

Reviewer 1#:

In my initial review, I indicated that their discussions on the mechanism of NH₃ on SOA leading to organonitrogen formation was both qualitative and speculative. In their response letter they claimed that “We cannot of course, be fully quantitative in these types of experiments for a variety of reasons. Such reasons include the inability to detect specific product molecules with the AMS, and the potential for other functional groups (ie: acids) to be formed from both precursors with oxidative aging. Regardless, the possible dominance of dicarbonyls in the aromatic system is a plausible reason for the enhanced NOC observed. While this cannot be confirmed we have nonetheless modified the manuscript to reflect this possibility”. They further revised the manuscript to indicate that “As discussed in Section 3.2, *α*-dicarbonyls are likely the most dominant products from the OH-initiated oxidation of *m*-xylene (Zhao et al., 2005), while organic acids are more likely the dominant SOA component from ozonolysis of *α*-pinene (Ma et al., 2013). This suggests an efficient reaction for *α*-dicarbonyls with NH₃ to form imine and/or imidazole and is consistent with the higher NOC content in the total SOA mass from OH oxidation of *m*-xylene”. I find that their argument was very confusing here. On what ground did they claim that the reaction of *α*-dicarbonyls with NH₃ to form imine and/or imidazole was more efficient than the acid-base reaction between organic acids and NH₃? Also, what was missing here was that the authors would need to provide a detailed account for both reaction types in the literature (see Zhang et al., 2015, Chem. Rev. for a review on heterogeneous reactions), both in the introduction and discussion sections.

Response: Thank you for your further comments and suggestions. We believe your confusion stems from the way in which those few lines were written. We did not intend to suggest that one reaction type was more efficient than the other, although we can see how one can derive this conclusion from the poor choice of words used in that sentence. What we were trying to point out was that in the *m*-xylene system, the reactions of carbonyls with NH₃ are likely more important than in the *α*-pinene system. This is based upon the fact that there was a higher NOC content in the *m*-xylene system, where NOC as defined here does not include NH_x AMS fragments. Acid-base reactions with ammonia will form ammonium salts which as far as the AMS is concerned would be manifested as NH_x fragments (as described on lines 380-383). Consequently, a higher NOC content would indeed be consistent with the dominance of carbonyl products in the oxidation of *m*-xylene compared to *α*-pinene. We have modified that paragraph to make this point clearer.

First, we have emphasized at the beginning of the aforementioned section (3.4) that

NOC cannot refer to acid base reactions (lines 455-457): *“Note that NOC as defined here is not likely to be a result of acid-base (organic acid-NH₃) reactions since NH_x fragments are excluded (See section 3.2).”*

We have also adjusted the wording of the lines in question to read as (lines 466-470): *“As discussed in Section 3.2, α -dicarbonyls are likely the most dominant products from the OH-initiated oxidation of m-xylene (Zhao et al., 2005), while organic acids are likely the dominant SOA components derived from the ozonolysis of α -pinene (Ma et al., 2013). This is consistent with the higher NOC content in the total SOA mass from the OH oxidation of m-xylene as shown in Figure 3.”*

We also leave open the possibility (lines 345-349) that acid-base reactions could have occurred despite the evidence described in lines 350-359 that suggests otherwise.

As you have suggested, both acid-base reactions and acid catalyzed reactions between amines or ammonia and carbonyl groups have been summarized in the introduction and discussion sections in our revised manuscript. For example, in lines 74-107, we have added to, and modified the existing paragraph. It now reads as: *“N-containing organic compounds (NOC) are an important class of heteroatom containing BrC compounds and can account for an appreciable fraction of organic aerosol mass (Beddows et al., 2004; Cheng et al., 2006 ;Kourtchev et al., 2014) which has been mainly attributed to biomass burning and cooking emissions (Cheng et al., 2006). As summarized in detail in a recent review paper (Zhang et al., 2015), heterogeneous reactions, which include acid-base reactions between amines and organic acids as well as acid-catalyzed reactions of carbonyl groups in OA with primary and secondary amines, are increasingly being considered an important source of particle bound organonitrogen compounds. For example, acid-base reactions between ammonia or amines and acid moieties (Liu et al., 2012b;Kuwata and Martin, 2012;Zhang et al., 2015) or exchange reactions of amines with inorganic ammonium salts (Chan and Chan, 2012;Bzdek et al., 2010;Qiu et al., 2011;Liu et al., 2012a) can lead to the formation of particle bound ammonium salts. Schiff base and/or Mannich reactions between NH₃, ammonium salts or amines with carbonyl functional groups in particles can also form organonitrogen compounds (Zhang et al., 2015), in which N atoms can be coupled to double bonds (imines) and act as effective chromophors since both π - π^* and n - π^* transitions are possible (Nguyen et al., 2013). It has also been proposed that Mannich reactions may be a possible formation mechanism for the high-molecular weight nitrogen-containing organic species observed in ambient particles (Wang et al., 2010b). Although it has not been confirmed with ambient data, the formation of light absorbing compounds has been*

inferred in laboratory studies during reactions between glyoxal, methylglyoxal and primary amines glycine, methylamine and ammonium (Zarzana et al., 2012; Yu et al., 2011; Powelson et al., 2014; Lee et al., 2013a; Trainic et al., 2011). Visible light absorption has also been observed from the reactions between O₃/OH initiated biogenic and anthropogenic SOA and NH₃ (Updyke et al., 2012; Nguyen et al., 2013; Lee et al., 2013b; Bones et al., 2010). Using High Resolution Time-of-Flight Aerosol Mass Spectrometry (HR-ToF-AMS) and Desorption Electrospray Ionization Mass Spectrometry (DESI-MS), characteristic fragments containing nitrogen (C_xH_yN_n and C_xH_yO_zN_n) from the above reactions have been identified (Galloway et al., 2009; Laskin et al., 2010; Lee et al., 2013a). Recent studies have found that BrC produced via such reactions is unstable with respect to degradation by oxidants (Sareen et al., 2013) and sunlight (Lee et al., 2014; Zhao et al., 2015), Regardless, NOC are likely to have very interesting chemical properties and atmospheric implications.”

