

## ***Interactive comment on “Effect of relative humidity on SOA formation from isoprene/NO photooxidation: role of particle-phase esterification under dry conditions” by H. Zhang et al.***

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Dear Editor,

Both reviewers gave invaluable suggestions to revise and improve the quality of our manuscript. Below are the detailed responses to the reviewers' comments. We thank both reviewers for their thoughtful comments and we have incorporated most of their suggestions into the revised manuscript. Sincerely,

Haofei Zhang and Jason Surratt

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Authors' Responses to Initial Report:

1. Comment: This manuscript describes series of experiments investigating the formation of SOA from isoprene in smog chamber, and focusing on the effect of relative humidity (RH) on the SOA yields. The experiments and chemical analyses are technically sound, the discussion is clear, and the manuscript well presented. This manuscript should thus be posted on the ACPD web site.

AUTHORS' RESPONSE: We want to thank the reviewer for their initial report before the ACP discussion. The initial feedback from this reviewer was very helpful to increasing the quality of the discussion in the manuscript.

2. However, I do have some reserve on the discussion and conclusions of this work that I will take in the scientific review:

- the main conclusion of this work (and justification for publishing it) is based on a very limited number of experiments: only 2 series of low RH/high RH comparisons, with 2 different concentrations of isoprene ! This does not seem enough to support with certainty a systematic difference of SOA mass between low and high RH, especially if the factor is 2 or less, as it is here.

AUTHORS' RESPONSE: Although we have performed only four experiments (two sets), the initial VOC/nitric oxide (NO) ratio ( $\sim 3$ ) was held constant for both sets of experiments, and thus, the initial peroxy radical (RO<sub>2</sub>) chemistry was similar in all 4 experiments (i.e., RO<sub>2</sub> + NO initially dominates). In addition, the SMPS, GC/MS, and LC/MS results are all very consistent between the experiments. We want to stress to the reviewer here that these experiments were done in an outdoor smog chamber facility. As a result, it is not possible to get reproducible experiments from day-to-day owing to the varying outside meteorological conditions. However, to get around the latter issue, our outdoor smog chamber facility is purposely designed as a dual chamber facility in which allows us to compare a variable experiment to a control experiment under the exact same meteorological condition. The control experiments in this case are the

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dry experiments, owing to the fact that isoprene SOA formation has been extensively examined under this condition and its aerosol constituents have been chemically characterized in detail at the molecular level using off-line MS techniques (i.e., Surratt et al., 2006, JPCA, 2010, PNAS; Kroll et al., 2005, ES&T, 2006, ES&T; Szmigielski et al., 2007a, JMS; Chan et al., 2010, ACP). Even though our limited number of experiments cannot adequately confirm the exact mechanism for the observed enhancements or derive alphas and Ks needed for the Odum two-product model commonly used in regional and global air quality models, our conclusion that more 2-methylglyceric acid, which is a known and commonly used molecular tracer used in SOA source apportionment methods (i.e., Kleindienst et al., 2007, Atmos. Environ.), and its corresponding oligoesters derived from the MPAN oxidation pathway (Surratt et al., 2010, PNAS; Chan et al., 2010, ACP) are enhanced under low-RH conditions is well justified from the off-line detailed chemical characterizations. The enhancement of 2-MG and its corresponding oligoesters under dry conditions is a novel finding and we feel deserves publication, especially considering that these aerosol constituents appear to dominate the aerosol mass that can be chemically characterized by ESI-MS and GC/MS techniques (Surratt et al., 2006, 2007, 2010; Chan et al., 2010; Szmigielski et al., 2007a) as well as seen by off-line MS techniques (such as the Aerodyne AMS) (Surratt et al., 2006, JPCA; Chan et al., 2010, ACP).

To further stress the significance of our work, it is important to note to the reviewers and the editor here that our findings are supported by another recent study by Nguyen et al. (2011) that is also currently in the ACP discussion, as well as the implied results from two Kroll et al. studies (2005 and 2006). The Nguyen et al. (2011) chemical characterization results are very consistent with our own (i.e., 2-MG and its corresponding oligoesters are enhanced under dry conditions); however, they did not observe enhancements in their SOA yields when comparing dry vs. humid conditions. This difference can be explained by a number of experimental factors, but most importantly, this difference likely results from the fact that their indoor chamber experiments relied on nucleation rather than condensation (or reactive uptake) of semivolatiles onto pre-

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existing ammonium sulfate seed aerosol. It is also possible that their use of H<sub>2</sub>O<sub>2</sub> as an OH radical precursor caused the differences between our studies, especially since H<sub>2</sub>O<sub>2</sub> could have partitioned into their wet aerosols, and as a result, this could have affected the SOA mass measurement as well as particle-phase chemistry in that study. To summarize, the detailed chemical findings from Nguyen et al. (2011, ACPD) are consistent with our chemical findings and the previous results of Dommen et al. (2006, GRL) (i.e., the volatility of the SOA decreased under dry conditions, consistent with the presence of more low volatility organics such as oligomers). Dommen et al. (2006, GRL) also conducted nucleation (no seed aerosol initially present) experiments like that of Nguyen et al. (2011, ACPD), and as a result, it is not too surprising to see they find common effects on the SOA yield; however, this shared result between Dommen et al. (2006) and Nguyen et al. (2011, ACPD) could be by coincidence owing to the fact that the oxidative conditions (i.e., initial VOC/NO ratios) are not the same between these two studies as well as the use of an OH radical precursor (H<sub>2</sub>O<sub>2</sub>) was not employed in both studies. Our measurements are correct; however, as suggested below in this reviewer's official comments, we more fully compared our results to many of the previously published studies to further support our current work. Specifically, we add the following plot of SOA yields from the various studies as Fig. 2 (see attached). In addition to Figure 2 attached, we include the following text in our discussion to explain the differences between these studies (pages 13-14, lines 262-285):

"Comparing the SOA yields found in the present study with several previous studies (Kroll et al., 2005; 2006; Dommen et al., 2006), the data in this study lie close to the data from Dommen et al. (2006), as shown in Figure 2. Note that among these four studies, the experiments performed by Dommen et al. (2006) did not use initial seed aerosol and the other three studies use ammonium sulfate as seed aerosol. As noted by Kroll et al. (2007), SOA yields are relatively lower in the system where inorganic seed aerosols are not initially present. This could potentially explain the lower SOA yields observed in the Dommen et al. (2006) study. The SOA yields presented by the Kroll et al. (2005; 2006) studies are relatively higher than this study that can be

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attributed to several reasons: (1) The SOA data reported in this study is not wall-loss corrected, and thus the SOA yields are likely under predicted, which may explain why SOA yields in this study are almost as low as the Dommen et al. (2006) study reported, even though seed aerosol was employed in this study; (2) OH radical precursor may also affect SOA yield. Kroll et al. (2006) used the photolysis of H<sub>2</sub>O<sub>2</sub> as an OH radical source and Kroll et al. (2005) used HONO photolysis to generate both OH radical and NO. However, Dommen et al. (2006) used xenon arc lamps to simulate solar light and this work was performed under natural sunlight. An extra source of OH radicals could also enhance SOA formation and hence, the SOA yield of the Dommen et al. (2006) and this work are relatively lower than the Kroll et al. (2005, 2006) results; (3) Systematical conditions such as temperature can be a possible reason as well. It should also be noted that the Kroll et al. (2005; 2006) studies were based upon the same chamber system except that the Kroll et al. (2005) experiments are performed under 40% < RH < 50%, while the Kroll et al. (2006) experiments are performed under RH < 10%. From Figure 2, the high-NO<sub>x</sub> experiments in Kroll et al. (2006) study showed higher yields than the similar experiments in Kroll et al. (2005) study. By comparing the two Kroll et al studies one may surmise there is an RH effect on isoprene SOA formation, but unfortunately these two studies had different sources of OH radicals and NO. This study, however, directly addressed RH effects and our observations reinforce the combined RH-SOA implications of Kroll et al. (2005; 2006).”

