Response to reviewers for "A functional group oxidation model (FGOM) for SOA formation and aging" by X. Zhang and J. H. Seinfeld

We thank both reviewers for their constructive comments, which have helped to note areas of ambiguity. Our specific responses can be found below, with reviewer comments in black and our responses in blue.

Response to Referee # 1

The paper presents a new simplified, yet flexible, model of SOA formation based on empirically fitted parameters. Sensitivities to processes are modeled by varying parameters within the fixed model framework. In all, the paper is quite interesting in that it assesses the ability of another semi-empirically formulated approach to understanding SOA formation. It is suitable for publication in ACP when some general issues have been addressed. Overall I would recommend more references are given to support various statements throughout. A few are mentioned below.

General comments.

The authors raise an interesting point, that being the trade-off between chemical fidelity and computational feasibility. I agree that the drive to include accurate SOA models in large scale schemes is critical. With this in mind it must also not be forgotten that the role of the more complex mechanistic approaches still holds for increasing our basic understanding of important aerosol processes. In the drive for developing reduced complexity models for use in large scale sensitivity studies, this parallel ethos must be maintained. Do the authors have a feel for which processes that might be occurring in real-world aerosol, that are not accounted for in this model, that might lead to biased sensitivities derived using this framework? One important statement is made at the beginning of the document. The authors state how 'laboratory chamber data on which current models are based generally do not exhibit the degree of oxidation observed in atmospheric organic aerosol'. If we are left with models that have to be tuned to such environments, it is then dangerous to prescribe 100% confidence in subsequent sensitivity studies for real-world scenarios? This is a harsh question perhaps, but with the rise of the tuned semi-empirical model that the authors concisely review, it is useful to think about this. There are numerous assumptions made in the inclusion of specific processes such as fragmentation. As the model is then fit to experimental data, do the authors have any mechanism for testing the sensitivity to these assumptions before even the sensitivity of the process?

1). The goal of developing a semi-explicit SOA model is to represent SOA formation and evolution in the atmosphere using a computationally accessible, yet chemically realistic, framework. In the current FGOM structure, dominant pathways, including gas- and particle- phase photochemistry, gas-particle partitioning, and particle-phase accretion reactions, have been incorporated with free parameters that are to be determined by fitting the model to experimental chamber data. One aspect that is not explicitly represented in the current model is the effect of RH. The interaction between water and organic uptake onto particles has both chemical and physical manifestations. As implicated in equation (1),

$$K_{p,i} = \frac{RT}{10^6 p_{L,i}^0 \gamma_i \overline{M_w}} \tag{1}$$

RH-driven changes in the gas-particle partitioning coefficient $K_{p,i}$ result from changes in both aerosol average molecular weight ($\overline{M_w}$) and activity coefficient (γ_i). The fractional partitioning fraction of compound *i* in the particle phase (ϕ_i^p) depends on the amount of water uptake (M_w), as shown in equation (2).

$$\phi_i^p = \frac{K_{p,i}(M_o+M_w)}{1 + K_{p,i}(M_o+M_w)} \tag{2}$$

In the current FGOM structure, the value of activity coefficients is assumed to be unity, which is known to be an over-simplification (Zuend et al., 2010 and 2012).

2). The extent of OH exposure is key to the extent to which chamber SOA data can exhibit the degree of oxidation observed in atmospheric organic aerosol. For the alkane experiments considered in this study, the photochemical ages, $\tau = \frac{1}{[OH]_{atm}} \int_0^t [OH]_{exp} dt$, for high- and low- NO_x conditions are, on average, 1 and 3 days, respectively, which are less than the average lifetime of secondary organic aerosols in the atmosphere. These are results typical of most chamber experiments. Thus, chamber data tend not to represent the entire lifetime of SOA formation in the atmosphere. An alternative is the flow tube, the PAMS, that can attain photochemical ages of a week or more (Lambe et al., 2012). Semi-explicit models such as the FGOM will need to fit such data in the future. Note that $[OH]_{atm}$ is the typical atmospheric OH concentration (here taken as 1×10^6 molecule cm^{-3}) and $[OH]_{exp}$ is the chamber OH concentration generated by the photolysis of H_2O_2 or HONO.

Another possible reason that chamber data do not replicate the degree of oxidation of ambient aerosol is that ambient particles may have been subject to aqueous phase photooxidation pathways due to cloud processing (Ervens et al., 2011).

