We thank the reviewers for their careful reading and helpful comments that improved the quality of our manuscript.

We believe that the major comments from reviewers are centered on our hypothesis of core-shell structure and its context with previous studies, especially by those of the UNC group. Although ample literature exists to support the hypothesis of core-shell morphology, as reviewer 1 pointed out, depending on the relative amount of seed material and organics condensing on it, we may not be able to detect SOA formation from glyoxal uptake onto aqueous ammonium sulfate during the seeded experiments. We found this to be a great question. Since the seed fraction was indeed minor after several hours of experiment, the seeded vs. non-seeded comparison by itself is not a strong evidence for core-shell morphology. Instead, the absence of a significant aqueous seed effect suggests that a non-glyoxal route dominated aromatic SOA formation in our experimental conditions (which is still our major conclusion). Impact of water content is discussed in more detail within the revised manuscript in the context with Kamens et al. studies.

Responses to specific comments are shown below.

Reviewer 1 comments:

1. What evidence do the authors have that the aerosols produced by photooxidation of aromatics in the presence of deliquesced inorganic seed have core-shell morphology? It is not at all obvious to me that it should be the case.

Response:

Although core-shell structures of aqueous salt – SOA have been proposed a number of times (Anttila et al., 2007; Anttila et al., 2006; Bertram et al., 2011; Warren et al., 2009), the argument on core-shell structure is removed in the revised manuscript because glyoxal uptake onto $(NH_4)_2SO_4$ would contribute only a minor fraction of the SOA as discussed below.

2. What is the relative amount of seed material vs organics condensed on it? If uptake of glyoxal was still going on at the same level as with pure ammonium sulfate, would the authors even notice it? An estimate would help.

Response:

Organic mass fraction reached approximately 90% (seed fraction 10%) in six hours (not shown). For pure ammonium sulfate experiment, org/sulfate mass ratio reached ~0.4 in six hours (Fig.2, AMS data). Assuming same extent of glyoxal uptake onto ammonium sulfate during the toluene + seed experiment (likely to be an upper limit), glyoxal SOA would comprise only minor mass fraction (<10%). Thus the results in Fig.7 cannot be strong evidence for the absence of glyoxal uptake into aqueous ammonium sulfate. Instead, this argument suggests that non-

glyoxal route dominates the SOA formation pathways, which is consistent with the other observations in this study.

3. The authors mentioned that glyoxal oligomers did not evaporate in the thermodenuder because of their low vapor pressure. Perhaps they similarly do not evaporate fully in the AMS ionizer? If this is the case, the evidence based on the conserved C4H9+ fraction becomes questionable.

Response:

The temperature of the AMS heater is ~600°C (well beyond the temperature range in Fig.1), thus expected to be high enough to vaporize glyoxal oligomers. The AMS has been successfully applied to glyoxal oligomer previously (Galloway et al., 2009; Lee et al., 2011).

4. The organic material produced by oxidation of aromatics generally has low water solubility. Aerosols made by oxidation of biogenic precursors, such as isoprene and alpha-pinene are generally more water soluble. Would the authors expect the same results for aerosols made for these biogenic precursors? I would avoid generalizing their conclusions to all types of SOA.

Response:

In the revised manuscript, we clarified that the conclusion is applicable to the compounds employed in this study and extrapolation to other compounds is currently speculative.

However, in previous studies, the hygroscopic growth factors (Gf) of biogenic SOA were observed to be approximately same as (or slightly less than) those of aromatic SOA:

Jimenez et al. (2009) – α-pinene, isoprene, and trimethylbenzene
Cocker et al. (2001) - α-pinene, *m*-xylene, and 1,3,5-trimethylbenzene
Qi et al. (2010) – α-pinene and *m*-xylene
Prenni et al. (2007) – α-pinene, β-pinene, Δ^3-carene, and toluene

Therefore, our conclusion has the potential to be applicable to biogenic species. This finding encourages further studies employing other important glyoxal precursors, such as isoprene.