3. - the main explanation proposed for the observed effects, that seed particles are more acidic a low RH (< 40 %) than high RH (40 – 90%) hence affecting the chemistry, is obviously wrong since it ignores the basic principles of the ammonium sulfate/water phase diagram and of water uptake: at RH < 40 % ammonium sulfate particles are dry, not acidic (Xu et al., JPC B, 1998). Over RH = 40 -90 %, their volume changes only once, either at deliquescence (RH = 90 %, if starting with dry seeds) or at efflorescence (RH = 40 % if starting with wet seeds). Over the range where they are liquid, the pH of these particles is practically constant (~ 5, the value at saturation) because their volume is constant as they do not take up much water. Only for RH > 133 %

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ammonium sulfate particles can become CCN and take up significantly more water. Thus, contrary to what suggested in the discussion, the pH of ammonium sulfate liquid particles is never lower than about 5, which barely qualifies as acidic. The seed particles being in different states (solid or liquid) over the two domains of RH explored, the discussion should probably consider more different mechanisms for SOA formation than only different chemical pathways . . .

AUTHORS' RESPONSE: We want to thank the reviewer for making this point, as this is not what we wanted to convey in the manuscript. What we wanted to convey is that acidity could be a misleading issue (Line 13-25, Page 5421 in ACPD). By comparing with Surratt et al. (2007b, 2010) and Jaoui et al. (2010) studies, we pointed out that the results in the present study is totally different from what they observed: 2-MG formation was substantially enhanced whereas 2-methyltetrols were not in this study; 2-methyltetrols were largely increased, but 2-MG formation was almost unchanged in both of the prior studies of Surratt et al. (2007b, 2010) and Jaoui et al. (2010, Atmos. Environ.). From this perspective, we concluded that acidity effect is not a dominant mechanism in the present study. We are taking into account the reviewer's concern and explain this section more clearly on pages 21-22 and lines 474-493 to better convey what we wanted the reader to understand from our explanation (or proposal):

“Particle-phase organic esterification is likely to be an acid-catalyzed process (Surratt et al., 2006; Szmigielski et al., 2007), which raises an important question: is acidity required in order to enhance SOA formation through the tentatively proposed organic esterification pathway? In the present study, the acidity effect is concluded not to contribute to SOA formation difference because the pH of ammonium sulfate aerosols cannot be lower than 5, which is the saturation value, and this value cannot change significantly in the RH regime investigated in this study (Xu et al., 1998). In addition, the formation of 2-methyltetrols was not significantly enhanced in the low-RH experiments. Surratt et al. (2007b, 2010) and Jaoui et al. (2010) both found under acidic conditions (acidity introduced by either acidic seed aerosol or injection of gaseous SO<sub>2</sub>) that the

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2-methyltetrols as well as the SOA mass were enhanced, but the formation of 2-MG remained fairly constant, which is contrary to the results of the present study. In this study, the formation of 2-methyltetrols was similar in both the high- and low-RH experiments, but the formation of 2-MG (and its corresponding oligoesters) increased by as much as a factor of two in the low-RH experiments. These opposite results indicate that it is more likely that low RH is playing a major role in accounting for the higher SOA yields through the particle-phase organic esterification process under dry conditions. Nevertheless, it is also possible that alternative mechanisms can explain the enhanced formation of the oligoesters. Further study is needed to confirm the exact processes leading to the enhanced formation of 2-MG and its corresponding oligoesters under dry conditions.”

4. - some important literature is missing in the discussion, such as the study of Volkamer et al., ACP, (2009) showing the effects of RH and Liquid Water Content of the particles on the SOA mass from glyoxal. The effects observed with glyoxal SOA (larger SOA mass at higher RH) are opposite to those reported here with isoprene, which confirms that, in this case, glyoxal chemistry is not the only contribution to SOA mass. This should be discussed in this paper.

AUTHORS' RESPONSE: The Volkamer et al. (2009, ACP) study and another relative study (Ervens and Volkamer, 2010, ACP), which showed the glyoxal aqueous-phase uptake and form SOA, have been discussed in the introduction section (page 5, lines 75-78):

“Owing to their high water solubilities, their uptake by aqueous-phase aerosols, followed by oxidation and oligomerization could be a significant SOA source (Volkamer et al., 2009; Carlton et al., 2009; Ervens and Volkamer, 2010).”

We have also added the following text to the discussion section (page 23, lines 510-516):

“Volkamer et al. (2009) and Ervens and Volkamer (2010) demonstrated that water

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uptake of glyoxal and methylglyoxal onto pre-existing aerosols contribute to larger SOA mass at higher RH. However, this work proposed a conflicting chemical process and the present results indicate that aqueous-phase chemistry of glyoxal and methylglyoxal is not the only SOA formation pathway affected by RH. Furthermore, in the system of isoprene/NO photooxidation, water uptake of glyoxal and methylglyoxal is not as important as the tentatively proposed organic esterification process.”

Responses to Anonymous Referee #1:

5. Comment: This paper presents interesting results on the effect of humidity on the yield of secondary organic aerosol of isoprene and on composition. Formation of SOA under dry conditions leads to a higher SOA yield and seemingly more oligomers compared to higher RH conditions. On the other hand organosulfates were enhanced under high RH conditions. These experiments are interesting and deserve publication in ACP. Yet, I have some major concerns regarding data evaluation and interpretation which might put into question some of the conclusions of the manuscript. These issues have to be addressed by the authors before publication.

SOA yield:

The authors determine the SOA yield from SMPS data. Figure 1B shows similar particle size distributions for the dry and humid experiment at the beginning of the experiment. In Figure 1A the time trend of the mass concentration of the particles is shown where the dry experiment exhibits a much larger increase. From the experimental description it is not clear if the SMPS measurements were done with dried aerosols. If not, increasing temperature during the experiment decreases RH and thus the water content of the particles. Therefore, starting with a similar size distribution for the dry and humid experiment, the size distribution of the high RH experiment would decrease with increasing temperature which results in a lower particle mass concentration. If the measurements were done without drying the aerosol, the determination of SOA mass concentrations is flawed as described.

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AUTHORS' RESPONSE: We thank the reviewer for pointing out that our description of the SOA mass concentration was not fully described in the text.

The SMPS measurements were not performed with dried aerosols; however, the reason we did not dry the aerosols before going through the SMPS system is that the drying process could likely affect the gas-to-particle partitioning of semivolatiles and/or subsequent particle-phase chemistry that could affect the SOA mass yields and chemical composition. To make this clearer to readers of our manuscript, we have added the following text to the Experimental Section starting on page 7 and line 126:

"SMPS measurements were not performed with dried aerosols. The reason for not drying aerosols before going through our SMPS system is that the drying process could affect the gas-to-particle partitioning of semivolatiles and subsequent particle-phase chemistry that could affect the SOA mass yields and chemical composition. However, the decay of ammonium sulfate seed aerosol and water uptake were corrected in the following method, with the assumption that the ammonium sulfate fraction dominated the hygroscopicity of the aerosol: Given the flow conditions of the SMPS, particles sizes, in counts per cm<sup>3</sup>, are recorded in 64 size bins for particles in the 14 to 661 nm size range. This can be translated into total particle volumes per cm<sup>3</sup>, and via particle densities to a total suspended particulate (TSP in  $\mu\text{g}/\text{m}^3$ ). TSP that is the sum of seed aerosol (which is ammonium sulfate (AS) in this work), particle liquid water content (LWC), and SOA:

$$\text{TSP} = \text{AS} + \text{LWC} + \text{SOA} \quad (1)$$

At the beginning of each experiment, there was no SOA in the chamber, and thus initially,  $\text{TSP}_0 = \text{AS}_0 + \text{LWC}_0$  (2)

A relationship between water uptake on ammonium sulfate particles and RH was developed from Kamens et al. (2011) based upon previous work (Chan et al., 1992; Kleindienst et al., 1999):

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$$\text{LWC} = \text{AS} \times f(\text{RH}) \quad (3)$$

Here  $f$  represents a functional relationship between LWC and RH for 1  $\mu\text{g}/\text{m}^3$  ammonium sulfate particle mass concentration.