3). Assumptions underlying the current class of SOA models, the 2D-VBS, the SOM, the CNPG and the current FGOM are based on our current knowledge in terms of SOA formation comprising both gas- and particle- phase chemistry (Kroll and Seinfeld, 2008; Jimenez et al., 2009). In each of these models, assumptions made for each process (functionalization, fragmentation, oligomerization, etc.) are used as a basis to represent the complex SOA formation mechanism piece by piece, through free parameters that are to be obtained from optimal fitting to chamber data. Fragmentation, for example, is considered to be more probable when OH attack occurs near an already existing oxygenated functional group, so that there is a positive relationship between the degree of oxidation and the probability of fragmentation (P_f). There are several ways to parameterize P_f, such as $P_f = f_v \times n_O$ and $P_f = (O:C)^{f_v}$, where f_v is a free parameter (Jimenez et al., 2009; Cappa et al., 2012). Different representations will lead to different f_v and thus P_f values. The exact value of P_f obtained from a specific chamber experiment is less meaningful, perhaps, than comparison of P_f values between experiments, which provide insight on the importance of fragmentation in the overall SOA formation mechanism. In this study, we have evaluated P_f as a function of NO_x levels and C_{12} alkanes chemical structures. The effect of different fragmentation parameterizations is not as important as the fact that each describes the positive correlation between the degree of oxidation and the probability of fragmentation.

Minor comments.

Page 32569. ‘This is in contrast to the fully explicit chemical model that has, in principle, no adjustable parameters’. On the contrary, the flexibility of parameter adjustment is huge in the ‘fully explicit models. Whilst often sold as a ‘black box’ there is much scope for testing, for example, the importance of specific reaction pathways. Or are the authors referring to something specific such as a process level phenomena?

The point is all that the rate constants and branching ratios in an explicit chemical model are generally assigned specific values, based on structure-activity relationships, for example. The semi-explicit models generally contain parameters, the values of which are to be obtained by optimal fitting to experimental data. The sentence in question has been revised as:

“This is in contrast to the fully explicit chemical model, for which rate constants and branching ratios are generally specified a priori based on structure-activity relationships, for example.”

Page 32573. I don’t think the statement that ‘a combination of these four groups is assumed to be a sufficient surrogate for all functional groups in terms of the contribution to vapor pressure..’ is technically correct. There is a large body of work on the correlation between vapor pressure and specific functionality. If referring to very simplified predictive techniques, that don’t actually perform very well for a large subset of atmospheric organics, this should be stated. Also, please add more supporting references in this paragraph.

It is true that these four functional groups do not represent all of those present in atmospheric organic molecules. An assumption underlying the FGOM is that the combination of the four functional groups, –C=O, –OH, –OOH, and $-ONO_2$, can serve as a sufficient surrogate in terms of contribution to the vapor pressure and oxidation state for most moieties during the parent VOC photooxidation. Progressive gas-phase oxidation of VOC leads to the formation of oxygenated products that include alcohol, ketone, aldehyde, carboxylic acid, alkyl nitrate, and hydroperoxide and/or peroxyacyl nitrate functional groups (Atkinson, 2000). Additional functionalities, such as ester and ether groups, are also found, usually in smaller amounts owing to significant emissions. The moieties mentioned above (–CHO, –C=O, –OH, –C(O)OH, –OOH, $–ONO_2$, –O–) are assumed to be represented by a combination of these four functional groups (–C=O, –OH, –OOH, $–ONO_2$) in terms of contribution to vapor pressure and oxidation state: 1) Carbonyl and aldehyde share similar chemical and physical properties. The decreases of the logarithm of vapor pressure upon the addition of –CHO and –C=O are predicted by SIMPOL.1 to be 1.3196 and 0.9364, respectively. In EVAPORATION, these two functional groups have the same contribution (ΔlVP = 1.1951) to the vapor pressure decrease; 2) Carboxylic acid can be represented by the sum of –C=O and OH: Based on the prediction of SIMPOL.1, the decrease of the logarithm of vapor pressure upon the addition of one –C(O)OH group is 3.5121, which is roughly similar to the sum of ΔlVP values, 3.3114, upon the addition of one –OH (ΔlVP = 2.1834) and one –C=O (ΔlVP = 1.1280) group. The increase of oxidation state resulting from the addition of –C(O)OH or the sum of –OH and –C=O is the same, i.e. $6/n_C$. In view of this, the formation of a carboxylic group, which results from the H-atom abstraction from aldehyde, can be considered as the addition of a –OH group onto a carbonyl group; and 3) The contribution of an ether group to vapor pressure is close to that from carbonyl. Epoxides have been observed from the photooxidation of isoprene under low-NO_x conditions (Paulot et al., 2009). The contribution of the formation of an epoxide group to ΔlVP and ΔOS_C are ~ 0.7948 and $4/n_C$, respectively, compared with 1.1280 and $4/n_C$ by the addition of one –C=O group.

