Author Response to the Referees' Comments on acp-2010-788

The authors thank the anonymous reviewers for their comments and specific suggestions to improve the manuscript. Because the reviewers shared some of the same concerns, we have addressed their comments together in the following:

Section 1: *Referee #2 is concerned that the introduction contains redundant detail that has been covered considerably in previous publications and suggests that the introduction be shortened, while Referee #1 states that the the introduction is written well with a sufficient amount of references to past work.*

The authors have chosen to keep the existing introduction for the following reasons: i) The basic chemical reactions and the literature review of laboratory and modeling studies provide context for the discussion of the potential mechanisms for the incorporation of amines in to aerosol, ii) The summary of online detection methods for amines in atmospheric aerosol provides context for the quantitative gas and particle composition measurements provided by the AIM-IC.

Section 2: *Both Referee #1 and Referee #2 suggest a more concise methodology to focus on the field measurements*.

The authors have reorganized the sub-sections and reduced the methodological content of this section by half to enhance the section's focus on the reported field measurements. Figures 1 and 3, and Tables 1 and 2 have been removed. Figures 2 and 4 were retained to highlight the quality of resolution of the amines in field samples by the reported methods, and the differing compromises of each approach.

Referee #1 - Page 27440, Line 2-5: write out the instrument names as opposed to just the acronyms

The Reviewer makes a good point and the instrument names have been written out in full for clarity.

Referee #1 – Page 27441, Line 29: Should it be "equivalent air concentrations of ng m-3" or "ng"?

The Reviewer is correct that 'ng' is used incorrectly here. 'ng' has been changed to 'pmol', describing the absolute detection limits of the ion chromatograph's conductivity detector as indicated in the abstract. This has been corrected.

Referee #1 – Page 27443, Line 15-18: Murphy et al. (2007) and Facchini et al. (2008) note in their methods sections that these species were targeted in those studies.

The references, taken together, potentially cover all of the amine compounds presented by the authors in this paper. Individually, however, Murphy et al. (2007) do not report observations of dimethylamine (DMA) which was present in all samples reported in this study, and in Facchini et al. (2008) it is indicated that mono- and trialkyl ammonium species could be detected using proton NMR, but a specific list of the amines that could be individually detected was not provided, nor in the referenced articles on the ion chromatography methodology (e.g. Matta et al. (2003), Decesari et al. (2000)). In any case, a reference to the Facchini et al. (2008) paper has been added and we reworded the statement to say 'measured' rather than 'investigated'.

Referee #1 – Page 27445, Line 15: can the authors delete "on the absolute amount of ammonia.."?

The suggested correction has been made to simplify the sentence.

Referee #1 – Section 2.2: Were denuders employed for the MOUDI sampling to account for artifacts from the gas phase?

The Reviewer presents a good question about potential interferences from reactive gases and whether they were corrected for through the use of denuders. Denuders were not used in the collection of these samples in order to limit possible size-dependent particle losses on the denuder walls. The authors have added this to the description of the MOUDI methodology with: "No denuders were used upstream of the MOUDI in order to limit possible size-dependent particle losses on the denuder walls. These losses can occur both in Aitken mode particles (< 0.1 μm) by Brownian diffusion (Ye et al., 1991)and in the coarse mode particles (> 2.5 μm) by impaction (Spurny, 1999).

Referee #2 – Page 27448, Line 25 and Page 27449, Line 10: Method detection limits need to be determined from a standard solution that still gives at least S/N = 3, not a blank solution. There is no guarantee that a detector responds to target analytes at an S/N = 3 concentration. Furthermore, a word of caution is warranted here for potentially much higher detection limits in the ambient samples due to matrix effects and extraction efficiencies.

The Reviewer raises an interesting point about the way in which the detection limits are calculated and the potential limitations of complex matrices and extraction efficiency. While the method of determining the detection limit as S/N = 3 in method blanks for chromatographic analyses (i.e. the instrument detection limit) is commonplace the Reviewer makes a good point that detector response at S/N=3 concentrations is not guaranteed. The authors have performed experiments to confirm a positive instrument response for all the analytes reported here at S/N=3 concentrations and, hence, this approach was deemed appropriate and consistent with the definitions provided by MacDougall and Crummett (1980). The authors have replaced 'method detection limits' with 'instrument detection limits' throughout the manuscript for clarity. A sentence has been added to clarify this further after Line 25: "Positive instrument response for target analytes at these concentrations was confirmed by offline injection of aqueous standards."

Matrix effects are only encountered in samples containing high concentrations of ions, which were dealt with by quantitation over multiple dilutions of the original sample as mentioned on

Page 27444, Line 27-28. (If high loadings were encountered during online sampling then the detection limit would indeed be higher, though this didn't occur in our sampling period). While we do not report the MOUDI extraction efficiency of the impactor filters, the extraction method is known to be nearly quantitative (~ 98 %) for water soluble compounds in the literature (e.g. Kouvarakis et al. (2002)). This information has been added to the manuscript. We did not measure the extraction efficiency of amines in the present study. Given the uncertainties associated with matrix effects and extraction efficiencies, the method detection limit could be higher than that calculated based on the instrument detection limit.

Referee #1 – Page 27450, Line 23: change 'was' to 'were'
done

Referee #2 – Page 27452, Line 18: Can the authors comment on a possible reason for an elevated concentration of amines in the 3.2–5.6 µm size range?

The Reviewer asks for hypotheses on the origin of coarse mode amines detected. The authors comment on a number of possible reasons for the presence of amines in the coarse mode aerosol (including the 3.2 – 5.6 µm range) at the end of section 3.1.

Referee #2 – Page 27455, Line 11 and Page 27460, Line 7: What do the authors mean by "... the fine aerosol population is internally mixed ..."? Do the authors mean that all fine particles are assumed to be internally mixed or the same chemical composition? It is not clear from the sentence if the authors state about the mixing state or chemical composition. Please clarify.

The authors agree that the terminology relating to 'internal mixing' is not appropriate here and have edited the following sentences for clarity:

"While the hourly measurements made using the AIM-IC provide data that can be used the evaluate the application of gas-particle partitioning models to amines, the strong size-dependence of the R3NH+/NH4+ ratio indicates that using bulk measurements ~~and an assumption of internal mixing~~ may not be appropriate."

"The observations in Fig. 7 demonstrate that an assumption that the fine aerosol population is internally mixed is not appropriate, especially with reference to the R3NH+/NH4+ ratio."
has been replaced with
"The observations in Fig. 7 demonstrate that there is a strong size-dependence to the fine aerosol composition, especially with reference to the R3NH+/NH4+ ratio."

"However the size dependence of the R3NH+/NH+4 ratio consistently seen in the MOUDI samples shows that an assumption that the fine aerosol population is internally mixed is not appropriate."
has been replaced with
"However the size dependence of the R3NH+/NH4+ ratio consistently seen in the MOUDI samples shows that an assumption that each size fraction of the fine aerosol population has the same relative composition as the bulk is not appropriate."

Referee #1 – Pg 27457, Line 16: Why is it written as C-ToF-AMS here and differently on Line 3 of Pg 27440? It should consistently be "C-ToF-AMS".

C-ToF-AMS has been applied consistently throughout the paper.

Referee #1 – Page 27452, Line 23: Other relevant studies that should be cited include. . .

The Referee noted that we had not covered all relevant studies in our Introduction and Discussion. The studies of (Miyazaki et al., 2010) and Sorooshian et al. 2009 were cited where appropriate.

References

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