Hence,

$$\text{TSP}_0 = \text{AS}_0 + \text{AS}_0 \times f(\text{RH}_0) = \text{AS}_0 \times [1 + f(\text{RH}_0)] \quad (4)$$

$$\text{AS}_0 = \text{TSP}_0 / [1 + f(\text{RH}_0)] \quad (5)$$

Wall-loss rates of particles at different RH in this smog chamber have been previously explored (Kamens et al., 2011). With known initial ammonium sulfate seed aerosol and their known decay rates under the exact same RH ranges employed in the present experiments, the ammonium sulfate particle mass concentration with time can be calculated, and thus, LWC can be estimated based upon equation (3). Therefore, SOA in the smog chamber can be estimated from the following:

$$\text{SOA} = \text{TSP} - \text{AS} - \text{LWC} \quad (6)$$

Background aerosol filter samples were collected before experiments started. SOA filter sampling was initiated after the aerosol volume concentration started to increase and before it reaches maximum value as detected by the SMPS. The duration of the background filter sample was one hour at a flow rate between 15–20 L min<sup>-1</sup>, and the duration of the SOA filter sample is two hours. The volumes of air sampled through each set of filter samples were approximately the same (within 1%) for the humid and the dry chambers."

After following the procedure outlined above, we determined SOA yields from our experiments. In addition, to make Figure 1A clearer and prevent confusion by our readers, we now revised it to show only the wall-loss uncorrected SOA mass during the course of the experiment instead of TSP (= AS + LWC + SOA). We want to note to the reviewer that we have modified Figure 1 B to only show the initial size distribution of the ammonium sulfate seed aerosol at the beginning of the experiment (before sun rise).

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Figure 1 B is used now to only show that the initial size distributions were similar in both experiments.

Below, please find our revised Figure 1A and 1B attached.

6. The authors claim to show wall loss corrected data. How was this done?

AUTHORS' RESPONSE: The SOA data presented in the revised manuscript, as well as in Figure 1A and Table 1, is not wall-loss corrected. The details of the processing for the SMPS data can be found in Appendix 2 of Kamens et al. (Atmos. Environ. 2011) and outlined above in comment 5.

7. Why does particle mass concentration decrease after the maximum? Is there a dilution flow?

AUTHORS' RESPONSE: We thank the reviewer for raising these questions. We did not add any dilution flow. The TSP concentration (now displayed in Figure 1A as SOA mass concentration) decreased owing to the following possibilities: (1) Wall losses of particles; (2) This decrease likely occurred since the temperature increased during the day, which could evaporate off and semivolatile/volatile organics; (3) organic peroxides could have formed after the initial NO concentration dropped to zero, and as a result, the RO<sub>2</sub> + NO reaction no longer dominated. Instead, since isoprene was still abundant around the time NO dropped to zero (i.e., ~500 ppb of isoprene still remaining), the RO<sub>2</sub> radicals that formed from further OH-initiated reactions of isoprene likely reacted either by RO<sub>2</sub> + RO<sub>2</sub> or RO<sub>2</sub> + HO<sub>2</sub> pathways, resulting in organic peroxide formations (ROOR or ROOH types). Aerosol-phase organic peroxides have been shown to quickly photolyze after reaching the peak in aerosol formation in previous chamber studies that examined isoprene photooxidation under low-NO<sub>x</sub> conditions (Kroll et al., 2006; Surratt et al., 2006). In comparison to the Caltech isoprene studies, our chamber studies do not keep the initial NO levels constant throughout the irradiation experiment. As a result, our RO<sub>2</sub> chemistry changes from an initial RO<sub>2</sub> + NO dominate case, to either a RO<sub>2</sub> + NO<sub>2</sub> or RO<sub>2</sub> + HO<sub>2</sub> or RO<sub>2</sub> + RO<sub>2</sub> case; (4) Finally, this decrease could have

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resulted from the heterogeneous oxidation of the aerosol, which could have resulted in evaporation of volatile products from these reactions (George and Abbatt, 2010; Kroll et al., 2009).

To take into account this reviewer's question, we have added the following text to the results and discussion section (on pages 12-13, lines 240-256):

"As can be observed from Figure 1A, the SOA mass concentrations decreased after reaching the maximum growth. These SOA mass decreases are likely due to the following possibilities: (1) Wall losses of particles; (2) Temperature increases observed during the course of the experiments could have evaporated semivolatile/volatile organics back into the gas phase; (3) Organic peroxides could have formed after the initial NO concentration dropped to zero, and as a result, the RO<sub>2</sub> + NO gas-phase reactions no longer dominated. Instead, since isoprene was still abundant around the time NO dropped to zero (i.e., ~ 500 ppb of isoprene still remaining), the RO<sub>2</sub> radicals that formed from further OH-initiated reactions of isoprene likely reacted either by RO<sub>2</sub> + RO<sub>2</sub> or RO<sub>2</sub> + HO<sub>2</sub> pathways, resulting in organic peroxide formations (ROOR or ROOH types). Aerosol-phase organic peroxides could have resulted and these have been shown to quickly photolyze after reaching the peak in aerosol formation in previous chamber studies that examined isoprene photooxidation under low-NO<sub>x</sub> conditions (Kroll et al., 2006; Surratt et al., 2006); (4) Finally, heterogeneous oxidation of the aerosol could have resulted in the evaporation of organic material from the aerosol phase, as shown in recent studies (e.g., George and Abbatt, 2010; Kroll et al. 2009). The exact cause of these decreases will be examined in future work."

8. The numbers given in Table 1, reported in the text (Page 9, last paragraph) and observed from Figure 1 are not consistent. For example, the initial particle concentration of the experiment 2010OCT21N is 29.8 ug/m<sup>3</sup> in Table 1 and text but larger as seen from Figure 1. The maximum SOA mass concentration is 40.5 ug/m<sup>3</sup> (Table 1) but only 37.1 ug/m<sup>3</sup> (66.9 – 29.8) in the text.

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AUTHORS' RESPONSE: We thank the reviewer for pointing out this apparent inconsistency. We failed to clearly describe if we were discussing/showing TSP or SOA mass data. Thus, we have described everything in terms of SOA mass only to prevent confusion for the readers trying to understand the text, Figure 1, and Table 1.

The text has been revised to state the following on Page 9, last paragraph:

“On 2010OCT21, the dry side started with 29.8  $\mu\text{g m}^{-3}$  of the ammonium sulfate seed aerosol, and upon photooxidation, reached a maximum SOA mass concentration of 60.2  $\mu\text{g m}^{-3}$ , with a SOA yield of 3.0%; the humid side started with 25.0  $\mu\text{g m}^{-3}$  of ammonium sulfate seed aerosol, and upon photooxidation, SOA peaked at 34.4  $\mu\text{g m}^{-3}$ , with a SOA yield of 1.6%. In the other set of experiments with relatively lower initial concentrations, the dry side SOA maximum is 17.5  $\mu\text{g m}^{-3}$ , with a SOA yield of 1.5%, and the humid side SOA maximum is 8.8  $\mu\text{g m}^{-3}$ , with a SOA yield of 0.7%. As a result, with approximately identical initial conditions, isoprene-derived SOA formed under low-RH conditions between 15–40% can be a factor of two higher than that formed under high-RH conditions between 40–90%.”

9. Unknown tracer. The large enhancement of the unknown tracer in the 2010OCT21N experiment could also be an artifact (Page 11, line 244). Looking at the other compounds one finds the ratio between high and low concentration experiments to be similar for dry and humid experiments respectively. Only the tracer compound strongly deviates.