Other functional groups, such as –C(O)OOH and $C(O)OONO_2$, are not represented well by the four functional groups. The set of functional groups that eventually characterize the photooxidation mechanism for a certain hydrocarbon can, in principle, be expanded and updated. Considering the generalized nature of a semi-explicit model and the fact that a combination of the four functional groups can describe the functionalization channel for C_{12} alkane systems, it is unlikely that additional moieties will improve the performance of the model for the parent alkane system.

According to the reviewer's suggestions, we have rewritten this paragraph, as shown below:

"The addition of various combinations of these four groups via photochemical oxidation accounts for a majority of the gas-phase reactions involving semi-volatile product aging. This assumption is based on observations pertinent to the photooxidation of VOCs and IVOCs (alkanes, alkenes, terpenes, and aromatics). Progressive gas-phase oxidation of VOC leads to the formation of oxygenated products that include alcohol, ketone, aldehyde, carboxylic acid, alkyl nitrate, hydroperoxide and/or peroxyacyl nitrate functional groups (Atkinson, 2000). Additional functionalities, such as ether and ester groups, are also found in smaller amounts. Most of these moieties can be represented by a combination of the four surrogate functional groups with comparable chemical identities (volatility and oxidation state): 1) Carbonyl and aldehyde share similar chemical and physical properties. The decreases of the logarithm of vapor pressure upon the addition of –CHO and –C=O are predicted by SIMPOL.1 to be 1.3196 and 0.9364, respectively. In EVAPORATION, these two functional groups have the same contribution (ΔlVP = 1.1951) to the vapor pressure decrease; 2) Carboxylic acid can be represented by the sum of –C=O and OH: Based on the prediction of SIMPOL.1, the decrease of the logarithm of vapor pressure upon the addition of one –C(O)OH group is 3.5121, which is roughly similar to the sum of ΔlVP values, 3.3114, upon the addition of one –OH (ΔlVP = 2.1834) and one –C=O (ΔlVP = 1.1280) group. The increase of oxidation state resulting from the addition of –C(O)OH or the sum of –OH and –C=O is the same, i.e. $6/n_C$. In view of this, the formation of a carboxylic group, which results from the H-atom abstraction from aldehyde, can be considered as the addition of a –OH group onto a carbonyl group; and 3) The contribution of an ether group to vapor pressure is close to that from carbonyl. Epoxides have been observed from the photooxidation of isoprene under low-NO_x conditions (Paulot et al., 2009). The contribution of the formation of an epoxide group to ΔlVP and ΔOS_C are ~ 0.7948 and $4/n_C$, respectively, compared with 1.1280 and $4/n_C$ by the addition of one –C=O group. Note that the structure-property relationships used in vapor pressure prediction models are more complicated (Camredon and Aumont, 2006) and the vapor pressures of a large subset of organics in the atmosphere can not be simply represented by the four functional groups identified in this study. The functionalization channel in FGOM is a generalized predictive technique that

is intended to capture key processes. The set of functional groups in FGOM that can sufficiently characterize the progressive oxidation reactions can eventually be expanded and updated for different hydrocarbon systems."

Page 32575: What is a 'Hockey Stick' in the O:C vs C* space? Is there a figure to refer to or can I assume something L-shaped?

Two steps occur upon the fragmentation of a precursor bin in 2-D VBS. First, it is assumed that the C-C bond scission from the precursor is randomly distributed along the carbon backbone. The distribution of products in each bin over the OS_C-n_C space after the first step of fragmentation is computed in such a way that the less volatile bins to the left of the midpoint bin (nominally $C_{n/2}$) have the same O:C as the precursor bin, while the more volatile bins to the right of the midpoint bin progress diagonally towards the bin with highest O:C (i.e., $C^*=10^9$ μg/m^3, O:C = 1.0). Thus, the distribution of fragments after the first step of fragmentation appears on the OS_C-n_C space like a "Hockey stick" or "L shape". Second, half of products formed from the first-step fragmentation are assumed to be intermediates that can undergo further functionalization. As a result, a number of heavy fragments with similar C^* and O:C as their precursors are produced, filling a relatively wide area in the 2D-VBS space. One can refer to Figure S3 in Jimenez et al. (2009) or Figure S1 in Donahue et al. (2012).

