

Response to Reviewer Comments

Effect of Humidity on the Composition and Yield of Isoprene Photooxidation Secondary Organic Aerosol

Tran B. Nguyen, Patrick J. Roach, Julia Laskin, Alexander Laskin and Sergey A. Nizkorodov

Atmos. Chem. Phys. Discuss., 11, 9217-9248, 2011
www.atmos-chem-phys-discuss.net/11/9217/2011/
doi:10.5194/acpd-11-9217-2011

Dear Editor,

We have chosen to provide a combined response to both anonymous reviewers. We have incorporated most of the suggestions into the text of the revised manuscript. The reviewers' comments are reproduced below, and are followed by our responses and/or a summary of revisions to the manuscript in italic.

Sincerely, on behalf of my co-authors,

Tran Nguyen

Response to Anonymous Referee #1

Received and published: 6 April 2011

The authors demonstrate the chemical composition of SOA changes substantially under high or low RH but that the SOA mass, and therefore SOA yield (using conventional definition) did not change. These results are consistent with Dommen et al., who studied the RH effect on SOA formed during isoprene + OH oxidation extensively and found no effect on the SOA mass/SOA yield. The finding that the chemical composition of the SOA changes though is quite important. There are implications for CCN suitability as well as other physio-chemical properties. The discussion at the end of the paper is important, but the introduction of new ideas and a new framing of the findings at the end of the manuscript is a bit awkward. There are some experimental details that require better justification. My main concern is that the use of signal-to-noise (S/N) ratio seems not well defended. The S/N could change due to changes in the signal (potentially due to increases in concentration) or due to changes in the noise (potentially due to higher variability). Usually, the signal is used to make statements regarding concentrations.

Provided the authors can defend the use of S/N and provide explanation or clarification to the comments below, this paper is suitable for publication in Atmospheric Chemistry and Physics

We thank the referee for the insightful comments. We will address the concerns brought up by the referee in the detailed comments below.

1. Abstract, Line 7: Is the word significant used colloquially or does it imply a statistical test?

We used the term colloquially to imply the change in SOA composition inferred from the apparent and reproducible differences between the high resolution mass spectra. A metric for quantification of the degree of chemical dissimilarity between different mixtures of organic compounds in environmental samples, such as different types of SOA, does not really exist. In order to come up with such a metric, the composition of the mixture would need to be tied to a specific property of interest such as toxicity, solubility, phase state, surface activity in aqueous solutions, etc. With improvement in analytical methods, atmospheric scientists should be able to accomplish this in the future.

2. Page 9218, line 4: I think the proper notation for 2 author works would make it Finlayson-Pitts and Pitts, not Finlayson-Pitts et al. That book has very useful descriptions of the gas phase oxidation products of isoprene + OH, but there is no discussion regarding subsequent SOA formation.

The notation “Finlayson Pitts et al.” was a typesetting mistake that we overlooked. We have changed it to “Finlayson-Pitts and Pitts” in the revised paper. We meant to refer the readers to a general description of the mechanism of isoprene photooxidation and we thought this book would be a suitable choice. However, the reviewer is correct in that the specific sentence is focused on SOA production. Therefore, the reference was moved to a more appropriate place in the text: introduction of the formation of nitrogen-containing organic compounds, which the text by Finlayson-Pitts and Pitts covers really well.

3. Page 9219, line 4: mechanism of SOA formation might be better wording

We have added “SOA” before the word “formation” in the revised manuscript.

4. Page 9219, line 7: the presence of liquid water not only affects chemical reactions. I think of partitioning as a physical process.

We have changed the sentence to include physical processes as well as chemical. The sentence now reads "...therefore any chemical reaction or physical process that involves water as a reactant, product, or solvent may be affected."

5. Page 9219, Line 10: This volume is sufficient to dissolve the most water soluble compounds. Is this volume not sufficient to accommodate water soluble compounds that are not the most soluble?

We agree that the sentence in question should be clarified as the term "most soluble" is qualitative and can be interpreted in different ways. Organic aerosols contain compounds, which range in their solubility properties from being miscible with water in all proportions to being completely insoluble for all the practical purposes. Our point is that 30% of the particle volume represented by an aqueous phase may be enough to have some water-soluble compounds partition in the aqueous phase. We have changed the sentence to say "This may be sufficient to have a substantial fraction of organic compounds partition in the aqueous phase."

6. Page 9219, Line 20: increased LWC can affect the rate of uptake, but the volatility of the VOC (or its oxidation products) does not change. The thermodynamics remain constant, just the kinetics change. This sentence should be re-worded.

The revised sentence reads "One possible consequence of LWC is an increase in reactive uptake kinetics of VOC into the aerosol phase..."

7. Page 9219, Line 24: This a curious sentence/reference mix. It is true that methylglyoxal hydrates in the condensed phase, but the first reference is about glyoxal. There is mention of the word "methyl glyoxal" in references cited but only in the introductions/discussions, not in the experiment. If the authors want to talk about methylglyoxal specifically (and not glyoxal, as I agree and think they should) a reference that studies methylglyoxal specifically might be more appropriate (a recent example that comes up in my ISI search is Tan et al., (2010) AE 44(9):5218-5226).

The revised sentence now reads “One possible consequence of LWC is an increase in reactive uptake kinetics of volatile organic compounds (VOC) into the aerosol phase because gas-phase carbonyls, like glyoxal and methylglyoxal, may hydrate on particles containing adsorbed water, and subsequently polymerize into less volatile products (Liggio et al., 2005b; Liggio et al., 2005a; Jang and Kamens, 2001; Jang et al., 2003; Axson et al., 2010; Loeffler et al., 2006; Altieri et al., 2008; Tan et al., 2010; Fu et al., 2009; Jayne et al., 1992; Corrigan et al., 2008).”

8. Page 9220, Line 4: can chemical reactions in the aqueous phase produce compounds that are not water soluble?

Yes, the reactions mentioned can produce compounds that are less water-soluble than the initial reactants. Both water-soluble and non water-soluble oligomer products are important to SOA growth because oligomer products are less volatile than the reactants and therefore more likely to stay in aerosol phase regardless of solubility behavior. The difference in solubility of compounds produced between the dry and humid SOA forming conditions is one of the main conclusions of the paper, as the two conditions favor different classes of chemical reactions.