AUTHORS' RESPONSE:

If the reviewer is arguing that this unknown SOA constituent is an artifact of our chamber system, then we respectfully disagree since our blank filters collected from our chamber system did not show this compound in our GC/MS data. Thus, we did not see this compound on any of our filter control samples. However, if the reviewer is arguing that this compound could be an artifact due to the GC/MS analyses then we cannot completely rule this out.

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To address this concern, we added the following text to the results and discussion (page 15, lines 320-323):

“Although we did not observe this unknown tracer on any of our control filters, we cannot completely rule out that this unknown tracer is not due to an artifact of the GC/MS analyses. Further chemical analyses will be needed to verify if this is a result of a GC/MS artifact.”

10. The tracer does not only correlate with 2-MG but with all other compounds (Page 13, line 296). Thus the correlation with 2-MG does not necessarily support the hypothesis of a C<sub>4</sub>H<sub>7</sub>NO<sub>6</sub> compound. Furthermore, the unknown tracer does not need to be C<sub>4</sub>H<sub>7</sub>NO<sub>6</sub> (Page 14, line 308) as e.g. C<sub>5</sub>H<sub>11</sub>NO<sub>5</sub> also has a MW of 165. This is a C<sub>5</sub> compound and would not be a product of MPAN chemistry. There is no proof that MPAN is the precursor of this unknown tracer as claimed on Page 15, line 336.

AUTHORS' RESPONSE: The disproportionate peak of the unknown tracer under the higher concentration experiments is likely due to a high amount of mass going through the RO<sub>2</sub>+RO<sub>2</sub> reaction pathways when initial isoprene concentrations are still high after the consumption of NO. However, this hypothesis needs further confirmation. We did not conclude that the unknown tracer is C<sub>4</sub>H<sub>7</sub>NO<sub>6</sub>, but tentatively proposed (or hypothesized) it as a possibility. It is also possible this tracer has a different structure, such as C<sub>5</sub>H<sub>11</sub>NO<sub>5</sub>, as the reviewer proposed. However, if this is the structure of the unknown tracer, it must have one –ONO<sub>2</sub> group and two –OH groups. During the atmospheric photooxidation or the filter extraction process, –ONO<sub>2</sub> groups could be hydrolyzed, resulting in the formation an –OH group (Sato et al., 2008). Thus, the hydrolyzed compound would be C<sub>5</sub>H<sub>12</sub>O<sub>3</sub> with three –OH groups, with a molecular weight (MW) is 120 (or MW is 336 after trimethylsilylation). If this is the case, since the unknown tracer has a huge peak area, this hydrolyzed compound should also have a relatively high concentration and have been observed directly by GC/MS. However, the only MW 336 compound observed on GC/MS is trimethylsilylated 2-MG, which has a totally different structure from this C<sub>5</sub>H<sub>12</sub>O<sub>3</sub>. By contrast, if the unknown tracer is what

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we have proposed, the hydrolyzed compound is 2-MG, which explains why we did not see another MW 120 (or trimethylsilylated MW 336) compound on GC/MS.

Taking into account the possibility that this unknown tracer could have a formula of C<sub>5</sub>H<sub>11</sub>NO<sub>5</sub>, we have added the following text to the discussion on page 18-19 lines 396-410:

“Although C<sub>4</sub>H<sub>7</sub>NO<sub>6</sub> is the likely composition of this unknown tracer, we cannot completely rule out the possibility that this unknown tracer has a C<sub>5</sub>H<sub>11</sub>NO<sub>5</sub> formula. However, if this is the structure of the unknown tracer, it must have one –ONO<sub>2</sub> group and likely two –OH groups. This composition is very hard to argue from known gas-phase chemistry of isoprene under initially high NO conditions. During the atmospheric photooxidation or the filter extraction process, –ONO<sub>2</sub> groups could be hydrolyzed, resulting in the formation an –OH group (Sato et al., 2008). Thus, the hydrolyzed compound would be C<sub>5</sub>H<sub>12</sub>O<sub>3</sub> with three –OH groups, with a MW 120 (or MW 336 after trimethylsilylation). If this is the case, since the unknown tracer has a huge peak area, this hydrolyzed compound should also have a relatively high concentration and have been observed directly by GC/MS. However, the only trimethylsilylated compound with MW 336 observed by GC/MS is the trimethylsilylated 2-MG, which has a different structure from this C<sub>5</sub>H<sub>12</sub>O<sub>3</sub>. By contrast, if the unknown tracer is what we have proposed, the hydrolyzed compound is 2-MG, which explains why we did not see another MW 120 (or trimethylsilylated MW 336) compound by GC/MS analyses.”

Shortly after this paper was posted in ACPD, another study investigating RH effect on isoprene SOA was published, which also found enhanced oligoester and nitrated aerosol (likely derived by C<sub>4</sub>H<sub>7</sub>NO<sub>6</sub>) under low-RH conditions (Nguyen et al., ACPD, 2011). This study supported some of our conclusions. Nevertheless, the reviewer is right that the data we currently have cannot adequately confirm the identity of the unknown tracer. More advanced measurements are required for further study, which is what directly stated on page 5419 lines 23-24 of the ACPD manuscript.

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11. Technical Comments: Page 4, line54: insert “of” at the end of the line Page 7, line 133: replace steam by stream Page 9, line 192: Figure 1A shows the second set of experiments not the first one. Interactive comment on Atmos. Chem. Phys. Discuss., 11, 5407, 2011.

AUTHORS' RESPONSE: Page 5, Line 55: “of” is inserted between “uptake” and “isoprene”. Page 9, Line 167: “steam” is replaced by “stream”. Page 11, Line 227: “first” is replaced by “second”.

Responses to Anonymous Referee #2:

12. Comment: This manuscript presents a study of the effect of relative humidity (RH) on the mass of Secondary Organic Aerosols (SOA) produced by isoprene, performed in an outdoor smog chamber. In a way, this study is the next step to the study of Surratt et al. (2010) where, in addition to identifying the products involved in SOA formation, the SOA mass is considered. This study is therefore very relevant for atmospheric chemistry currently. But while the experimental work presented is generally of good quality, I have some serious concerns about the very limited number of experiments performed (4 in total). In comparison, other studies of the same topic (Dommen et al., 2006) have involved 17 experiments! It is not clear that a discussion or conclusion can be based on such a limited dataset and therefore that this work is publishable. Perhaps the only way to compensate for the limited dataset would be to compare the results with those of previous works to confirm the trends observed here (see below).

AUTHORS' RESPONSE: The reviewer's comments are well taken, and this concern was addressed above in response to comment #2 above from the reviewer's initial report. However, to summarize here, we respectfully disagree with this comment. One of the major reasons for this disagreement is that our 4 experiments were all conducted under the same initial VOC/NO ratio (~ 3). In the study of Dommen et al. (2006), the initial VOC/NO ratio was not always held constant between all experiments; in fact, it varied from ~2–8. Holding the initial VOC/NO ratio constant between experiments is

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incredibly important to consider in the reaction of isoprene (as with any other VOC) as this dictates the fate of the initially formed RO<sub>2</sub> radicals, and thus, the amount and chemical composition of the resultant SOA (Kroll et al., 2006, ES&T; Surratt et al., 2006, JPCA; 2010, PNAS; Chan et al., 2010, ACP). It is not equitable to compare the 17 experiments from Dommen et al. (2006) to our 4 experiments as Dommen et al. (2006) not only varied the RH but they also varied the initial VOC/NO ratio, which also affects the SOA yield. Our study is systematic because we keep the initial VOC/NO ratio constant in all 4 experiments; the only variable to change is RH in this case. Naturally, in our experiments with higher isoprene mixing ratios, however, we will get higher Mo (or SOA mass) values. We did this to explore if the same chemical effect happened at lower Mo values. The purpose of our study was not to determine the alphas and Ks by fitting our data with the “two product model” over a wide range of Mos (and thus have a need for a large number of experiments); however, our study was designed to gain insight into the differences of the SOA composition and yield at one VOC/NO ratio. Future work is certainly needed to derive a parameterization, such as the two-product model, to be used in regional and global models to take into account the effect of RH on SOA yields. However, this is out of the scope of our present work and will likely require many other groups to also closely examine this issue. The effect of RH at higher VOC/NO ratios could be also strikingly different from the current set of experiments and also warrants future study. Thus, this is not a simple system to study, and thus, we started off here by only examining the effect of RH on one initial VOC/NO ratio. It will be interesting to examine the effect of RH on isoprene SOA formation when RO<sub>2</sub> + RO<sub>2</sub> or RO<sub>2</sub> + HO<sub>2</sub> initially dominate the gas-phase chemistry. This will dictate what types of semivolatile products form and go onto to make SOA from isoprene. These products may very well have different interactions with an irradiated wet aerosol as compared to what we found here when RO<sub>2</sub> + NO initially dominates the gas-phase chemistry.

