Responses to the Comments of Referee 1

(1) This paper describes the simulation of ground-based and vertical profile measurements of organic aerosol mass loading and O:C ratio during the PEGASOS campaign. The multiple simulations use a variety of different parameterizations of functionalization and fragmentation, different for anthropogenic and biogenic SOA, and also vary assumed vaporization enthalpy. The offsetting nature of functionalization, fragmentation, and vaporization enthalpy result in no unique simulation scheme having clearly superior prediction skill metrics.
We have done our best to address the various suggestions and comments of the referee. Our responses follow the corresponding comments of the referee (in italics) below.

General comments:
(2) In the introduction, you describe the Murphy et al modeling studies and point out that they found the simplest approach to parameterization (for anthro compound aging) did better than the more complex formulation (lines 72-75). It seems like this is your conclusion, too, based on your figures focusing on your simplest 1-bin parameterization. But, I didn't see that stated clearly as the conclusion. I suggest to explain somewhere why you focused on that 1-bin model for the figures, and if you conclude it was the best, make that clearer. In the end I came away feeling that no parameterization was necessarily superior but then was confused by your focus on the one in the figures. (Also in that discussion of Murphy 2011 and 2012: I would have found it easier to make the comparison between parameterizations if you included some metrics from each model on average volatility reduction and O addition at each step.)
Murphy et al. tried a few parameterizations without try to select optimum parameters (e.g., the fragmentation probability) and concluded that the simplest approach performed better. In this study, the different parameterizations with fitted parameters perform a lot better and their performance is quite close to that of the simple parameterization. The performance metrics shown in Table 2 and 3 indicate that different parameterizations perform better than the others depending on the metric. For example, the detailed functionalization scheme (DET with b=0.3) has the lowest mean square error for OA mass concentration, while the 2-bin shift with bSOA aging an b=0.4 scheme has the lowest fractional bias for O:C. Given that the performance of the seven best performing parameterizations is quite close to each other and that this is based on just one measurement set, we do not think that it makes sense to try to declare a winner. So, we agree that no parameterization (from the seven best) is superior. We have added the above discussion in the paper.

We had to choose one set of simulations based on one of the parameterizations to illustrate the results of the model. Figures 2-4 were quite messy with the results of all 11 or even 7 parameterizations. We have chosen the results of the simple scheme because they are discussed first in the paper. To avoid confusion, we clarify in the revised paper that this is just an example and the results of the other six best performing parameterizations are quite similar to those shown.

(3a) The discussion of temperature dependence / enthalpy of vaporization confused me. In the introduction (lines 97-103), can you comment a bit on the stark difference between the Sheehan & Bowman and Murphy results you report? Because you also find a surprising result, it would be useful to understand what is known about why this has not been found to have consistent results in past studies.

The main difference is the chemical aging process. Sheehan and Bowman (2001) focused on the first generation of SOA production. They found (as expected) that temperature affected significantly the partitioning of the mostly semivolatile SOA components and therefore the predicted SOA concentration was quite sensitive to the assumed enthalpy of evaporation. Murphy et al. (2011) simulated both the first and later generation of reactions in the system. The inclusion of the chemical aging processes reduced dramatically the sensitivity of the predicted SOA concentration to the enthalpy of evaporation. This explanation has now been added to the introduction.

(3b) Related, around lines 431-434: I don't understand your result. Why would aging mechanism change in response to deltaHvap? Or is this just that your optimization will adjust fragmentation correspondingly? This discussion could be clearer.
The aging mechanism did not change (the fragmentation probability is fixed in these tests), the amount of SOA produced from these later generation reactions did. When a high evaporation enthalpy was used, the first generation SOA evaporated more at high temperatures and its concentration was reduced. However, now there were more semivolatile vapors available for the aging reactions with the OH. So, these reactions produced more later-generation SOA. The reduction of first generation SOA (due to evaporation) was offset by the higher SOA from the chemical aging reactions, so the total SOA did not change much. The opposite happened when a lower enthalpy was used. This interplay between the two processes (first generation production/partitioning and chemical aging) resulted in a small sensitivity of the predicted SOA to the enthalpy of evaporation. We have added the above explanation to Section 3.6.