9. Page 9220, Line 16 due to increased LWC

The word “increased” has been inserted.

10. Page 9220, Line 16/17 I think the correct term is keto-enol tautomerism
The sentence is changed to “...due to shifts in the keto-enol tautomerism.”

11. Page 9221, Experimental section: The authors provide uncertainty estimates for temperature and relative humidity. How about for O₃, NO/NO_x/NO_y?

The accuracy of measurement for the mentioned compounds were inserted in the appropriate places in the experimental section.

12. Page 9221, Experimental section: The authors state the RH was initially 90% for “humid” experiments, but during the experiment RH was “somewhat” lower due to a slight rise in temperature (5 deg. C). A quick estimation of potential RH change for the system suggests

changes of more than 20%, which is substantial (e.g., 90% RH vs. 70%). The authors do not need to be qualitative, they can quantitatively explain what the RH values were.

We have changed the sentence to reflect the more quantitative assessment of RH. “The actual RH experienced by the reacting mixture was lower at the end of the reaction period (70-80% RH) due to a slight rise in temperature (3-5 °C) in the chamber during the photooxidation.”

13. Experimental section: The reference provided for the 1.2 g cm^{-3} density assumption is from a study investigating α -pinene ozonolysis. The VOC was different and ozonolysis is an inherently different oxidation process with very different products. Can the authors defend their selection for particle density a little more robustly? How sensitive are the findings to this assumption?

Particle density measurements have been conducted for a number of SOA produced from oxidation of monoterpenes or aromatic VOC (Kostenidou et al., 2007; Malloy et al., 2009; Bahreini et al., 2005; Zelenyuk et al., 2008b; Shilling et al., 2009). From these studies, SOA from biogenic VOC are reported to have densities of approximately 1.2 g cm^{-3} . We are not aware of a density measurement for the isoprene photooxidation SOA. An estimation of the density of isoprene photooxidation SOA can be inferred from comparing the AMS aerodynamic size and DMA mobility size measurements ($\sim 1.25 \text{ g cm}^{-3}$) (Surratt et al., 2006); however, the estimation from that specific work was for particles containing inorganic seeds. Density measurements may also be mass loading-dependent: experiments with SOA loadings similar to our work ($\sim 20 \mu\text{g m}^{-3}$), for α -pinene SOA, corresponds to a density value of 1.23 g cm^{-3} (Shilling et al., 2008).

Particle density is needed to calculate the absolute values of the SOA yields from the SMPS data. However, it is not necessary to know the density to compare the relative yields between the dry and humid conditions. What is of more importance is the effect an exposure to humidity can have on the particle density. We are making an assumption that the density of a particle formed under dry conditions, and that of a particle formed under humidified conditions, followed by drying, are similar. We are not in a position to verify this assumption, and to the best of our knowledge such an experiment has not been done before. Therefore, the relative SOA yields need to be treated as approximate, and we acknowledge this in the paper. As the main focus of the manuscript is the effect of RH on the SOA chemical composition, the assumption of a particle density of 1.2 g cm^{-3} based mainly on α -pinene ozonolysis experiments do not change the

main conclusions of the paper. However, we will insert the citations provided here in this response into the text to further support our decision to use the assumed density.

14. Page 9224, Line 22 typo with lacetaldehyde?

We believe the sentence is correct as written. We mentioned acetic acid and lactaldehyde in line 20 as possible interferences, if present in the chamber, at the two aforementioned masses (m/z 61.03 and 75.04, respectively). We explained why acetic acid was unlikely in line 21 and why lactaldehyde is unlikely in lines 22-23.

15. Page 9225, Line 9/10: The fact that the conventional definition of SOA yield is insufficient is an important point. They might also want to mention this in the caption for Figure 2. The authors should state explicitly the formula they used.

We inserted the following into the caption of Figure 2: “The time-dependent SOA yield in panel (d) is defined as $[(mass)_{SOA}/(mass)_{Reacted\ Isoprene}]_t$ [note: oxidation of MAC and MVK also contributes to SOA mass].”

16. Page 9226: Changes in the S/N could be due to higher variability or less mass at a particular m/z correct?

Based on our past experiments, the relative S/N is very reproducible in the ESI-MS analysis of SOA extracts. As long as the tuning parameters for the instrument do not change repeated spectra for the same sample or spectra of different samples prepared under identical conditions are very reproducible. We demonstrate in Figure S1 by using the same S/N range on the vertical axis that for the same type of SOA, even at different SOA loadings, the S/N of most peaks do not vary between experiments. Furthermore, we typically re-take mass spectra several times in the window of a few days, after instrument calibration, in order to assure reproducibility and stability of the signal of extracted SOA compounds. Because of these reasons, we are confident that S/N can be used as a measure of ion abundance in the mass spectra.

17. Page 9228 Line 18, increase in the gas phase would be surprising, but not in the condensed phase.

The sentence has been changed to refer only to the gas-phase compounds: “...the increase in the abundances of these products in the gas phase under higher RH conditions is unexpected.”

18. Atmospheric Implications: The discussion of chain length, solubility, viscosity all seems very important. However it is awkward to introduce new ideas at the end of the paper. Perhaps the authors can find a better spot in the manuscript to begin this discussion?

In response to this comment, we have added a sentence to introduce the topic “The changes in composition affects the physical characteristics of the SOA (Zelenyuk et al., 2008a), e.g. hygroscopicity, viscosity, etc., which may have profound implications in the atmosphere.”

19. Page 9234, starting at line 19: the hygroscopicity of SOA formed from α -pinene ozonolysis? Are the chemical properties of compounds formed via ozonolysis similar enough to isoprene + OH oxidation to say that the results are expected or in agreement? I think we can say they are not inconsistent with each other. The sulfate/CCN sentences as written seem non-sequitor. The work here also does not investigate CCN activity.