13. In addition, the discussion of the mechanisms is at odd with some basic facts of inorganic and organic chemistry. Thus, the title of this paper could be unfortunate, as  
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esterifications are unlikely to explain the observations.

AUTHORS' RESPONSE: Although the chemical characterization of 2-methylglyceric acid and its corresponding oligoesters in our manuscript are well supported by our chemical data and by both previous studies, such as Surratt et al. (2006, JPCA; 2010, PNAS) and Szmigielski et al. (2007, Journal of Mass Spectrometry), and more recent studies by Chan et al. (2010, ACP) and by Sato et al. (2011, ACPD) that employed both on-line (e.g., high-resolution AMS) and off-line MS techniques, we agree with this reviewer that these oligoesters could have resulted from alternative pathways other than organic esterification (see our detailed response below to this detailed comment raised by this reviewer). What is known at this time from previous studies is that the further oxidation of alpha-beta-unsaturated aldehydes, such as MACR, yield 2-methylglyceric acid and its corresponding oligoesters. What happens after the further oxidation of MPAN that leads to these oligoesters is still unknown (Surratt et al., 2010, PNAS; Chan et al., 2010, ACP). We want to stress here to the reviewer and the editor that we are only tentatively proposing that these oligoesters are formed by organic esterification reactions. To make this clear we have revised the following sentence in the abstract to read (lines 19-22):

“Based upon detailed chemical characterization results, particle-phase organic esterification is tentatively proposed to explain the observed enhancements of isoprene SOA mass under lower RH conditions. Alternative mechanisms explaining the enhancement of 2-MG and its corresponding oligoesters cannot be completely ruled out.”

In addition, taking into account the reviewer's suggestion, we have revised the title of the paper to be:

“Effect of Relative Humidity on SOA Formation from isoprene/NO Photooxidation: Enhancement of 2-methylglyceric Acid and its Corresponding Oligoesters under Dry Conditions”

It is important to also note here to the reviewer and editor that 2-methylglyceric acid

and its corresponding oligoesters have been chemically characterized at the molecular level using GC/MS with prior single derivatization (i.e., trimethylsilylation only) or double derivatization (i.e., ethylation followed by trimethylsilylation) approaches (Surratt et al., 2006, JPCA; Szmigielski et al., 2007, JMS), LC/ESI-MS/MS or LC/ESI-HR-TOFMS techniques (Surratt et al., 2006, JPCA; Chan et al., 2010, ACP; Nguyen et al., 2011, ACPD; Sato et al., 2011, ACPD), and more recently by high-resolution AMS (Chan et al., 2010, ACP; Sato et al., 2011, ACPD). The GC/MS with prior single or double derivatization approaches have helped to tag the ester linkages to further support the LC/ESI-HR-TOFMS, LC/ESI-MS/MS, and more recently the HR-AMS data. Currently, it is very difficult to argue against the identity of these oligomers as oligoesters.

To make sure the above is clear to readers of our manuscript, we have added the following text to the results and discussion (page 21, line 457-473):

“It is important to also note that 2-MG and its corresponding oligoesters have been chemically characterized at the molecular level using GC/MS with prior single derivatization (i.e., trimethylsilylation only) or double derivatization (i.e., ethylation followed by trimethylsilylation) approaches (Surratt et al., 2006; Szmigielski et al., 2007), LC/ESI-MS/MS or LC/ESI-HR-TOFMS techniques (Surratt et al., 2006; Chan et al., 2010; Nguyen et al., 2011; Sato et al., 2011), and more recently by high-resolution AMS (Chan et al., 2010; Sato et al., 2011). The GC/MS with prior single or double derivatization approaches have helped to tag the ester linkages to further support the LC/ESI-HR-TOFMS, LC/ESI-MS/MS, and more recently the HR-AMS data. Thus, currently, it is very difficult to argue against the identity of these oligomers as oligoesters.”

Last, we want to add that the oxidation of other VOCs, such as cyclohexene ozonolysis (Hamilton et al. 2006, ACP; Müller et al., 2008, ACP), cyclohexene/ $\alpha$ -pinene ozonolysis (Müller et al., 2008, ACP),  $\alpha$ - $\beta$ -unsaturated aldehydes (e.g., acrolein, crotonaldehyde, MACR) photooxidations under initially high NO<sub>2</sub>/NO ratios (Chan et al., 2010, ACP), and butadiene photooxidation under high-NO<sub>x</sub> conditions (Angove et al., 2006), have been shown to lead to oligoesters in the resultant SOA. Most of these

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prior systems have been investigated under dry conditions.

We've added the following text to the discussion to take into our account our point above on page 21 lines 467-473:

“Last, we want to add that the oxidation of other VOCs, such as cyclohexene ozonolysis (Hamilton et al. 2006, ACP; Müller et al., 2008, ACP), cyclohexene/ $\alpha$ -pinene ozonolysis (Müller et al., 2008, ACP),  $\alpha$ - $\beta$ -unsaturated aldehydes (e.g., acrolein, crotonaldehyde, MACR) photooxidations under initially high NO<sub>2</sub>/NO ratios (Chan et al., 2010, ACP), and 1,3-butadiene photooxidation under high-NO<sub>x</sub> conditions (Angove et al., 2006), have been shown to lead to oligoesters in the resultant SOA. Most of these prior systems have been investigated under dry conditions.”

14. Finally, some works directly relevant to this study (effect of RH on SOA yield), which have not been quoted, must absolutely be discussed.

AUTHORS' RESPONSE: We are grateful to the reviewer for recommending the missing references suggested below. As the reviewer points out below, these references help to support our findings here, as well as to point out the likely insignificant role of glyoxal-forming SOA in this initially high-NO system.

15. In conclusion, the editor would have to decide if this paper is publishable in view of the limited dataset. But, should it be the case, it is essential that the issues addressed below are completely answered before publication can be considered.

Detailed comments: 1) Insufficient dataset and comparison with Dommen et al., 2006  
The main concern about this work is the small number of experiments. While a trend between the SOA mass produced and RH can be seen, it is rather small (less than a factor 2) and borderline from being significant. The concentrations of isoprene and NO have almost the same effect on SOA mass than RH, which add some uncertainties in the results.

AUTHORS' RESPONSE: Please see our detailed reply above about the limited number

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of experiments after the first paragraph of the reviewer's comments.

Moreover, no detail is given on how the SOA mass is determined (see comment below), but it is also likely to include large uncertainties.

AUTHORS' RESPONSE: Please see our response to this issue in our reply to Reviewer #1 above, comment # 2. We addressed there how we determined the SOA mass.

16. The discussion - and the entire paper - being based on these 4 experiments, it is not clear that this work is publishable. At the very least this paper should discuss other works which have examined the SOA mass from isoprene as function of RH: Dommen et al., (2006). This study is barely mentioned and no comment is made on how the results compare.