Page 32576, line 20. In what way advantageous? Easy to use? Equation.2 Where has this equation come from?

Semi-explicit models, such as 2D-VBS, SOM, and FGOM, tend to represent an actual molecule using a certain combination of carbon, oxygen, and hydrogen atoms. For example, the "non-volatile" species in the FGOM are represented by [C_x, H_y, O_z], where the values of x, y, z are to be tuned from the chamber data. In this case, the linear relationship between C^* and elemental composition, developed by Donahue et al. (2011), proves to be convenient to use.

Equation. 2 is developed in this study in order to estimate the lowest carbon number for a combination of functional groups that can be considered as a semi-volatile product, as shown in Figure 3 in the ACPD version.

Page 32577. Line 27. This isn't correct, if using mole fractions the activity coefficient should be on a mole fraction scale not molality based (1 for the pure liquid). Also, please refrain from placing equations in line with the text.

This has been corrected.

Section 3. What boundaries are placed on the fitted variables?

The range of values applied to the free parameters were given in Table 2 in the ACPD version.

Page 32585, line 6. Please state and reference range for which 'AMS measurements are less reliable'.

For a typical experiment, we first sample the purified chamber air with a filter in line to measure the organic loadings by AMS for three replicates and obtain the average organic loading value as the AMS detection limit. If the organic aerosol mass growth in the chamber is below the detection limit, the reliability of that AMS measurement is suspect. For low-NO_x experiments, particle growth usually starts after about 4 hours of reaction. During this initial period, the noise to signal ratio is high and data are deemed not reliable.

References:

Atkinson, R.: Atmospheric chemistry of VOCs and NO_x, Atmos. Environ., 36, 1483-1498, 2000.

Aumont, B., Valorso, R., Mouchel-Vallon, C., Camredon, M., Lee-Taylor, J., and Madronich, S.: Modeling SOA formation from the oxidation of intermediate volatility n-alkanes, Atmos. Chem. Phys., 12, 7577-7589, 2012.

Blando, J. and Turpin, B.: Secondary organic aerosol formation in cloud and fog droplets: a literature evaluation of plausibility, Atmos. Environ., 34, 1623-1632, 2000.

Camredon, M. and Aumont, B.: Asessment of vapor pressure estimation methods for secondary organic aerosol modeling, Atmos. Environ., 40, 2105-2116, 2006.

Chhabra, P. S., Flagan, R. C., and Seinfeld, J. H.: Elemental analysis of chamber organic aerosol using an aerodyne high-resolution aerosol mass spectrometer, Atmos. Chem. Phys., 10, 4111-4131, 2010.

Donahue, N. M., Epstein, S. A., Pandis, S. N., and Robinson, A. L.: A two-dimensional volatility basis set: 1. organic-aerosol mixing thermodynamics, Atmos. Chem. Phys., 11, 3303-3318, 2011.

Donahue, N. M., Henry, K. M., Mentel, T. F., Kiendler-Scharr, A., Spindler, C., Bohn, B., Brauers, T., Dorn, H. P., Fuchs, H., Tillmann, R., Wahner, A., Saathoff, H., Naumann, K.-H., Möhler, O., Leisner, T., Müller, L., Reinning, M.-C., Hoffman, T., Salo, K., Hallquist, M., Frosch, M., Bilde, M., Tritscher, T., Barmet, P., Praplan, A. P., DeCarlo, P. F., Domenn, J., Prévôt, A. S. H., and Baltensperger, U.: Aging of biogenic secondary organic aerosol via gas-phase OH radical reactions, Proc. Natl. Acad. Sci., 109, 13503-13508, 2012.

Ervens, B., Turpin, B. J., and Weber, R. J.: Secondary organic aerosol formation in cloud droplets and aqueous particles (aqSOA): a review of laboratory, field and model studies, Atmos. Chem. Phys., 11, 11069-11102, 2011.