To the best of our knowledge, there are currently no studies performed on the impact of chamber relative humidity on hygroscopicity of isoprene/OH SOA. We cited the study on α -pinene ozonolysis SOA as an example of the way the hygroscopicity of biogenic SOA could change based on the initial water vapor concentration affecting the SOA composition. We mentioned in the text that a similar study done with isoprene SOA would be very interesting and would expand upon these conclusions to a wider range of SOA.

The second point the reviewer makes that CCN activity and hygroscopicity should not be used interchangeably is valid. Hygroscopicity and CCN activity are closely related to each other as more hygroscopic compounds are more likely to activate cloud droplets at lower values of relative humidity (King et al., 2010; Hori et al., 2003; Poulain, 2010). We referred to a study by King et al (2010) that reported CCN activity for isoprene photooxidation products that related the CCN activity to a “hygroscopicity parameter (κ)” (King et al., 2010). Because of the relation, we changed the sentence in question to refer to hygroscopicity instead of CCN activity to be in better keeping with the logical flow of the paragraph.

20. Table 1: caption: number of carbons in the in the monomer unit. Why not call “kmax” what it is, that is “homologous units” or homologues? Kmax wet and dry should be identified in the column heading similar to “total signal”.

We believe that k_{max} is more consistent with the notation we used in other parts of the text which is (parent molecular formula) + (oligomer unit)_k, e.g. $C_xH_yO_zN_w + (C_4H_6O_3)_k$. The k_{max} values corresponding to humid and dry conditions are now more explicitly identified in Table 1 under the respective headings.

21. Figure 2. The secondary y-axis in (a) shouldn't go to 50. It seems there are important differences at t_30 minutes for 3MF, if the axis went to _10, readers would be able to see this better. Figure 2 is small and difficult to read in general.

There is a small difference between the concentration of 3MF at around t=40 minutes (6.8 ppb humid vs. 5.4 ppb dry). The difference may stem either from user error in the injection of isoprene (notice that isoprene and MVK/MAC traces under dry vs. humid conditions also do not perfectly overlap) causing a slight difference in oxidation, or perhaps it is genuinely induced by humidity effects. The point we are making is that compared to the > 20 ppb difference in glycolaldehyde and hydroxyacetone between dry and humid conditions, the variation in mixing ratios of other VOC appears to be insignificant. We state that formaldehyde concentrations also show an important difference that is discernable even with a much larger concentration scale (in this case the difference is around 12 ppb and may be attributed to differences in loss mechanisms after the formaldehyde is produced.) We do not think that the ~ 1 ppb difference in the 3MF concentration warrants a larger scale on the right hand vertical axis, which would make the graph even harder to read as the traces for the VOC will overlap.

22. Figure 3. Why not show the arbitrary units of the signal. The S/N can change due to changes in signal or in the variability (noise). The signal could actually be higher, suggesting more mass, but with more variability there could be a lower S/N. There seems to be a higher potential for mis-interpretation.

See our response to comment #16. S/N is a reproducible metric of ion abundance as the variability of the noise level in the instrument is minimal.

23. Figure S-1: the caption states “the S/N of the peaks in the 10 ug/m³ sample is noticeably smaller than for the 40 ug/m³ sample”. This is apparent for the m/z of _125, but not elsewhere in the spectrum.

The reviewer is correct. Our point is that the intensity distribution does not change significantly, which is showcased in the figure and mentioned in the text of the manuscript. The sentence referred to by the reviewer can indeed be misinterpreted. We have deleted this sentence to improve the clarity of the caption.

23. Editorial: define VOC and m/z at first use 4 digit zip code for Roach affiliation

We have edited the introduction to properly define VOC at first use, and added the zip code for Roach & Associates affiliation (54165)

Response to Anonymous Referee #2

Received and published: 14 May 2011

Overall Comments:

This paper examines the effect of RH on SOA formed from the photooxidation of isoprene under high-NO_x conditions; specifically, this study employed H₂O₂ photolysis to generate sufficient OH radicals to drive the chemistry forward as was done in Kroll et al. (2006, ES&T) and Surratt et al. (2006, JPCA). This is a well-presented and concise study that will certainly be of high interest to the atmospheric aerosol research community, especially since the effect of RH on isoprene SOA formation has not yet been extensively examined. Most of the prior work has examined the effects of NO_x (Dommen et al., 2006, GRL; Kroll et al., 2005, GRL; Kroll et al., 2006, ES&T; Surratt et al., 2006, JPCA; Surratt et al., 2010, PNAS) and aerosol acidity (Edney et al., 2005, Atmos. Environ; Surratt et al., 2007, ES&T; Surratt et al., 2010, PNAS) on isoprene SOA formation under dry conditions only. Importantly, the present manuscript's chemical composition results are quite consistent with the recent findings of the Surratt research group at UNC (i.e., Zhang et al., 2011, ACPD); specifically, oligoesters of 2 methylglyceric acid (2-MG) are enhanced under dry conditions. The Zhang et al. (2011, ACPD) study was published about 1 month before this study appeared in the online discussion of ACP, and thus, the authors were probably unaware of the Zhang et al. (2011) study. With that said, the authors should include this new study in their discussion, as there are some important differences that need to be compared and discussed thoroughly. For example, there were several differences in how the experiments were designed in these studies. These experimental differences might explain why the SOA yield results differ between these two studies. As will be mentioned below in my specific comments, these experimental differences include the different oxidative conditions employed (i.e., an OH precursors versus no OH precursor) and also nucleation versus condensation of semivolatiles onto preexisting seed aerosols. This study should be published in ACP only when the authors fully address the detailed and technical comments outlined below in this review.

We thank the reviewer for the thorough review of this scientific problem, and for providing useful information about additional relevant citations. At the time of submission, we

were not aware of the study by Zhang et al which appeared in APCD shortly before our paper was submitted. We will expand the discussion in the manuscript to include this study.