Specific minor comments:
Page 30601, line 16: acquired -> attracted

Response: Done

Page 30602, line 10: insert a comma before Calvert

Response: Done

Page 30602, line 19: the extent of the contribution : : : is poorly understood

Response: Done

Page 30602, line 25: radical or non-radical reactions -> free-radical initiated and various condensation reactions

Response: Done

Page 30603, line 10: use SI units

Response: Done

Page 30603, line 11: 272 115 is not the best way to start a sentence, and also can be confused for 271,115

Response: The description is modified appropriately.

Page 30607, line 3: available -> possible

Response: Done

Page 30609, line 2: added to match OH levels in previous experiment – it is not clear from the text how OH was measured or estimated

Response: The description is modified appropriately.

Table 1: The notation involving EPA may be confusing, people may think these are abbreviations of some EPA standard operating procedures.

Response: "EPA" is removed from RunID.

Reviewer 2 comments:

- One of my concerns is regarding the conclusion stated in lines 6-7 of the abstract: "Glyoxal is found to only influence SOA formation by raising hydroxyl (OH) radical concentrations."
It seems that this phenomenon will be mainly important in the chamber studies conducted here (and other similar controlled studies). Or do the authors think that this would be significant in the atmosphere as well? If not, strong statements such as

this one must be reworded to make the specific relevance to chamber experiments clear.

Response:

The text and the title are modified to clarify the importance in the chamber studies.

- What kind of glyoxal uptake did the authors expect to observe in the toluene SOA uptake experiments (section 3.2)? As the authors state in lines 5-6 of page 30601, the vapor pressure of glyoxal is far too high to partition to organic aerosol. If this was basically a control experiment designed to evaluate the effect of glyoxal on the chamber photochemistry, this should be made clear.

Response:

It was often assumed that glyoxal partitions to small amount of water associated with SOA even under medium humidity and then forms oligomers. For instance, Kalberer et al. (2004, Science) proposed that the oligomer pattern observed in SOA formed from 1,3,5-trimethylbenzene is due to methylglyoxal uptake at RH less than 50%.

Although previous studies observed SOA formation from pure glyoxal uptake onto seed particles, the significance of glyoxal uptake in the complex aromatic hydrocarbon oxidation system has never been directly evaluated. Currently it is assumed that glyoxal uptake can play a major role in aromatic SOA formation under humid conditions (Kamens et al., 2011; Kalberer et al., 2004). If the assumption is correct, addition of high concentration of glyoxal (~100ppb) into toluene SOA system should result in additional SOA formation. Section 3.2 scrutinizes thus hypothesis in terms of PM volume and volatility. The results indicate that the role of glyoxal under our experimental conditions was a gas-phase OH radical source, not an oligomer precursor.

- Section 3.3. I agree with the other referee that more discussion of these experiments is in order. Is there evidence for core-shell morphology in the aerosols, from this group or from the literature? How thick is the coating? There is a large body of literature on the uptake of gas-phase molecules to aqueous particles coated with organic films; this phenomenon depends greatly on the thickness of the coating and the molecular identity of the film organics and the incoming gas molecules. So, statements such as "glyoxal uptake onto aerosol is minor when the surface (and near-surface) of aerosols are primarily composed of secondary organic compounds" are much too general to be made based on the results here (especially when no actual knowledge about the particle morphology seems to be available).

Response:

As mentioned in the reply to reviewer 1, we confirmed that the mass fraction of seed is so small (<10% in approximately 6 hours) that even if ammonium sulfate is fully available for glyoxal uptake, oligomer formation from glyoxal would be minor.

Although recent studies (Bertram et al., 2011; Zuend et al., 2011) suggest that liquid-liquid phase separation (LLPS) is likely to occur in our experimental conditions, morphology plays minor role in these experiments.

- The phrase ": : : lack of these enhancements by sulfate ion and ammonium ion in water associated with SOA can contribute to the lack of reactive uptake of glyoxal onto
SOA" is a bit cryptic. Please elaborate on what is meant here. That the salts were inaccessible to the incoming glyoxal, and glyoxal will just interact with water in the organic phase of the toluene SOA?

Response:

The sentence was rephrased to reflect arguments shown above (minor seed mass fraction).