AUTHORS' RESPONSE: The reviewer states here that the Dommen et al. (2006) study was barely mentioned and no comment is made on how the results compare. But this is not the case. We have cited this study several times both in the introduction section and the discussion section. It is a very important reference in our paper. Although the reviewer is correct in stating that Dommen et al. (2006) examined the effect of RH on some of the experiments from that study, 12 of the experiments kept the RH constant at around 50%; for these 12 experiments, the VOC/NO ratio was varied from ~2–8. Interestingly, two sets of their experiments could be compared at relatively the same initial VOC/NO ratios. These included the experiments 6 and 7 as one pair (VOC/NO ~ 7) and experiments 9 and 10 as another pair (VOC/NO ratio ~ 5–6). The RH effect on their SOA yields was almost similar to what we observe here with our seeded experiments; however, this could be a result of the higher VOC/NO ratios employed in Dommen et al. (2006). In the two pairs of nucleation experiments pointed out from this study by Dommen et al. (2006), the dry experiments had an RH < 2% and the more humid experiments had an RH at ~ 53%. In any case, this result is encouraging and does support our initial results. Again, we can't stress enough that to compare the RH effect between different experiments, it is important to con-

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sider only those experiments with the same oxidative conditions (i.e., VOC/NO ratios) as well as seed aerosol conditions. Kroll et al. (2007, ES&T) demonstrated a systematic lowering of SOA yields from the photooxidation of aromatics when ammonium sulfate seed aerosol was not initially present. This lowering was proposed to be due to longer induction periods in the nucleation case. Induction periods were defined in this prior study to result from the buildup of semivolatile products in the gas phase prior to gas-particle partitioning. Induction periods may arise not only from the lack of seed aerosol, but also from photooxidation reactions carried out under high-NO<sub>x</sub> conditions, in which SOA formation does not begin until the NO mixing ratio falls close to zero, and/or due to reactions involving multiple rate-limiting steps to SOA formation. Thus, if semivolatiles remain in the gas phase for long periods, it is very possible they could be lost to further oxidation reactions in the gas phase or lost to the surfaces of chamber walls. The presence of seed aerosol may allow for these semivolatiles to not be lost, resulting in increased SOA yields compared to the nucleation experiments. One of the major conclusions of Kroll et al. (2007) was that their results highlighted the need to conduct SOA formation studies in the presence of atmospherically relevant aerosol loadings. We should note that it took ~ 7 hrs in the Dommen et al. (2006) study to reach the maximum SOA mass concentration, whereas in our experiment it took ~ 3 hrs. This difference between our experiments is likely a combination of both different seed aerosol and oxidative conditions.

17. Yet, this previous work might be the only way to compensate for the limited dataset: Two plots comparing the results from this paper and Dommen et al. (2006) are attached to this review and show how the discussion could be made and would benefit this paper.

The first plot, "SOA mass", shows that the SOA masses obtained in this work are generally consistent with the "high NO" (> 280 ppb) data from Dommen et al., which reinforces the present discussion of a "high NO<sub>x</sub>"-type mechanism involving MPAN and MG. In addition, this plot shows that the SOA mass varies almost as the square of the initial concentration of isoprene (in fact, slightly below order 2), suggesting that most of

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the SOA mass is under the form of "dimers", such as 2-MG. The SOA mass produced at lower NO concentration seems, however, to vary with a higher degree in [isoprene]o suggesting the implication of larger "oligomers".

**AUTHORS' RESPONSE:** We are grateful to the reviewer for kindly putting this plot together to compare our data with Dommen et al. (2006). However, as we outlined above, in the study of Dommen et al. (2006) the initial VOC/NO ratio was not always held constant between all experiments; in fact, it varied from ~2–8. Holding the initial VOC/NO ratio constant between experiments is incredibly important to consider in the reaction of isoprene as this dictates the fate of the initially formed RO<sub>2</sub> radicals, and thus, the amount and chemical composition of the resultant SOA (Kroll et al., 2006, ES&T; Surratt et al., 2006, JPCA; 2010, PNAS; Chan et al., 2010, ACP). It is not equitable to compare the 17 experiments from Dommen et al. (2006) to our 4 experiments as Dommen et al. (2006) not only varied the RH but they also varied the initial VOC/NO ratio, which also affects the SOA yield. Our study is systematic because we keep the initial VOC/NO ratio constant (~3) in all 4 experiments; the only variable to change is RH in our experiments.

The reviewer mentioned that "the only way to compensate for the limited dataset would be to compare the results with those of previous works to confirm the trends observed here" and the reviewer kindly suggested that we compare our results with Dommen et al. (2006) study in detail. However, Dommen et al. (2006) performed only non-seed aerosol experiments, and as a result, the SOA formation was mostly from nucleation. In this study, by contrast, we are using ammonium sulfate as the initial seed aerosol and the SOA formation is mostly based upon gas-to-particle partitioning. Kroll et al. (2007, ES&T) has compared SOA formation with and without initial ammonium sulfate seed aerosol for aromatic compounds, finding that SOA yields varied under different initial seed conditions (i.e., a systematic lowering of SOA yields without the presence of seed aerosol). This was recently confirmed by Kamens et al. (2011, Atmos. Environ.). By having initial seed aerosol we allow semivolatiles to uptake to the aerosol,

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which in turn prevents them from being lost to the walls of the smog chamber or being further removed by further gas-phase oxidation reactions. Also, the ammonium sulfate seed aerosol allows for a reactive surface to exist for the partitioning organics. Recent work by Loza et al. (ES&T, 2010) has demonstrated that semivolatiles, such as 2,3-epoxy-1,4-butanediol (BEPOX) and glyoxal, can be irreversibly or reversibly lost to smog chamber walls, respectively. Instead of using this plot here provided by the reviewer, we have added Figure 2 to the manuscript so we can discuss the differences between our SOA yields and those previously published by Kroll et al. (2005, GRL; 2006, ES&T) and Dommen et al. (2006).

18. The second plot, "RH", confirms that, once the SOA mass is divided by the square of [isoprene]o, it does vary inversely with RH, the results of the present work being consistent with those of Dommen et al. (2006) (note, however, that RH was not varied in the high NO experiments of Dommen et al. (2006), and these points are thus not shown). This strongly reinforces the main conclusion of this paper and shows the interest of discussing this previous study.

**AUTHORS' RESPONSE:** We are grateful to the reviewer for kindly providing this plot to further support our data set. Even though this plot suggests our results are consistent with Dommen et al. (2006), we must be careful to not read into this too much. One might expect different yields from systems that generate SOA via nucleation vs. partitioning as well as with differing initial VOC/NO ratios. In the study of Dommen et al. (2006), the initial VOC/NO ratio was not always held constant between all experiments; in fact, it varied from ~2–8. Holding the initial VOC/NO ratio constant between experiments is incredibly important to consider in the reaction of isoprene (as with any other VOC) as this dictates the fate of the initially formed RO<sub>2</sub> radicals, and thus, the amount and chemical composition of the resultant SOA (Kroll et al., 2006, ES&T; Surratt et al., 2006, JPCA; 2010, PNAS; Chan et al., 2010, ACP). Although the reviewer is correct in stating that Dommen et al. (2006) examined the effect of RH on some of the experiments from that study, 12 of the experiments kept the RH constant at around 50%; for