Detailed/Specific Comments:

Note: comment #1 was split into three separate sections to improve clarity of the presentation

1a. SOA Yields – Use of H₂O₂ as an OH precursor: The biggest issue that needs to be resolved by the authors is related to the SOA mass measurements (or yields). The reason for this concern is it is unclear how the authors of this study deal with H₂O₂ partitioning into wet aerosols in their humid experiments, and thus, further reacting with semivolatiles or nonvolatiles in the aerosol phase. The latter could cause undesired chemistry to occur. More importantly, how can the authors correct their SOA mass measurements due to absorption of H₂O₂ in wet aerosols? This absorption could cause an overestimate of the true SOA mass yield under humid conditions. As Kroll et al. (2006) pointed out, the use of H₂O₂ as an OH precursor required that isoprene SOA generation be done under dry conditions due to its relatively high Henry's law constant. H₂O₂ is known to be miscible in water.

We acknowledge the referee's concern about H₂O₂ partitioning in the humid conditions and we have indeed thought about this issue when designing our experiments. We support our decision to use H₂O₂ as an OH precursor in our experiments for the following reasons:

- 1) Our results are consistent with the Dommen et al (2006) who investigated SOA formation over a broad range of conditions and did not use H₂O₂ as an OH precursor. Rather, Dommen et al (2006) studied the "classical photooxidation" conditions the referee mentioned in further comments, and came to the conclusion that isoprene SOA yield were not detectably different between the dry vs. humid conditions which is consistent with our work. The difference in the Kroll et al (2006) study and the studies of our group and Dommen et al (2006) is the latter two studies did not use inorganic seed particles. We specifically wanted to avoid inorganic seeds (e.g. (NH₄)₂SO₄) in humidified experiments because such particles would condense much more water than organic particles would. Inorganic particles commonly used as seeds in aerosol experiments are considerably more hygroscopic than typical organic particles. Addition of organics to the inorganic*

seeds suppresses their hygroscopic properties somewhat but even such mixed particles remain sufficiently hygroscopic to attract significant quantities of water at elevated RH. For example, pure adipic acid or succinic acid aerosol had a hygroscopic growth factor (GF) of 1.00-1.01 at RH = 90% but if one mixes these organics with inorganic seeds, even at a modest 1:1 mixture the GF increases to 1.33-1.52 (Prenni et al., 2003). For model biogenic SOA from photooxidation of monoterpenes (unfortunately data for isoprene is not available), GF=1.05-1.10 in the absence of (NH₄)₂SO₄ throughout the oxidation period at RH = 85% (Virkkula et al., 1999). In seeded experiments, Virkkula et al (1999) observed GF ≈ 1.5 at the beginning of the experiment that decreased to GF=1.05-1.13 at the end of the oxidation period because the inorganic seeds were thoroughly coated with SOA mass. With GF of 1.5, the particle's water:solute ratio becomes of the order of 2:1. In our experiments, the goal was to have liquid water content (LWC) characteristic of purely organic particles, and we have chosen to do seedless experiments.

- 2) The issue of H₂O₂ partitioning is a valid one; however, it more important in experiments where inorganic seeds are used. With significant LWC in seeded experiments, H₂O₂ can partition into aqueous phase already at the beginning of the experiment. We made our particles through nucleation, as Dommen et al did. With LWC appearing only by the end of the experiment the H₂O₂ aqueous photochemistry should be suppressed. We have estimated the fraction of OH produced through aqueous vs gas-phase photochemistry under our conditions – the aqueous fraction is negligibly small. PTR-MS measurements support this - we do not observe a reduction in the gas-phase concentrations in the presence of organic particles and humidity*

As other readers may have similar concerns, we have amended the manuscript's experimental section with the following text:

“Under high RH conditions, H₂O₂ may partition into the adsorbed water on particles and potentially contribute to aqueous photochemistry (Kroll et al., 2006). We estimate that the contribution of aqueous photochemistry to the production of OH is negligible under our experimental conditions, largely because we do not use inorganic seeds. The hygroscopic growth factors (GF) for model biogenic OA are in the range of 1.05-1.10 (Virkkula et al., 1999), which

are much smaller than the corresponding GF of 1.5-2.1 reported (Virkkula et al., 1999; Cruz and Pandis, 2000) for inorganic salts typically used as seeds in aerosol chamber experiments. This helps suppress the particle LWC, and minimize the rate of the aqueous photochemistry. The rates of gas-phase oxidation of isoprene and its derivatives do not change between dry and humid conditions (Fig. 2a) confirming that the gas-phase OH is not significantly depleted due to partitioning of H₂O₂ in the particle aqueous phase.”

1b. In addition to this concern, the observation of similar amounts of 2-MG monomer under both humid and dry conditions is at odds with the Zhang et al. (2011, ACPD) study. In Zhang et al. (2011) they observed enhanced concentrations of both 2-MG and its corresponding oligoesters under dry conditions. This raises the concern now that H₂O₂ is not only affecting the SOA mass measurements, but it is also absorbed in the wet aerosol (or humid) experiments of the present manuscript causing formation of 2-MG from H₂O₂ + methacrylic acid or H₂O₂ + methacrolein pathways, which these pathways were demonstrated by Claeys et al. (2004, Atmos. Environ).

At the time of writing, we were not aware of the manuscript of Zhang et al (2011, ACPD) reporting that 2MGA is produced in higher the quantity in the drier conditions. We have presented arguments in the text that H₂O₂ aqueous chemistry is unlikely to be important in the non-seeded experiments, but may potentially be more important in seeded experiments conducted under high RH conditions. We are citing the Claeys et al. (2004, Atmos. Environ) paper in the text.

1c. I caution the authors to tone down their conclusion that RH does not seem to affect the SOA yields from isoprene photooxidation under high-NO_x conditions. Have the authors considered examining this system again but without the use of H₂O₂ as an OH radical precursor? For example, rely on the “classical photooxidation” experimental approach where one only injects NO and VOC into chamber and then irradiate the mixture. I wonder what the authors will find with their SOA mass measurements in that case. It should be noted here that 2-MG and its corresponding oligoesters have now been demonstrated to form from the further oxidation of methylacryloylperoxynitrate (MPAN), especially under increasing NO₂/NO ratios (Surratt et al., 2010, PNAS; Chan et al., 2010, ACP).

