

Interactive comment on “The 2005 Study of Organic Aerosols at Riverside (SOAR-1): instrumental intercomparisons and fine particle composition” by K. S. Docherty et al.

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Responses to interactive comment No. 1

IC.1. P6328L20: "For instance, characteristic mass spectral fragments have been observed to indicate the presence of amines in particles sampled in a number of locations". Our recent paper (Ge et al., Atmos. Environ., 45, 2011, 524-546) summarized the observation of particle amines, and indeed some of them came from Riverside studies. Sun et al. (Atmos. Chem. Phys., 11, 1581–1602, 2011) were able to separate a unique nitrogen-enriching OA from NYC aerosols with high correlation with C₂H₄N⁺, C₃H₈N⁺ and C₄H₁₀N⁺ which are clearly indicative of amines.

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Response: We have added citations to Ge et al. (2011) and Sun et al. (2011) in P6328 L21, to acknowledge these additional studies. We note that the component reported by Sun et al. is unique for that study, but similar components have been observed by Aiken et al. (ACP 2009) in Mexico City and in this study (as discussed on P6333 L11-14 of the current ACPD manuscript).

IC.2: P6333L1-5: "The influence of amines on the HR-AMS ion balance is unknown. Amines may contribute to fragments nominally assigned to NH₄ (e.g., m/z 16, 17, and 18) in which case they would artificially increase both measured "ammonium" and apparent particle basicity." This is somehow in consistent with a recent paper (Hersey et al., Atmos. Chem. Phys. Discuss., 11, 5867–5933, 2011). They suggested the presence of amines led to the observation of significant excess of particulate ammonium.

Response: The subject of this comment is our discussion in the text regarding the impact of amines on the AMS ion balance. We have changed the first two sentences of this text for improved clarity to read:

"The influence of amines on the HR-AMS ion balance is unknown. Amines may contribute to fragments nominally assigned to NH₄ (e.g., m/z 16, 17, and 18) in which case they would artificially increase both measured "ammonium" and apparent particle basicity. As discussed above, amines can compete with NH₄ for particulate anions such as inorganic SO₄ and NO₃ forming ammonium salts (Murphy et al., 2007; Lloyd et al., 2009), thereby increasing nominal anion concentrations."

As we explain later in the text (L4-6) "However, amines can compete with NH₄ for particulate anions such as inorganic SO₄ and NO₃ forming salts (Murphy et al., 2007; Lloyd et al., 2009)..."

Each of these 2 possibilities (stand-alone organic amines, and amine salts) will have a different impact on the resulting ion balance which we discuss in the text. Both organic amines and amine salts may inflate the apparent NH₄ concentration if they contribute

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to signals at m/z 16, 17, and 18. Indeed, this is precisely the point that Hersey et al. (2011) makes with the following statement:

The AMS uses the ion signal at m/z 16, 17, and 18 to derive the concentration of NH_4 . Hersey et al. correctly point out that the AMS has no way to distinguish what, if any, fraction of NH_4 is due to amines. E.g.

p. 5884, l. 8: The AMS has difficulty distinguishing whether NH , NH_2 , and NH_3^+ (m/z 15, 16, and 17, respectively) are contributed by inorganics or organic amines.

Therefore, if amines contribute signal at these masses, the result would be to inflate the amount of nominally inorganic NH_4 reported by the standard AMS data analysis software.

Hersey et al. go on to state:

p. 5897, l. 6: An ammonium ratio of 1.28 ± 0.30 ... suggests that ammonium was in excess and that organic amines may have been an important constituent of submicron aerosol. . .

Here is where our results differ: the ammonium ratio of Hersey et al. was >1 which led them to conclude that organic amines were contributing to the concentration of NH_4 . However during SOAR-1 the ammonium ratio was <1 . Hersey et al. assume that the amines present in their aerosol samples were purely organic amines and not amine salts. In the case of amine salts the contribution to the NH_4 signal arising from amines will likely be buffered (in the ion balance calculation) by the associated anion signal. As we could not conclusively identify the nature of the amines in the aerosol during SOAR-1, we raised both possibilities. We believe this is clear in our text, with the one clarification discussed above.

IC.3: P6333L5: "amines can compete with NH_4 for particulate anions such as inorganic SO_4 and NO_3 forming salts..." Our recent work (Ge et al., *Atmos. Environ.*, 45, 2011, 561-577) proved that this could be true for a lot of amines based on thermody-

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amic calculations. Also, there are some other related studies might also be valuable: Barsanti et al. (*Atmos. Chem. Phys.*, 9, 2949-2957, 2009) and Rehbein et al., (*Environ. Sci. Technol.*, [dx.doi.org/10.1021/es1042113](https://doi.org/10.1021/es1042113).)

Response: The three additional references provided in this comment present similar results to those already cited in the manuscript. We believe that the references provided are sufficient for this point and have not added further references.

IC.4: At last, about Section 2. In my opinion, if the title is changed to "...Overview of results and instrumental intercomparison...", then the lengthy Section 2 will be inside the scope of the paper.

Response: The organization of the manuscript has been changed substantially in response to comments R1.5, R2.3, and R2.5, among others, and we believe this issue has thus been addressed already.

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/11/C9658/2011/acpd-11-C9658-2011-supplement.pdf>

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 11, 6301, 2011.

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