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these 12 experiments, the VOC/NO ratio was varied from  $\sim 2$ –8. Interestingly, two sets of their experiments could be compared at relatively the same initial VOC/NO ratios. These included the experiments 6 and 7 as one pair (VOC/NO  $\sim 7$ ) and experiments 9 and 10 as another pair (VOC/NO ratio  $\sim 5$ -6). The RH effect on their SOA yields was almost similar to what we observe here with our seeded experiments; however, this could be a result of the higher VOC/NO ratios employed in Dommen et al. (2006). In the two pairs of nucleation experiments pointed out from this study by Dommen et al. (2006), the dry experiments had an RH  $< 2\%$  and the more humid experiments had an RH at  $\sim 53\%$ . In any case, this result is encouraging and does support our initial results. Again, we can't stress enough that to compare the RH effect between different experiments, it is important to consider only those experiments with the same oxidative conditions (i.e., VOC/NO ratios) as well as seed aerosol conditions. It is not equitable to compare the 17 experiments from Dommen et al. (2006) to our 4 experiments as Dommen et al. (2006) not only varied the RH but they also varied the initial VOC/NO ratio, which also affects the SOA yield. Our study is systematic because we keep the initial VOC/NO ratio constant in all 4 experiments; the only variable to change is RH in this case. Naturally, in our experiments with higher isoprene mixing ratios, however, we will get higher Mo (or SOA mass) values. We did this to explore if the same chemical effect happened at higher Mo values. The purpose of our study was not to determine the alphas and Ks by fitting our data with the "two product model" over a wide range of Mos (and thus a number of experiments); however, our study was designed to gain insight into the differences of the SOA composition and yield at one VOC/NO ratio. Future work is certainly needed to derive a parameterization, such as the two-product model, to be used in regional and global models to take into account the effect of RH on SOA yields. However, this is out of the scope of our present work and will likely require many other groups to also closely examine this issue. The effect of RH at higher VOC/NO ratios could be also strikingly different from the current set of experiments and also warrants future study. Thus, this is not a simple system to study, and thus, we started off here by only examining the effect of RH on one initial VOC/NO ratio. It will be

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interesting to examine the effect of RH on isoprene SOA formation when RO<sub>2</sub> + RO<sub>2</sub> or RO<sub>2</sub> + HO<sub>2</sub> initially dominate the gas-phase chemistry. This will dictate what types of semivolatile products form and go onto to make SOA from isoprene. These products may very well have different interactions with an irradiated wet aerosol as compared to what we found here when RO<sub>2</sub> + NO initially dominates the gas-phase chemistry.

In our discussion of our SOA yields, we include the following on page 14 and lines 286-297:

"Dommen et al. (2006) examined the effect of varying the initial isoprene/NO<sub>x</sub> ratio on SOA formation from isoprene; the specific focus was on examining this effect on SOA yields, the presence of oligomers, and on the volatility of the resultant SOA. However, in a few circumstances, they examined the effect of varying RH under similar VOC/NO ratios. One pair of their experiments had an initial VOC/NO ratio of  $\sim 7$  and in another pair of experiments this ratio was  $\sim 5$ -6. In both pairs, the dry experiments had an RH  $< 2\%$  where as the more humid experiments had an RH of about 53%. The SOA yields observed in the drier experiments were found to be higher by a factor of  $\sim 2$ . Interestingly, for the experiments that had an initial VOC/NO ratio of  $\sim 5$ -6, the SOA was found to have a much lower volatility under dry conditions, which was consistent with the observation of oligomeric SOA constituents found in Dommen et al. (2006). These results further support our findings."

18. Experimental determination of SOA mass No detail is given in the Experimental section on how the SOA mass was determined. This is essential because this is likely to include some uncertainties impacting the results. In addition, as pointed out by Reviewer 1, it would be important to know if a potential uptake of water has been taken into account.

AUTHORS' RESPONSE: This issue has been explained in the response to reviewer #1's comment. Water uptake has been taken into account as described in our response to reviewer #1.

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19. Discussion of other relevant studies While the introduction discusses other studies of SOA mass vs RH (for aromatics, for instance) and even the potential role of glyoxal in isoprene SOA, the study of SOA formation from glyoxal by Volkamer et al., 2009 is completely overlooked. This previous work evidenced an effect of the liquid water content of the aerosol on the SOA yield, directly relevant to the present work. This would also reinforce this paper, even though the trend reported is opposite, as an effect of RH on SOA yield is demonstrated. A discussion of this work (albeit short) is indispensable in this paper.

AUTHORS' RESPONSE: We thank the reviewer for kindly pointing this out and also suggesting including this into our discussion. The Volkamer et al. (2009) study is now included in this revised manuscript. Also, as outlined above, we have also added detailed text to the discussion that includes the results from this study.

20. pH and reaction mechanisms Some of these points were already addressed in my preliminary review. The identification of the products in the SOA at high and low RH is probably the most interesting results of this work. However, some aspects of the discussion of the possible mechanisms are plagued by some misconceptions.

AUTHORS' RESPONSE: We agree with the reviewer here that the varying chemical composition between low and high RH is probably the most interesting part of this work, but is consistent with our observed SOA yields.

21. - the main explanation proposed for the differences in SOA mass between low and high RH is that the seeds are more acidic at low RH, which should enhance esterification reactions (by acid catalysis). Unfortunately, by definition, the pH of ammonium sulfate seeds cannot be lower than 5, the value at saturation. This can hardly be considered as "acidic". Moreover, this value cannot change significantly between RH = 15 % and RH = 90 % because, in order to change, the particles have to take up large amounts of water, causing an increase of volume and a "dilution" toward pH = 7. But such water uptake occurs only above critical supersaturation, i.e. well above

C3384

RH = 100% for ammonium sulfate. The pH of the seeds in these experiments was therefore close to 5 over the entire range of RH. This should be easy to confirm with measurements.

AUTHORS' RESPONSE: The pH issue has been addressed in the responses to the initial report by this reviewer.

22. - Another aspect to take into consideration is that at RH = 15- 42 % a large fraction of the ammonium sulfate particles are likely to be solid, according to the phase diagram of Xu et al., J. Phys. Chem. B, 102, 7462, 1998.

AUTHORS' RESPONSE: We completely agree here that the dry aerosol case likely has solid ammonium sulfate seed aerosol. This could be helping to drive the enhancements in the SOA yields.

23. - The discussion of the reaction mechanisms in this paper starts from the assumption that esterifications are involved, because the previous work of Surratt et al., (2010) proposed (but did not prove) that esterifications were involved in these processes. Esterification reactions are well known to be extremely slow, as supported by a plethora of literature.

AUTHORS' RESPONSE: We would like to restate our response here to this concern by the reviewer. Although the chemical characterization of 2-methylglyceric acid and its corresponding oligoesters in our manuscript are well supported by our chemical data and by both previous studies, such as Surratt et al. (2006, JPCA; 2010, PNAS) and Szmigielski et al. (2007a, Journal of Mass Spectrometry), and more recent studies by Chan et al. (2010, ACP) and by Sato et al. (2011, ACPD) that employed both on-line (e.g., high-resolution AMS) and off-line MS techniques, we agree with this reviewer that these oligoesters could have resulted from alternative pathways other than organic esterification. Currently, it is known from previous studies that the further oxidation of alpha-beta-unsaturated aldehydes, such as MACR, yield 2-methylglyceric acid and its corresponding oligoesters due to the formation and further oxidation of MPAN. What

C3385

happens after the further oxidation of MPAN that leads to these oligoesters is still unknown (Surratt et al., 2010, PNAS; Chan et al., 2010, ACP). We want to stress here to the reviewer and the editor is that we are only tentatively proposing that these oligoesters are formed by organic esterification reactions. To make this clear we have revised the following sentence in the abstract to read:

“Based upon detailed chemical characterization results, particle-phase organic esterification is only tentatively proposed to explain the observed enhancements of isoprene SOA mass under lower RH conditions. Alternative mechanisms explaining the enhancement of 2-MG and its corresponding oligoesters cannot be completely ruled out.”

We want to add here that the oxidation of other VOCs, such as cyclohexene ozonolysis (Hamilton et al. 2006, ACP; Müller et al., 2008, ACP), cyclohexene/alpha-pinene ozonolysis (Müller et al., 2008, ACP), photooxidation of alpha-beta-unsaturated aldehydes (e.g., acrolein, crotonaldehyde, MACR) under initially high NO<sub>2</sub>/NO ratios (Chan et al., 2010, ACP), and 1,3-butadiene photooxidation under high-NO<sub>x</sub> conditions (Angove et al., 2006), have all been shown to lead to oligoesters in the resultant SOA. Most of these prior systems have been investigated under dry conditions.