We believe that our conclusions regarding the small effect of RH on the overall aerosol yield are correct. Both our work and the work of Dommen et al (2006) demonstrated that SOA yield from isoprene under high-NO_x conditions is not significantly affected by RH in non-seeded chamber experiments. Dommen et al (2006) performed “classical photooxidation” experiments suggested by the reviewer and we used H₂O₂ as an OH precursor. We do, however, think it is important to distinguish between seeded and non-seeded scenarios, as there could be differences between these two types of experiments. Hence, we have taken the referee’s advice to mention clearly in the abstract, introduction, experimental and results & discussion sessions that we did not use inorganic seeds in the datasets from which these conclusions were derived. We have toned down the statements mentioned by the reviewer.

2. SOA Yields – Nucleation versus Seed Aerosol Experiments. Both the present study and the Dommen et al. (2006, GRL) study did not use seed aerosol. That is probably why they also both did not observe SOA yield changes between the dry and humid experiments. This is at odds with the recent study by Zhang et al. (2011, ACPD). However, in the ambient atmosphere, there is background aerosol. How does seed aerosol affect SOA yield? Kroll et al. (2007, ES&T) pointed out that SOA yield may vary with or without seed aerosol (higher SOA yield with seed aerosol). It is very likely that the isoprene SOA yield under different RH could be different in the presence of seed aerosol, such as demonstrated by Zhang et al. (2011, ACPD). Thus, the yield result in this study is not sufficient to conclude that RH does not significantly affect isoprene SOA yield in the atmosphere.

We agree with the referee that the discrepancy in yield results is likely due to the initial presence or absence of inorganic seeds. In our opinion, the observation that the chemical composition changes dramatically without an accompanying change in organic mass (the total particle mass) is very interesting, and it should inspire additional work in this area. We have not had a chance to explore the full dimensionality of this possible trend (different types of seeds, effect of temperature, broader range of RH values, adding humidity after vs before the particle formation, ext.), and we hope that the community will address these interesting questions in the future. In the present set of experiments, the particle mass comes exclusively from the production of organics. Although this is not the most realistic scenario, it may be applicable to SOA formed in remote atmosphere or SOA formed after a recent nucleation event (when the seed particles

are still relatively small). We understand that the yield results are not applicable to conditions with high initial concentration of particulate matter, and we were careful to avoid making claims to the contrary. For example, our “atmospheric implications” section is focused entirely on the discussion of the composition of the SOA and how it could potentially affect SOA properties. However, we will make the following changes for clarity:

- a) In the introduction at the first mention of Dommen et al study, we note that they did not use inorganic seeds. We also added a citation to the Zhang et al study in the text:

“Isoprene photooxidation SOA has been studied under a variety of RH conditions (Carlton et al., 2009). Dommen et al (2006) studied SOA yields from isoprene photooxidation generated without inorganic seeds under 2-84% RH and found that high RH does not considerably change the SOA yields and gas-particle partitioning in the SOA formation process (Dommen, 2006). However, a recent study by Zhang et al (2011) found an approximately 2-fold increase in SOA yield in the dry vs. humid conditions when using ammonium sulfate seed aerosol (Zhang, 2011). The conclusions from these two studies are not consistent with the modeling predictions that isoprene SOA yield is enhanced under humid conditions (Couvidat, 2011). The disagreement between the isoprene SOA yields measured under different RH conditions in Dommen et al (2006) vs. Zhang et al (2011) experiments is likely due to the absence and presence of seed particles, but other factors could also contribute. The present work does not use seed particles and therefore is more comparable to the work of Dommen et al (2006) with respect to the RH effect on the SOA yields.”

- b) Section 3.1, when discussing Figure 2, we revised the caption as follows “Figure 2d clearly demonstrates that RH does not substantially affect SOA yield from isoprene photooxidation in the absence of inorganic seeds”

3. In the manuscript, the authors mentioned “several types of processes may be induced by LWC, with conflicting effects”. Based upon their results, apparently, the enhanced SOA from aqueous-phase uptake of glyoxal, methylglyoxal, and glycolaldehyde under higher RH and the enhanced SOA from oligomerization, such as esterification under lower RH conditions, are two major conflicting processes. The same SOA yields indicate that these conflicting processes offset each

other. However, the experimental setting of this study only investigated one pair of high RH and one low RH (90% and <2%). Also, this study only investigated one isoprene/NO ratio (1:3). As the RH changes from dry to humid and isoprene/NO ratio varies, the contribution to SOA formation and the extent of these process may alter as well. Therefore, the SOA yield could also be different under varying RH conditions and oxidative conditions (i.e., RO₂ + NO or RO₂ + RO₂ or RO₂ + HO₂ dominates the gas-phase chemistry).

The referee's point is well taken. However, as we mentioned above, the focus of our paper is not on SOA yield. If it was the main focus, we would indeed study the yield from isoprene (as have been done previously) at many different RH and NO_x conditions and dedicate a major fraction of the paper to the discussion of yields. The subject of SOA yield under different NO_x and RH conditions has, in our opinion, been explored by several groups in a number of works that we have cited in the manuscript. We mentioned in the text that the detailed molecular composition is something that is much less studied, and we focus our efforts on understanding composition changes and chemistry. In addition, analyzing the composition changes by high-resolution mass spectrometry is a time-consuming process and therefore, we picked just two extreme cases of RH in order to determine the most dramatic changes. Doing these experiments over a very broad range of conditions would take prohibitively long.

4. DMA Measurements: RH in the DMA was set to be <10%. When the particles in the humid experiment go through the SMPS, will this much lower RH change the chemistry before detection? For example, assuming glyoxal, methylglyoxal, and glycolaldehyde aqueous-phase uptake is not reversible, drying the aerosol will not change these SOA mass. But reactions like esterification will likely be driven towards more SOA formation by drying, which increases SOA yield. If this is the case, a higher SOA yield under dry conditions would be expected.