(3c) And, lines 472-484: these conclusions could use more discussion. Why is the low sensitivity surprising? Is this result mainly a function of not having explored a wide enough temperature range because of the season? If so, could say this at the end: e.g., "wintertime predictions would explore a larger range of temperature and thus better constrain delHvap."
The low sensitivity is surprising because all the SOA models rely on the partitioning of the semivolatile organic vapors between the gas and particulate phases. In any simulation of the atmosphere, this process is very sensitive to the evaporation enthalpy and changing temperature. The fact that in the SOA model used in this work, there is a quite different process (chemical aging) that cancels to a large extent this sensitivity is unexpected. This is now clarified in the paper.

The suggestion of the referee about exploring the sensitivity of the model to the enthalpy of evaporation during winter is quite interesting. This interplay should still be present, but the chemical aging should be slower. We will try to explore this suggestion in future work.

(4) I also had some confusion about the exact use of the back-trajectories. On line 115, are you simulating along the clustered average back-trajectory, or each one? Perhaps a bit more additional explanation of how the CTM incorporates the back-trajectories would be helpful. At line 142, I suggest to begin this paragraph with stating that these are 72-hour back trajectories (you mention this much later), and clarify that the ground site is the trajectory receptor – the list of times at the beginning was confusing. At line 161: "receptor site around Po Valley"-does this refer to the Zeppelin flights? Were 72-hr back-trajectories run for a series of points along the flight trajectory too? Or did you only use zeppelin measurement above the ground site and thus use the same back trajectories? At the end of this paragraph, maybe segue to the next section with a brief reacp of

how they are fed into the chemistry schemes. (If you discuss this more above it may not be necessary to do much here).
We have followed the reviewer's suggestion and added information about the calculation and use of the back-trajectories. We are simulating along the clustered average back-trajectory in this work and not along each one of the individual trajectories. We now clarify in the beginning of the paragraph that these are 72-hr back trajectories with the ground site as their end point. The Zeppelin trajectories were based on the actual Zeppelin position every hour, so that we could use all the measurements from all the flights. We have added a couple of sentences in the end of this paragraph explaining that the trajectories are used to select the corresponding emissions from the emissions inventory files and also the meteorological parameters (temperature, humidity, rain, etc.) from the meteorological input schemes.

(5) Around lines 178-182: What is the reasoning for using different aging rate constants for some classes of OA and not others? Explain choices.
We now explain in the revised paper that these choices of different rate constants by Murphy et al. (2011) were based on the average size of the corresponding organic compounds, with higher values for bigger organic molecules.

(6) Around line 208-209: Why would aging of bSOA result in negligible change in volatility and an increase in O:C? And around line 215: why would bSOA be different than other OA aging?
Please note that the fundamentals of the aging scheme are the same for all compounds: it is assumed that homogeneous reactions with OH radicals are the main chemical aging pathway. The effect of these reactions on the volatility distribution of the secondary compounds is allowed to be different between biogenic and anthropogenic SOA components. This is due to the available findings that suggest that there is significant second and later generation production of SOA from anthropogenic precursors (e.g., Hildebrandt-Ruiz et al., 2015), while the corresponding later production of SOA from biogenic precursors may be a lot smaller (Ng et al., 2006; Szidat et al., 2006; Tritscher et al., 2011; Gilardoni et al., 2011; Yttri et al., 2011; Zhao et al., 2015). As a result, we have treated the chemical aging of anthropogenic and biogenic compounds independently following previous modeling efforts (Murphy and Pandis, 2009; 2010; Murphy et al., 2012). This independent treatment allowed us to explore better the effect of the various assumptions used in the various chemical aging schemes. We have added some additional information about this issue in the Introduction and we have added as well more information in the Section 2.2.2 describing the bSOA aging parameterizations. A similar comment was made by the second reviewer (see Comment 3).