Additionally, these reaction mechanisms were discussed in the discussion section (lines 298-306). Note that we had already described these reactions in section 3.2 and provided a generic mechanism in Scheme S1. Given that the various reactions of ammonia have now been noted in the introduction and discussion sections, with appropriate references, we feel this amount of discourse on possible reactions is sufficient, particularly since the conclusions of this paper do not depend on knowing the exact chemical mechanisms involved. The kinetics of uptake remain accurate regardless of mechanism.

Also, I found the manuscript could be benefitted by a more careful editing for its usage of English. A few examples are given below in the abstract, and there are many others throughout the manuscript.

Response: Thank you for your suggestion. Various grammar errors have been fixed throughout the paper by a native English speaker.

Line 21. “The uptake coefficients of NH₃ to SOA leading to organonitrogen compounds are reported for the first time and were in the range of ~10⁻³-10⁻²”. Inconsistent tense usage.

Response: Thanks. The line 22 was revised as: “*Ammonia uptake coefficients onto SOA which led to organonitrogen compounds were reported for the first time, and were in the range of ~10⁻³-10⁻²,.....*”.

Line 33. “NOC from such a mechanism may be an important and unaccounted for source of PM associated nitrogen, and a mechanism for medium or long-range transport and dry/wet deposition of atmospheric nitrogen” is awkward.

Response: Thanks. This sentence (line 34) has rewritten as:

“NOC from such a mechanism may be an important and unaccounted for source of PM associated nitrogen. This mechanism may also contribute to the medium or long-range transport and wet/dry deposition of atmospheric nitrogen”.

Reviewer 2#

I am satisfied with the revisions done by the authors. Minor things remain:

Response: Thanks.

L76: remove extra space after “2006”

Response: It has been deleted in the revised manuscript in line 78.

L100: replace comma by period

Response: It has been corrected (line 106, in the revised manuscript).

L128: In the current -> In this

Response: It has been corrected (line 136, in the revised manuscript)

L138: Bunce et al. (Bunce et al., 1997) -> Bunce et al. (1997)

Response: It has been corrected (line 146, in the revised manuscript)

L233 and everywhere else m/z should be italicized

Response: It has been corrected throughout the paper (line 243....)

L269, L277, L336: Lin-Vien reference is missing the publication year

Response: It has been corrected lines 280, 289, 352 in the revised manuscript.

L340, L399, L465, L588, L610, etc. – please find and replace all: ie: -> i.e.,

Response: It has been corrected throughout the paper.

L342: See -> see

Response: It has been corrected in line 358 in the revised manuscript.

L348, L553: there is no reaction that is called “Schiff-base reaction”. There is a class of compounds called Schiff bases. There is indeed a reaction called “Mannich

reaction”. Please rephrase.

Response: Thanks. We have checked this term in Web of Science. Schiff-base reaction is correct in organic chemistry. For example, the following patent (F. C. Ford and P. A. Diocos, PH1200002351-B1) mentioned it as “Formation of **Schiff base reaction** product for use as perfume in laundry detergent composition, by combining perfume component, methyl anthranilate and acid catalyst in solvent, agitating reaction mixture, and neutralizing with mild base”. In other papers “Schiff base reaction” has also been used such as “Multifunctional Electrochemical Platforms Based on the Michael Addition/Schiff Base Reaction of Polydopamine Modified Reduced Graphene Oxide: Construction and Application” (Huang et al., ACS Appl. Mat.&Inter., 2015, 7(32), 17935-17946). Schiff-base reaction is the first step for Mannich reaction.

L415: Hence -> hence

Response: It has been corrected in [line 435](#) in the revised manuscript.

L470: Total -> total

Response: It has been corrected in [line 493](#) in the revised manuscript.

L515: check references on this line – it is not clear what “a” is attached to

Response: Thanks. Two papers from the same author was cited and it was corrected in [line 539](#) in the revised manuscript.

L583: 1.95 is the ratio between sulfuric acid and sodium sulfate but it may be misinterpreted as acidity (pH) in this sentence. I would use “=” instead of “:”

Response: Thanks. It has been replaced with “**content of particle-phase sulfuric acid**” in [line 607](#) in the revised manuscript. And “:” was replaced with “=”.

L589: Poschl -> Pöschl

Response: It has been corrected in [line 613](#).

Reference section: capitalization of titles is not uniform between different reference, not a big deal, perhaps.

Response: It has been corrected throughout the revised manuscript.

L747: the superscript after SO₄ should be 2-

Response: It has been corrected in [line 775](#).

L841: missing space

Response: It has been fixed in [line 870](#).

L960: different font used

Response: It has been fixed in [line 989](#).

L970. L975: interchange the order of “a” and period in the top –left cell

Response: It has been fixed in [lines 1003 and 1008](#).

L971: removed period after “a”

Response: It has been fixed in [line 1009](#).

Figure 3: panel indexes C and D are not visible – I would change their font color to yellow.

Response: It has been fixed in [Figure 3](#).