We have not verified whether these particles are achieving equilibrium with respect to their content of liquid water and content of reversibly absorbed organics on a times scale of passing through the DMA. We agree with the reviewer that if such equilibria are slow, the apparent particle size and therefore the apparent yield will be affected. The proper way to do this experiment is to let particles go through driers, and vary the drying time to make sure the equilibrium is achieved. The next level of sophistication in this experiment would involve using thermodenuders to drive the more volatile organic compounds off the particles.

5. ESI-MS and DESI-MS Analyses. The analytical techniques employed are appropriate here; however, why was chromatographic separation not employed before ESI-MS detection? ESI is commonly known to easily form clusters or artifacts, and as a result, can cause for misinterpretation of mass spectral data. How do you know that what you observe in terms of oligomers is not simply a result of ions clustering together in the mass spectrometer? The use of chromatographic separation, like that done by Surratt et al. (2006, JPCA) and Zhang et al. (2011, ACPD), clearly show that these oligoesters are real and resolvable on a chromatographic (in these prior cases a reverse-phase column) column. This further supports that these constituents are not artifacts in these prior studies.

There are several ways to prove that high-molecular weight compounds detected by the ESI-MS instrument are real molecules and not ion clusters generated by the ESI process. In our work, we chose to do this with MSⁿ instead of LC, which is an effective method to estimate the stability of these molecules with respect to collision induced dissociation. We explained in the text that ion selection by the linear ion trap and further collision-induced dissociation (CID) in MSⁿ experiments prove the molecules are real due to the relatively high CID energy necessary to fragment the ions. We understand that other groups, and our own group (unpublished results on limonene SOA), have done LC and came to the same conclusions. It should be well-established at this point that high molecular weight compounds detected in ESI-MS spectra of dilute SOA extracts are real molecules, and not ionic clusters.

6. Comparison with other studies in Discussion Sections. I suggest that the authors also compare their yields and chemical results with priors studies of Kroll et al. (2005, GRL), Kroll et al. (2006), Surratt et al. (2006, JPCA), Dommen et al. (2006, GRL) and Zhang et al. (2011, ACPD). It would be of use to include the discussion of how differences in seed aerosol conditions, oxidative conditions, etc., lead to differences in yields between the present study and these prior studies.

As our SOA yield measurements were done under different conditions than the references suggested by the referee, and are a relatively minor focus in this manuscript, we believe that a detailed discussion of the measured absolute yields is unwarranted. Furthermore, we have not waited for the SOA generation to come to completion, and have not corrected the measurements

for the wall loss effect (as done in proper yield measurements). However, we agree that the differences in oxidative conditions need to be clearly explained. As the work of Zhang et al (2011) is directly relevant to our work, we have also included a comparison to that work in addition to the comparison to the Dommen et al (2006) work. We have added the following clarifying sentences to the end of the 3.1 section (SOA yield and gas-phase reaction products):

“Figure 2d demonstrates that RH does not substantially affect the SOA yield from isoprene photooxidation in the absence of inorganic seeds. This result qualitatively agrees with conclusions of Dommen et al (2006) who reported no significant change in the SOA yields at different RH (Dommen, 2006), also for SOA generated in the absence of inorganic seeds. However, our observations are different from the recent study of Zhang et al (2011) who reported an enhancement of the SOA yield under dry conditions from isoprene photooxidation in (NH₄)₂SO₄-seeded experiments (Zhang, 2011). The presence of inorganic seeds in the chamber is an important difference between the seeded and non-seeded experiments. (NH₄)₂SO₄ particles exhibit significant hygroscopic growth at elevated RH (GF~ 1.5 at 85% RH for (NH₄)₂SO₄ seeds (Virkkula et al., 1999; Cruz and Pandis, 2000)), compared to organic particles (GF~ 1.0-1.1 for biogenic SOA (Virkkula et al., 1999; Varutbangkul et al., 2006)). The increased LWC in the seeded experiments likely has an effect on the SOA formation, and may account for the different conclusions of Zhang et al (2011) vs. Dommen et al (2006) and this work.

Under humidified conditions, the use of H₂O₂ as an OH precursor may lead to aqueous photochemistry occurring directly inside the wetted particles, potentially affecting the final SOA yield. This would be more of an issue for the seeded experiments, which have higher LWC. Dommen et al (2006) performed "classical photooxidation" experiments without OH precursors. The good agreement between this work and that of Dommen et al (2006) with respect to the RH effect on the SOA yields suggests that the specific choice of OH precursor and presence of H₂O₂ in the chamber is not important for the non-seeded experiments.”

Technical Comments:

7. Abstract:

The use of H₂O₂ as an OH radical precursor should be mentioned in the abstract to clearly designate to readers how aerosol from isoprene was generated under these varied conditions.

We have inserted this sentence into the abstract “Experiments were performed with hydrogen peroxide as the OH precursor and in the absence of seed aerosol”.

8. Introduction:

The authors don't mention that 2-MG and its corresponding oligoesters have now been shown to form by the further oxidation of MPAN, especially under increasing NO₂/NO ratios. This was demonstrated recently by both Surratt et al. (2010, PNAS) and Chan et al. (2010, ACP). Since 2-MG and its corresponding oligoesters are of focus in this study, I suggest that the authors include these references here. I would also cite the work of Zhang et al. (2011, ACPD) here since they also recently examined the effect of RH on isoprene SOA formation; however, no OH radical precursor was used in that study.

We agree that the pathways of formation for 2MGA should be discussed in the text. We feel that the discussion section, after the first mention of the detection of 2MGA in the aerosol phase by HR-MS, is the appropriate position to insert this information. Citation to the Zhang et al (2011) work was done in response to comment #2 and #6. We have included the following text:

“For example, one formation pathway for 2MGA and its oligomers is the photooxidation of a second-generation product from isoprene methacryloylperoxynitrate (MPAN) (Surratt et al., 2010; Chan, 2010).”

9. Introduction, Page 9219, Lines 1:

Citation needed for the sentence ending in “..of organic nitrogen (ON) compounds.”