Reviewer 3 comments:

1. These experiments are carefully done. However, the conclusion of this paper does not take into consideration an important lesson that should have been gleaned from the examination of other recent papers. A discussion of the results of these experiments in comparison with the others is required.
Zhou et al. (xylenes and toluene; Atmospheric Environment, 45, 2011, 3882-3890) clearly demonstrated that the aerosol water concentration, rather than the RH, is critical to the formation of SOA through aqueous chemistry in wet particles. The type of aerosol seed, the concentration of that seed aerosol, and the RH together determine the liquid water concentration in the chamber. Kamens et al (toluene SOA; Atmospheric
Environment, 45, 2011, 2324-2334) explain differences between the work of Cocker (2001) who concluded that RH had no effect on aromatic SOA and Volkamer (2009) who concluded that it has a dramatic effect on SOA from glyoxal (an aromatic intermediate).
The concluded that Cocker's experiments were conducted at much lower liquid water content. The Kamens et al (2011) experiments found that more toluene SOA formed at higher liquid water concentrations. And when they conducted experiments with ambient seed particles and with ammonium sulfate seed particles

adjusting RH to give the same liquid water concentration, more SOA forms from the ambient seed than from the ammonium sulfate seed.
Nakao et al must discuss their own results in the context of the Kamens and Zhou results. They must add the concentration of liquid water to Table 1.

Response:

Liquid water content (LWC) is now included in Table 1. Our results also indicate that higher LWC resulted in higher SOA yield, which is consistent with UNC group's study. However, what is unique in this study is that we directly evaluated the role of glyoxal by using synthesized glyoxal and direct measurement of glyoxal. Our results indicate that although high LWC resulted in high SOA yield, it was not due to glyoxal uptake in our experimental conditions. Since the goal of this study is evaluation of the role of glyoxal in aromatic SOA formation, detailed investigation of the non-glyoxal route SOA formation in a high LWC condition is beyond the scope of this study. One of the possible explanations is aqueous reaction of phenolic compounds (Sun et al., 2010). Also, their lower SOA concentration range might result in higher contribution from glyoxal uptake because glyoxal uptake is not driven by partitioning to organic phase, but dissolution into water.

Direct comparison of our study with UNC's study is difficult due to different experimental conditions such as light source, different level and composition of background, different RH range, and PM concentration range.

They must revise their title, as I believe they can only say that "gas-phase reaction trumps reactive uptake" for their experimental conditions (i.e., liquid water concentration). They must acknowledge and discuss the Kamens and Zhou results to put their work into context.

Response:

The title is revised as follows: "Chamber studies of SOA formation from aromatic hydrocarbons: observation of limited glyoxal uptake"

We believe that the significance of glyoxal uptake during aromatic SOA formation was surprisingly limited at least in the experimental conditions of this study. The title still leaves room for the possibility of glyoxal uptake under different conditions such as different aerosol composition (e.g., wet ammonium sulfate) or ambient studies.

3. OH concentrations also matter to the aqueous chemistry in these experiments. Increasing OH radical can increase SOA through gas phase or aqueous phase chemistry.

Response:

Addition of OH may result in enhanced aqueous chemistry of glyoxal (Galloway et al., 2011; Volkamer et al., 2009). This is clarified in the revised manuscript. We would like to emphasize that our experiments of additional glyoxal vs. H_2O_2 are not intended to rule out the possibility of enhanced aqueous reaction via "OH"; rather, the idea is to evaluate the role of "glyoxal". The fact that enhanced OH level (as confirmed from faster toluene decay rate) in both experiments resulted in similar SOA formation indicates the enhanced SOA formation was due to the OH reaction in gas-phase and/or aqueous phase.

4. page 30606 line 24 "particulates" should be "particulate matter"

Response: Done

5. what is the effect of retained water and sulfate on the reported glyoxal oligomer volatility?

Response:

We do not have measurement of volatility with the presence of water and sulfate. Since dehydration is the key process in glyoxal oligomer formation, vapor pressure could be higher if water is retained in particles. Organo sulfate formation has been reported; however, the volatility of organo-sulfate is still poorly characterized.

