spectrum for each season). b. The discussions in this section appear to be built on the assumption that secondary organic aerosols dominate the total OA observed in these campaigns. Yet, the authors did not provide any data to support this. Do the authors have some ideas on the contributions of primary organic aerosols (POA) in these campaigns? One way to get some ideas on the relative importance of POA is to look at m/z 57. How does the times series / diurnal cycles of m/z 57 look like? c. The authors wrote that the changes in organic oxidation levels are mainly examined through m/z 44 and 43 (mostly C₂H₃O⁺). The authors seem to have framed their discussions based on that m/z 43 is mainly C₂H₃O⁺, but no data were included to support this statement. Is the statement “m/z 43 is mostly C₂H₃O⁺” based on the HR analysis of their data? What do the authors mean by “mostly” (What % of m/z 43 is C₂H₃O⁺ actually?)? m/z 43 can be C₃H₇⁺ or C₂H₃O⁺. How does the diurnal cycle of these two fragments (instead of the “total m/z 43”) look like? Do the relative contributions of these two fragments change at different times of the day (e.g., in the afternoon hours

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when the photochemical activity is stronger, I would imagine the m/z 43 would be more dominated by C₂H₃O⁺)? d. m/z 44 can be used as an indication of the oxidation level of the aerosols, however, the data here at HR-AMS data, so instead of relying on m/z 44 the authors should present the O:C ratios calculated from elemental analysis of their data. e. Page 11622, the sentence “Moreover, it is known that f₄₄>f₄₃ characterized a highly oxygenated and low volatile OA, while f₄₄<f₄₃ characterized a less oxygenated and semi-volatile OA (Ng et al., 2010)”. I think the authors are over-generalizing the results from Ng et al. (2010). Ng et al. (2010) put all the PMF OOA components from multiple sites into the f₄₄ vs. f₄₃ space and found that all components fall into a triangular region, with the LV-OOA components concentrating on the top of the triangle and the SV-OOA components concentrating on the bottom of the triangle. In this case, the authors did not perform any factor analysis on their data. First of all, they have to at least show that the m/z 43 is indeed dominated by the C₂H₃O⁺ fragment. Secondly, the statement “f₄₄<f₄₃ characterized a less oxygenated and semi-volatile OA” is not always true, for instance, in Ng et al. (2010), the f₄₃ of SV-OOA components range from ~7% to 18%, there are actually SV-OOA components with f₄₄>f₄₃. Overall, I think the authors over-emphasized on f₄₄ and f₄₃ and ignored many other information they could have obtained from the analysis of their HR-AMS data. f. Page 11624, line 10. Is this true for all m/zs? Otherwise the authors cannot say “organic compounds”. What about m/z 55, 57 etc? g. Page 11624, line 28. The authors stated that the local sources of OA in winter time are limited. Does this include POA? If so, it is not necessarily true that the POA contribution is lower in winter? What about biomass burning OA (BBOA)? Are there any BBOA in winter time?

13. Section 4.3. This section is highly speculative, mainly owing to the lack of many important gas-phase measurements, such as NH₃, HNO₃, HONO etc required for their hypothesis.

a. The authors discussed the partitioning of nitrate as if this was a pure ammonium nitrate system. In reality, as the authors have shown, the aerosols consisted of organ-

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ics, sulfate, chloride, and soot. These other components are present in non-negligible amounts. How does the presence of these components (esp. organics and sulfate) affect the discussions and conclusions in this section? b. The authors should include RH and T in Fig. 4 c. Figure 5 is difficult to follow – I think scatter plots will serve the purpose better. d. The argument regarding the surface chemistry of HONO and HNO₃ is speculative owing to the lack of HONO and HNO₃ measurements. If the morning peak of NO is indeed produced by photolysis of HONO, shouldn't the authors expect OH also to have a peak around the same time NO peaks? (This is not seen from Fig. 6).

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