We have inserted a citation to the Finlayson-Pitts and Pitts text (and references therein) because the book thoroughly describes formation of organic nitrogen compounds from the NO + RO₂ reaction for a variety of hydrocarbon precursor molecules.

10. Introduction, Page 9219, Line 4:

Delete the word “organic”

Amended.

11. Introduction, Page 9219, Line 11-12:

Insert “, and references therein)” into the “Carlton et al, 2009)” citation, especially since this is a review article and not the actual studies that have studied isoprene SOA under variety of RH conditions.

Agreed, and amended.

12. Introduction, Page 9220, Lines 11-12:

It turns out that hemiacetals observed in low-NO_x SOA by Surratt et al. (2006) have now been demonstrated to form from the acid-catalyzed reactive uptake of isoprene epoxydiols (IEPOX) (Surratt et al., 2010, PNAS).

The information and citation suggested by the referee are relevant to our manuscript. We have inserted the following sentence “The addition products may stem from heterogeneous chemistry; for example: hemiacetals derived from isoprene have been demonstrated to form in the acid-catalyzed reactive uptake of gas-phase epoxydiols (Surratt et al., 2010).”

13. Experimental Section:

Just to be clear, what are the temperature ranges of these experiments? This should be clearly listed. Also, to be clear, were 6 total experiments conducted (i.e., 3 dry and 3 humid)? If so, please state that here.

We have inserted the temperature information: “Experiments were performed in the temperature range of 22-26°C.” We already state “At least three samples were generated for each set of conditions.” Some experiments were performed up to seven times for reproducibility and to gather all the necessary gas-phase and particle-phase data.

14. Mass Spectrometry Analysis of SOA Samples Section, Page 9226, Line 6:

Add “, consistent with the findings of Surratt et al. (2006).” to the sentence “Methyltetrols were not observed in the high-NO_x data.”

Amended.

15. Figure 3:

Have these abundances been corrected for sampling volume differences?

As we observe the same particle mass concentration for the dry and humid experiments, and perform each experiment in an identical manner, we do not expect any sampling volume discrepancies. Furthermore, as we explained in the text, the signal-to-noise ratios detected in ESI-LTQ-Orbitrap are remarkably reproducible. Please see Figure S1 where we show the mass spectra obtained from a filter with 10 $\mu\text{g}/\text{m}^3$ SOA mass loading vs. 40 $\mu\text{g}/\text{m}^3$ SOA mass loading for the same type of SOA. When we apply the technique to a different type of SOA, the mass spectrum looks different. Therefore, we are confident the mass spectral differences we present in the manuscript are due to RH effects, and not due to sampling discrepancies.

16. Figure 2:

The authors should add a detailed plot of NO, NO₂, and O₃ to this figure. From this figure, do you find that isoprene all primarily reacts away by the time NO reaches zero? This could explain why the 2-methyltetrols were not observed. Specifically, as Surratt et al. (2010, PNAS) study showed, the route to SOA formation under RO₂ + NO dominate conditions is isoprene -> MACR -> MPAN -> SOA. The latter is a C₄-preserving pathway.

We presented a plot of NO and O₃ in a recently submitted paper (Nguyen, 2011) where it is clear that isoprene has not reacted away completely by the time NO reaches zero. From approximately 250 ppb of isoprene present initially, we estimate (based on PTR-ToF-MS data) that 50 ppb of isoprene remains in the chamber by the time NO reaches zero. With the set of data we have, we cannot explain why 2-methyltetrols are not produced in the chamber in the time period after all NO has reacted away (around the 40 minute photooxidation mark in our experiments) but before isoprene has reacted away (around the 80 minute mark in our experiments). This is an interesting question, and we feel more experiments are needed to obtain insight into the mechanism of 2-methyltetrol production from isoprene, as a function of NO_x.

References:

Altieri, K. E., Seitzinger, S. P., Carlton, A. G., Turpin, B. J., Klein, G. C., and Marshall, A. G.: Oligomers formed through in-cloud methylglyoxal reactions: Chemical composition, properties, and mechanisms investigated by ultra-high resolution ft-icr mass spectrometry, *Atmos. Environ.*, 42, 1476-1490, 2008.

Axson, J. L., Takahashi, K., De Haan, D. O., and Vaida, V.: Gas-phase water-mediated equilibrium between methylglyoxal and its geminal diol, *Proc. Nat. Acad. Sci. USA*, 107, 6687-6692, 10.1073/pnas.0912121107, 2010.

Bahreini, R., Keywood, M. D., Ng, N. L., Varutbangkul, V., Gao, S., Flagan, R. C., Seinfeld, J. H., Worsnop, D. R., and Jimenez, J. L.: Measurements of secondary organic aerosol from oxidation of cycloalkenes, terpenes, and m-xylene using an aerodyne aerosol mass spectrometer, *Environ. Sci. Technol.*, 39, 5674-5688, 2005.

Chan, A. W. H., Chan, M. N., Surratt, J. D., Chhabra, P. S., Loza, C. L., Crouse, J. D., Yee, L. D., Flagan, R. C., Wennberg, P. O., and Seinfeld, J. H.: Role of aldehyde chemistry and nox concentrations in secondary organic aerosol formation, *Atmos. Chem. Phys.*, 10, 7169-7188, doi:10.5194/acp-10-7169-2010, 2010.

Corrigan, A. L., Hanley, S. W., and Haan, D. O.: Uptake of glyoxal by organic and inorganic aerosol, *Envir. Sci. Technol.*, 42, 4428-4433, 10.1021/es7032394, 2008.

Fu, T. M., Jacob, D. J., and Heald, C. L.: Aqueous-phase reactive uptake of dicarbonyls as a source of organic aerosol over eastern north america, *Atmos. Environ.*, 43, 1814-1822, 10.1016/j.atmosenv.2008.12.029, 2009.

Hori, M., Ohta, S., Muraio, N., and Yamagata, S.: Activation capability of water soluble organic substances as ccn, *Journal of Aerosol Science*, 34, 419-448, 2003.