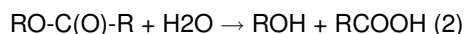
24. For instance, under typical aerosol conditions, the kinetics experiments of Minerath et al. 2008 showed that they would have a typical half-life of 4600 days. Thus, unlike what is discussed in the text, they are extremely kinetically limited. And at pH = 5- 7 these reactions would be nowhere near observable in these experiments.

AUTHORS' RESPONSE: The reviewer referred to the Minerath et al. (2008) study to show that esterification reactions in the aerosol-phase are very slow. However, the Minerath et al. (2008) study was focused on examining alcohol sulfate esterification. But what we proposed in this study is the organic esterification, which involves an organic acid condensing with an alcohol that is different from the Minerath et al. (2008) study.

25. Other reactions, however, would be favored in “less aqueous” media: dehydrations, for instance, but not only.

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AUTHORS' RESPONSE: The reviewer pointed out that other reactions may also be favored in “less aqueous” media such as dehydrations. However, the nature of the low-RH favored organic esterification process is dehydration.



In the reversible organic esterification process, the kinetics of the forward reaction (1) does not differ from different RH conditions (March, J. “Advanced Organic Chemistry” 4th Ed. J Wiley and Sons, 1992). But the kinetics of the backward reaction (2) highly depends on water concentration. Thus, removal of water by physical means could improve the yield of the ester (according to Le Chatelier's principle). Under low-RH conditions, this backward reaction is impeded and hence more oligoesters stay in this system. In addition, under high-NO<sub>x</sub> conditions these reactions could be acid-catalyzed by the formation and presence of HNO<sub>3</sub> in the particle phase, as previously proposed by Lim and Ziemann (2009, AS&T).

26. Moreover, other products of the same brut formula than 2-MG and the higher “oligomers” proposed in Surratt et al. (2010) could account for the exact masses found in the SOA – and results from reactions very different from esterification. The discussion is still open. But the title of this manuscript could turn out to be unfortunate once these mechanisms are elucidated. I would suggest the authors to use more caution in the title and refer to the high-molecular weight products or “oligomers” rather than to the reactions.

AUTHORS' RESPONSE: It is important to clarify here for the reviewer and the editor that 2-methylglyceric acid and its corresponding oligoesters have been chemically characterized at the molecular level using GC/MS with prior single derivatization (i.e., trimethylsilylation only) or double derivatization (i.e., ethylation followed by trimethylsilylation) approaches (Surratt et al., 2006, JPCA; Szmigielski et al., 2007, JMS), LC/ESI-MS/MS or LC/ESI-HR-TOFMS techniques (Surratt et al., 2006, JPCA; Chan et al.,

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2010, ACP; Nguyen et al., 2011, ACPD; Sato et al., 2011, ACPD), and more recently by high-resolution AMS (Chan et al., 2010, ACP; Sato et al., 2011, ACPD). The GC/MS with prior single or double derivatization approaches have helped to “tag” the ester linkages and carboxylic acid moieties to further support the LC/ESI-HR-TOFMS, LC/ESI-MS/MS, and more recently the HR-AMS data. Currently, it is very difficult to argue against the identity of these oligomers as oligoesters. However, we certainly agree that it could be possible that alternative mechanisms enhance these oligoesters under dry conditions. We do argue in the text that this is a tentative proposal and not final.

However, taking into account the reviewer’s suggestion, we have revised the title of the paper to be:

“Effect of Relative Humidity on SOA Formation from isoprene/NO Photooxidation: Enhancement of 2-methylglyceric Acid and its Corresponding Oligoesters under Dry Conditions”

27. Minor comments:

- at several places in the text, references to Paulot et al. (2009) are inappropriate. For instance, in the introduction (li 11), referring to Paulot et al. for global estimates of SOA from isoprene is not justified. Only global models can do that. Also, on li. 27-28, it is incorrect that Paulot et al. has elucidated SOA formation mechanisms. This work focused exclusively on gas-phase mechanisms and only suggested that the results could bring some explanation on the SOA formation, nothing more.

AUTHORS’ RESPONSE: The Paulot et al. (2009) citation has been removed from the sentence in the introduction on line 11. We thank the reviewer for finding this error. We respectfully disagree with the Reviewer about the citation of Paulot et al. (2009) on lines 27-28 in the introduction section. Paulot et al. (2009) conducted preliminary chamber experiments with acidic seed aerosol when finding the presence of IEPOX in the gas phase with their CIMS technique. They observed SOA formation from this process; however, the detailed chemistry was not discussed. Thus, these initial findings

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by Paulot et al. (2009) helped guide the detailed SOA studies by Surratt et al. (2010). As a result, we feel it is only fair to credit the work of Paulot et al. (2009) in helping guide the further work of Surratt et al. (2010). In total, there are only now two references to Paulot et al. (2009) in our manuscript.

28. - the reference to Froyd et al., 2010 to support a SOA enhancement due to organosulfates (li. 14 of p. 5410) is not correct either. Froyd et al. reported atmospheric observations, not chamber studies, and could thus not observe an “enhancement”. The next sentence is fully correct, but the term “ambient” should be replaced by “high-altitude”, since these measurements were made in the free troposphere-lower stratosphere.

AUTHORS’ RESPONSE: We thank the reviewer for finding that this reference was improperly cited in this sentence. We have removed this reference from this citation.

We have also replaced the term “ambient” with the term “high-altitude” to more precisely reflect where these measurements were made by Froyd et al. (2010).

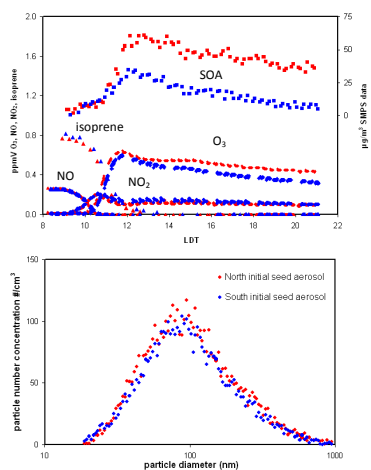
29. - References to the gas-phase oxidation mechanism of isoprene and the formation of MACR and MPAN are off. These mechanisms have been elucidated well before the 2000’s. For MACR: Paulson, Flagan, Seinfeld, “Atmospheric photooxidation of isoprene”, *Int. J. Chem. Kinet.*, 24, p. 79 and 103 (2 articles), 1992 and Paulson and Seinfeld, “Development and evaluation of a photooxidation mechanism for isoprene”, *JGR*, 97, 20703, 1992. For MPAN: Bertman and Roberts, “A PAN analog from isoprene photooxidation”, *GRL*, 18, 1461, 1991. Interactive comment on *Atmos. Chem. Phys. Discuss.*, 11, 5407, 2011. New references to the gas-phase oxidation of MACR and MPAN are added in the revised manuscript (page 19-20, line 429-430).

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Interactive comment on *Atmos. Chem. Phys. Discuss.*, 11, 5407, 2011.

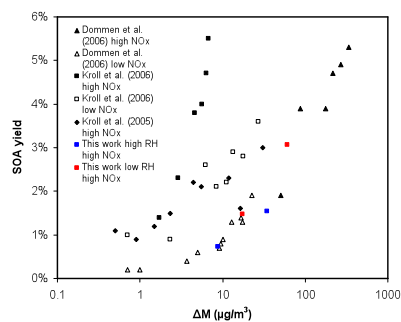
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**Fig. 1.** (A) Gas-phase measurement of O<sub>3</sub>, NO<sub>x</sub>, and isoprene and wall-loss uncorrected SOA data. (B) Particle size distributions under low-(red dots) and high-(blue dots) RH conditions when experiments began.

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**Fig. 2.** Summary of SOA yields reported from previous literature and this work as a function of organic mass concentration ( $\Delta M$ )

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