(7) Fragmentation parameterization, around lines 223-224 and following section: Were fragmentation probabilities simulated separately per time step or at all times, or at endpoint, or at "average" timestep? Why would b not be dependent on O:C? At line 233: what is Figure C.4?
In all tests described in this work a constant fragmentation probability was assumed during the full corresponding simulation. In principle this probability should depend on O:C. However, the fact that the model could reproduce the observations with a fixed value, discouraged us from using a more complicated parameterization in which the *b* would be a function of O:C introducing more free parameters in the scheme. Clearly, this fragmentation probability should be better constrained in all similar schemes. These points are clarified in the revised paper. We have corrected the typo and Figure C.4 is now Figure S5.

(8) Lines 243-253: Aren't these skill metrics pretty standard definitions? Is it necessary to include the equations in the body text, or could they be in the supplemental info, or referenced?
We have moved the definition of the metrics to the Supplementary Information.

(9) On the binning of model results (lines 269-270): why 4 hours? Did you try single hours and how did it look? If 4 hours is all that works from the model perspective, why not bin your data onto the same time base as the model output that you are comparing too? It looks awkward to have the difference. The wording also made me wonder if you binned over the same hour of the day on multiple days – clarify how you did the averaging, how many days averaged, etc.
The use of 4 hr long time bins was a compromise between keeping the computational cost of the hundreds of simulations performed and maintaining most of the variability of OA and O:C. We tried the single hour simulations for selected schemes and the differences were marginal. We did bin the measurements in exactly the same time base as the model output. This is now clarified in the paper and the comparisons to avoid confusion. Please note that the diurnal averages are shown for illustrative purposes in Figures 2 and 4. We have added additional text to explain our choice of the number of trajectories per day and the corresponding model evaluation.

(10) A big question I have about the observations is why the error bar suddenly changes above 700 m (the top 3 points in the vertical profiles), and there is a striking discontinuity in the data at those points as well. This needs to be addressed in the text (around lines 279-287, caption for Fig. 3) – what could explain this unusual behavior? You mention it is a single flight – how many flights do the other points represent? How were the locations different? Are those points truly better known (as suggested visually by the smaller error bars) or were the others just spatially or temporally more diverse? If the latter, maybe rethink how you determine your error bars, or how you portray the different points to show this. One thought: Are the top 3 points at lower temperature? Although, this would suggest a stronger delHvap sensitivity …
The measurements below 700 m represent averages from all flights. Given that these took place during several different days they have a higher variability. The three data points above 700 m are from a single flight (June 20). The measurements suggest that there was a layer with higher OA levels at these altitudes during that day that cannot be explained by the model. It is difficult to draw any reliable conclusions from such an event without additional information. We have added some additional explanation about these three data points in the corresponding section.

(11) Around line 314: It doesn't make sense to me that aggressive functionalization would underpredict O:C – would it oxidize faster?
This is one more relatively counterintuitive result due to the interplay of different processes. The aggressive reduction of the volatility of the organic compounds in this parameterization moves them rapidly to the particulate phase where they cannot be oxidized further (at least in this modeling scheme). So the scheme moves the compounds to the left of the 2D-VBS but with a small slope, so the final predicted O:C is low and actually lower than observed. This additional discussion has been added to the paper.

(12) Around lines 347-354: The range in b's you find optimized for the various parameterizations is enormous – it seems to just be a correction factor you can use to tune your model. Can you contextualize what would be a reasonable value for b, e.g. by citing some experimental results that

might help one choose? Same questions generically at the end of section 3.5 (line 412) about bSOA parameterizations – these also span a huge range. How could we decide which assumptions are more reasonable? If no data exists to constrain this, might you suggest some experiments that should be done?
We do agree that the resulting range for the "optimal" average fragmentation probability (0.1 to 0.7) is large and the model appears to use it as a correction factor to reduce the SOA produced by the most aggressive schemes. However, both the low and high values of this range are reasonable for lightly and highly substituted organic compounds (Donahue et al., 2012). There have been a number of studies that have tried to constrain this process for selected systems like squalene particles (Kroll et al., 2009) and a series of alkanes, ketones, aldehydes and acids (Chacon-Madrid et al., 2010; Chacon-Madrid and Donahue, 2011). While these studies have provided useful insights we are far from constraining this parameter. Additional emphasis on the production of volatile organic compounds (including small organic molecules) during the aging process will clearly help. These issues related to the fragmentation probability are discussed in a new paragraph in the paper.