Jang, M., and Kamens, R. M.: Atmospheric secondary aerosol formation by heterogeneous reactions of aldehydes in the presence of a sulfuric acid aerosol catalyst, *Environ. Sci. Technol.*, 35, 4758-4766, 2001.

Jang, M., Carroll, B., Chandramouli, B., and Kamens, R. M.: Particle growth by acid-catalyzed heterogeneous reactions of organic carbonyls on preexisting aerosols, *Envir. Sci. Technol.*, 37, 3828-3837, 10.1021/es021005u, 2003.

Jayne, J. T., Duan, S. X., Davidovits, P., Worsnop, D. R., Zahniser, M. S., and Kolb, C. E.: Uptake of gas-phase aldehydes by water surfaces, *The Journal of Physical Chemistry*, 96, 5452-5460, 10.1021/j100192a049, 1992.

King, S. M., Rosenoern, T., Shilling, J. E., Chen, Q., Wang, Z., Biskos, G., McKinney, K. A., Poschl, U., and Martin, S. T.: Cloud droplet activation of mixed organic-sulfate particles produced by the photooxidation of isoprene, *Atmos. Chem. Phys.*, 10, 3953-3964, 2010.

Kostenidou, E., Pathak, R. K., and Pandis, S. N.: An algorithm for the calculation of secondary organic aerosol density combining ams and smps data, *Aerosol Sci. Technol.*, 41, 1002 - 1010, 2007.

Liggio, J., Li, S.-M., and McLaren, R.: Heterogeneous reactions of glyoxal on particulate matter: Identification of acetals and sulfate esters, *Envir. Sci. Technol.*, 39, 1532-1541, 10.1021/es048375y, 2005a.

Liggio, J., Li, S. M., and McLaren, R.: Reactive uptake of glyoxal by particulate matter, *J. Geophys. Res.-Atmos.*, 110, D10304, 10.1029/2004jd005113, 2005b.

Loeffler, K. W., Koehler, C. A., Paul, N. M., and De Haan, D. O.: Oligomer formation in evaporating aqueous glyoxal and methyl glyoxal solutions, *Envir. Sci. Technol.*, 40, 6318-6323, 10.1021/es060810w, 2006.

Malloy, Q. G. J., Nakao, S., Qi, L., Austin, R., Stothers, C., Hagino, H., and Cocker, D. R.: Real-time aerosol density determination utilizing a modified scanning mobility particle sizer aerosol particle mass analyzer system, *Aerosol Sci. Technol.*, 43, 673 - 678, 2009.

Nguyen, T. B., Nizkorodov, S.A., Roach, P.J., Laskin, J. and Laskin, A. : Nitrogen containing organic compounds and oligomers in secondary organic aerosol formed by photooxidation of isoprene

In Preparation, 2011.

Poulain, L., Wu, Z., Petters, M. D., Wex, H., Hallbauer, E., Wehner, B., Massling, A., Kreidenweis, S. M., and Stratmann, F.: Towards closing the gap between hygroscopic growth and ccn activation for secondary organic aerosols - part 3: Influence of the chemical composition on the hygroscopic properties and volatile fractions of aerosols. , *Atmos. Chem. Phys.*, 10, 3775-3785, 2010.

Prenni, A. J., DeMott, P. J., and Kreidenweis, S. M.: Water uptake of internally mixed particles containing ammonium sulfate and dicarboxylic acids, *Atmos. Environ.*, 37, 4243-4251, 2003.

Shilling, J. E., Chen, Q., King, S. M., Rosenoern, T., Kroll, J. H., Worsnop, D. R., McKinney, K. A., and Martin, S. T.: Particle mass yield in secondary organic aerosol formed by the dark ozonolysis of alpha -pinene, *Atmos. Chem. Phys.*, 8, 2073-2088, 2008.

Shilling, J. E., Chen, Q., King, S. M., Rosenoern, T., Kroll, J. H., Worsnop, D. R., DeCarlo, P. F., Aiken, A. C., Sueper, D., Jimenez, J. L., and Martin, S. T.: Loading-dependent elemental composition of alpha-pinene soa particles, *Atmos. Chem. Phys.*, 9, 771-782, 2009.

Surratt, J., Chan, A. W. H., Eddingsaas, N. C., Chan, M., Loza, C. L., Kwan, A. J., Hersey, S. P., Flagan, R. C., Wennberg, P. O., and Seinfeld, J. H.: Reactive intermediates revealed in secondary organic aerosol formation from isoprene, *Proc. Natl. Acad. Sci.*, 107, 6640-6645, 2010.

Surratt, J. D., Murphy, S. M., Kroll, J. H., Ng, N. L., Hildebrandt, L., Sorooshian, A., Szmigielski, R., Vermeylen, R., Maenhaut, W., Claeys, M., Flagan, R. C., and Seinfeld, J. H.: Chemical composition of secondary organic aerosol formed from the photooxidation of isoprene, *J. Phys. Chem. A*, 110, 9665-9690, 2006.

Tan, Y., Carlton, A. G., Seitzinger, S. P., and Turpin, B. J.: Soa from methylglyoxal in clouds and wet aerosols: Measurement and prediction of key products, *Atmos. Environ.*, 44, 5218-5226, 10.1016/j.atmosenv.2010.08.045, 2010.

Virkkula, A., Van Dingenen, R., Raes, F., and Hjorth, J.: Hygroscopic properties of aerosol formed by oxidation of limonene, a-pinene, and b-pinene, *J. Geophys. Res.*, 104, 3569-3579, 1999.

Zelenyuk, A., Imre, D., Han, J. H., and Oatis, S.: Simultaneous measurements of individual ambient particle size, composition, effective density, and hygroscopicity, *Anal. Chem.*, 80, 1401-1407, 2008a.

Zelenyuk, A., Yang, J., Song, C., Zaveri, R. A., and Imre, D.: A new real-time method for determining particles' sphericity and density: Application to secondary organic aerosol formed by ozonolysis of alpha-pinene, *Envir. Sci. Technol.*, 42, 8033-8038, 10.1021/es8013562, 2008b.