Gao, S., Keywood, M., Ng, N. L., Surratt, J., Varutbangkul, B., Bahreini, R., Flagan, R. C., Seinfeld, J. H.: Low-molecular-weight and oligomeric components in secondary organic aerosol form the ozonolysis of cycloalkenes and α-pinene, J. Phys. Chem. A., 108, 10147-10164, 2004a.

Gao, S., Ng, N. L., Keywood, M., Varutbangkul, V., Bahreini, R., Nenes, A., He, J. W., Yoo, K. Y., Beauchamp, J. L., Hodyss, R. P.: Particle phase acidity and oligomer formation from secondary organic aerosol, Environ. Sci. Technol., 38, 6582-6589, 2004b.

Iinuma, Y., Müller, C., Berndt, T., Böge, O., Claeys, M., Herrmann, H.: Evidence for the existence of organosulfates from β-pinene ozonolysis in ambient secondary organic aerosol., Environ. Sci. Technol., 41, 6678-6683, 2007a.

Iinuma, Y., Müller, C., Böge, O., Gnauk, T., Herrmann, H.: The formation of organic sulfate esters in the limonene ozonlysis secondary organic aerosol (SOA) under acidic conditions, Atmos. Environ., 41, 5571-5583, 2007b.

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., Rautiainen, J., 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., 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., and Worsnop, D. R.: Evolution of organic aerosols in the atmosphere, Science, 326, 1525-1529, 2009.

Lambe, A. T., Onasch, T. B., Croasdale, D. R., Wright, J. P., Martin, A. T., Franklin, J. P., Massoli, P., Kroll, J. H., Canagaratna, M. R., Brune, W. H., Worsnop, D. R., and Davidovits, P.: Transitions from functionalization to fragmentation reactions of laboratory secondary organic aerosol (SOA) generated from the OH oxidation of alkanes precursors, Environ. Sci. Technol., 46, 5430-5437, 2012.

Paulot, F., Crounse, J. D., Kjaergaard, G., Andreas, K. Clair, J. M. S., Seinfeld, J. H., and Wennberg, P. O.: Unexpected epoxide formation in the gas-phase photooxidation of isoprene, Nature, 325, 730-733, 2009.

Surratt, J. D., Murphy, S. M., Kroll, J. H., Ng, N. L., Hilderbrandt, L., Sorroshian, 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.

Surratt, J. D., Kroll, J. H., Kleindienst, T. E., Edney, E. O., Claeys, M., Sorooshian, A., Ng, N. L., Offenberg, J. H., Lewandowski, M., Jaoui, M., Flagan, R. C., and Seinfeld, J. H.: Evidence for organosulfates in secondary organic aerosol, Environ. Sci. Technol., 41, 517-527, 2007a.

Surratt, J. D., Lewandowski, M., Offenberg, J. H., Jaoui, M., Kleindienst, T. E., Edney, E. O., and Seinfeld, J. H.: Effect of acidity on secondary organic aerosol formation from isoprene, Environ. Sci. Technol., 41, 5363–5369, 2007b.

Szmigielski, R., Surratt, J. D., Vermeylen, R., Szmigielska, K., Kroll, J. H., Ng, N. L., Murphy, S. M., Sorooshian, A., Seinfeld, J. H., and Claeys, M.: Characterization of 2-methylglyceric acid oligomers in secondary organic aerosol formed from the photooxidation of isoprene using trimethylsilylation and gas chromatography/ion trap mass spectrometry, J. Mass Spectrom., 42, 101–116, 2007.

Yasmeen, F. Sauret, N., Gal, J. –F., Maria, P. –C., Massi, L., Maenhaut, W., and Claeys, M.: Characterization of oligomers from methylglyoxal under dark conditions: a pathway to produce secondary organic aerosol through cloud processing during nighttime, Atmos. Chem. Phys., 10, 3803-3812, 2010.

Ziemann, P. J. and Atkinson, R.: Kinetics, products, and mechanisms of secondary organic aerosol formation, Chem. Soc. Rev., 41, 6582-6605, 2012.

Zuend, A., Marcolli, C., Peter, T., and Seinfeld, J. H.: Computation of liquid-liquid equilibria and phase stabilities: implications for RH-dependent gas/particle partitioning of organic-inorganic aerosols, Atmos. Chem. Phys., 10, 7795-7820, 2010.

Zuend, A. and Seinfeld, J. H.: Modeling the gas-particle partitioning of secondary organic aerosol: the importance of liquid-liquid phase separation, Atmos. Chem. Phys., 12, 3857-3882, 2012.