(13) On line 456, you refer to "more than a hundred" tested aging schemes, but your tables have a much smaller number. Do you mean the multiple tested b values in each scheme?
This is correct. We count the different values of the fragmentation probability as a different scheme because additional simulations need to be performed for each value before we can arrive at the optimum b. A brief explanation has been added.

Specific comments / technical suggestions:

(14) Line 26: define SOA (first instance)
The definition has been added.

(15) Line 28: "contribute around 5%"
The typo was corrected.

(16) Line 29: define HOA, define (& explain) PMF-AMS
Done.

(17) Line 32: "intricate interplay" is unclear, replace with something more descriptive?
We have added a new paragraph to deal with this issue and added a brief explanation at this point.

(18) Line 37: perhaps you meant to cite the IPCC 2013 WG1 report?
The reference has been corrected.

(19) Line 68: "(PMCAMx-Trj) as the" (this is one of several places where I think a comma should be removed or added)
Corrected.

(20) Line 75: "chemical aging assumed"
Corrected.

(21) Line 82: “(2012), formation”
Corrected.

(22) Line 98: “Bowman (2001) concluded”
Corrected.

(23) Line 99: are you refering to SOA mass yields increase? Or mass concentrations?
This refers to an increase in SOA mass concentrations.

(24) Line 106: “The Po Valley”
Corrected.

(25) Line 108: “evaluated by comparing the resulting 2D-VBS”
Corrected.

(26) Line 115: “2011; 2012) simulating the”
Corrected.

(27) Line 118-119:”aerosols, vertical turbulent dispersion, and area and”
Corrected.

(28) Line 132: “from terrestrial ecosystems”
Corrected.

(29) Line 133: “emissions, and wildfire emissions are included following Sofiev et al. (2008a,b).”
Corrected.

(30) Line 267: “ground level is”
Corrected.

(31) Line 270: “concentrations of 4 hours instead of”? I think this is what you mean? But not clear why you chose 4 hours. See general comment above.
We have rewritten this. The choice of 4 hours is explained in our response to Comment 9 above.

(32) Line 278: “measurement in Figure 3a … predictions agree with”
Corrected.

(33) Line 299: “error for altitudes”
Corrected.

(34) Line 311: “scheme underpredicted the”
Corrected.

(35) Line 313: “; 2012) about the”
Corrected.

(36) Line 461-462: “with similar average”
Corrected.

(37) Line 464: “evaporation of primary OA and subsequent”
Corrected.

(38) Lines 479-480: “small temperature differences for altitudes up to 600 m … this low sensitivity to … evidence that the higher values (150 kJ mol-1) are”
Corrected.

(39) Fig 1: In caption, mention that these are 20 72-hour trajectories. On maps: can you make the map boundaries the same in both panels?
We have added the suggested text. Unfortunately, it is not easy to make the map boundaries the same.

(40) Fig. 2: As mentioned above, it feels strange to me that the binning is different for model and measurements – consider unifying? Maybe state in caption how many days of coverage this is to help contextualize the variability / error bars. And, could interrupt / truncate the y axis to miss all the white space up 0 – 0.4 and see the variation better.
We prefer to keep the hourly resolution for the measurements because this provides an idea of the variability that the model is missing by using 4-hr bins. We do explain this difference in the new figure caption together with the number of days that have been averaged. The range used for the y-axis reflects the reasonable range for O:C of ambient aerosol.

(41) Fig. 3: As mentioned, say something about the weird discontinuity at the top. Mention in caption how many measurements are averaged at each height (or find a way to show this with symbology in the figure).
We have added the corresponding information in the figure caption.

(42) Fig 2-4: somewhere, explain why you picked the 1-bin case for all comparisons.
We mention now that this is shown as an example.

(43) Fig 6 caption: “Diurnally averaged (a)”
Corrected.