References

Anttila, T., Kiendler-Scharr, A., Mentel, T., Tillmann, R. (2007). Size dependent partitioning of organic material: evidence for the formation of organic coatings on aqueous aerosols. *Journal of Atmospheric Chemistry* 57(3): 215-237.

Anttila, T., Kiendler-Scharr, A., Tillmann, R., Mentel, T. F. (2006). On the reactive uptake of gaseous compounds by organic-coated aqueous aerosols: theoretical analysis and application to the heterogeneous hydrolysis of N2O5. *J. Phys. Chem. A* 110: 10435-10443.

Bertram, A. K., Martin, S. T., Hanna, S. J., Smith, M. L., Bodsworth, A., Chen, Q., Kuwata, M., Liu, A., You, Y., Zorn, S. R. (2011). Predicting the relative humidities of liquid-liquid phase separation, efflorescence, and deliquescence of mixed particles of ammonium sulfate, organic material, and water using the organic-to-sulfate mass ratio of the particle and the oxygen-to-carbon elemental ratio of the organic component. *Atmos. Chem. Phys.* 11(21): 10995-11006.

Cocker, D. R., Mader, B. T., Kalberer, M., Flagan, R. C., Seinfeld, J. H. (2001). The effect of water on gas-particle partitioning of secondary organic aerosol: 2. m-xylene and 1,3,5-trimethylbenzene photooxidation systems. *Atmospheric Environment* 35: 6073-6085.

Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prevot, A. S. H., Zhang, Q., Kroll, J. H., DeCarlo, P. F., Allan, J. D., Coe, H., Ng, N. L., Aiken, A. C., Docherty, K. S., Ulbrich, I. M., Grieshop, A. P., Robinson, A. L., Duplissy, J., Smith, J. D., Wilson, K. R., Lanz, V. A., Hueglin, C., Sun, Y. L., Tian, J., Laaksonen, A., Raatikainen, T., Vaattovaara, P., Ehn, M., Kulmala, M., Tomlinson, J. M., Collins, D. R., Cubison, M. J., Dunlea, E. J., Huffman, J. A., Onasch, T. B., Alfarra, M. R., Williams, P. I., Bower, K., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Salcedo, D., Cottrell, L., Griffin, R. J., Takami, A., Miyoshi, T., Hatakeyama, S., Shimono, A., Sun, J. Y., Zhang, Y. M., Dzepina, K., Kimmel, J. R., Sueper, D., Jayne, J. T., Herndon, S. C., Trimborn, A. M., Williams, L. R., Wood, E. C., Middlebrook, A. M., Kolb, C. E., Baltensperger, U., Worsnop, D. R. (2009). Evolution of organic aerosols in the atmosphere. *Science* 326: 1525-1529.

Prenni, A. J., Petters, M. D., Kreidenweis, S. M., DeMott, P. J., Ziemann, P. J. (2007). Cloud droplet activation of secondary organic aerosol. *Journal of Geophysical Research* 112(D10223): doi:10.1029/2006JD007963.

Qi, L., Nakao, S., Malloy, Q., Warren, B., Cocker, D. R. (2010). Can secondary organic aerosol formed in an atmospheric simulation chamber continuously age? *Atmospheric Environment* 44: 2990-2996.

Warren, B., Malloy, Q., Yee, L. D., Cocker, D. R. (2009). Secondary organic aerosol formation from cyclohexene ozonolysis in the presence of water vapor and dissolved salts. *Atmospheric Environment* 43: 1789-1795.

Zuend, A., Marcolli, C., Booth, A. M., Lienhard, D. M., Soonsin, V., Krieger, U. K., Topping, D. O., McFiggans, G., Peter, T., Seinfeld, J. H. (2011). New and extended parameterization of the thermodynamic model AIOMFAC: calculation of activity coefficients for organic-inorganic mixtures containing carboxyl, hydroxyl, carbonyl, ether, ester, alkenyl, alkyl, and aromatic functional groups. *Atmos. Chem. Phys.* 11(17): 9155-9206.