Responses to the Comments of Referee #2

(1) Summary/recommendation: This paper seeks to model total OA concentrations and O:C ratios from ground and airborne measurements from the PEGASOS field campaign. A number of chemical aging schemes were used, and although several schemes performed well, no one chemical aging scheme yielded superior model-measurement fits. This is a well-conducted study and I recommend that this paper be in published in ACP but with revisions, as discussed below.
We do appreciate the constructive comments and suggestions of the referee. We have done our best to address them and revise the paper accordingly. Our responses follow the comments of the referee (in italics) below.

General Comments:

(2) Pg 3 lines 65-67: is this paper also using all those classifications of OA? Not clear from the "Lagrangian CTM description section". How do you distinguish SOA-sv and SOA-iv from and/or between aSOA-v and bSOA? In general, this work assumes a knowledge of the Murphy et al. 2011 and 2012 papers and model that the modelling work was built upon. As a reviewer not familiar with the model used in this work, it was difficult to follow some of the more complicated nuances of how the model treats different OA types. I suggest that more details about the model be added to assist the reader.
Yes, we use the classification proposed by Murphy et al. (2011) to address the complexity of components of OA. The following five OA components are resolved: (1) aSOA is OA formed from the oxidation of anthropogenic VOCs (aromatics, alkenes, and alkanes); (2) bSOA is OA formed from the oxidation of biogenic VOCs (isoprene, monoterpenes and sesquiterpenes); (3) POA is fresh emitted OA which may evaporate and recondense during its atmospheric lifetime, but once it reacts with OH it becomes secondary OA; (4) SOA-sv which is SOA formed from the oxidation of semivolatile organic compounds, that is POA that has evaporated and reacted and (5) SOA-iv that is SOA formed during the oxidation of intermediate volatility organic compounds. We have followed the suggestion of the reviewer and added more information about the OA simulated OA components and their simulation in the revised manuscript.

(3) Sec 2.2.2: Need to give clear justification as to why there are two aging schemes of bSOA, and not any other type of SOA. These details need to be included.
Please note that the fundamentals of the aging scheme are the same for all compounds: it is assumed that homogeneous reactions with OH radicals are the main chemical aging pathway. The effect of these reactions on the volatility distribution of the secondary compounds is allowed to be different between biogenic and anthropogenic SOA components. This is due to the available findings that suggest that there is significant second and later generation production of SOA from anthropogenic precursors (e.g., Hildebrandt-Ruiz et al., 2015), while the corresponding later production of SOA from biogenic precursors may be a lot smaller (Ng et al., 2006; Szidat et al., 2006; Tritscher et al., 2011; Gilardoni et al., 2011; Yttri et al., 2011; Zhao et al., 2015). As a result, we have treated the chemical aging of anthropogenic and biogenic compounds independently following previous modeling efforts (Murphy and Pandis, 2009; 2010; Murphy et al., 2012). This independent treatment allowed us to explore better the effect of the various assumptions used in the various chemical aging schemes. We have added some additional information about this issue

in the Introduction and we have added as well more information in the Section 2.2.2 describing the bSOA aging parameterizations.

(4) Pg 6, simple scheme description: were any sensitivity studies done on the rate constants used for reactions with OH? A comment should be included about this assumption.
Murphy et al. (2011) have investigated the sensitivity of the results of the 2D-VBS scheme to a number of assumptions in the framework including the assumed rate constants with OH. The sensitivity of the results was small to moderate. We have added a reference to that work in the end of Section 2.2.1.

(5) Pg 10, Lines 299-300: There could be a brief discussion here of the potential problems of basing best-fit model conclusions on just one flight.
Please note that the conclusions for altitudes lower than 700 m here are based on the measurements of all seven flights. We have clarified this point. Only the three data points for the higher altitudes are based on one flight. Potential problems with the use of data from just one flight include the existence of a pollution layer aloft that day that was not captured by the model or some other relatively rare event that took place at that time. We have added a brief discussion about this in the manuscript.

(6) Sec 3.4 How valid is it to tune fragmentation to the measurements with just 7 cases?
Obviously the validity of this scheme that was tuned to the measurements in a specific area and period will need to be tested in future work. For the time being, this can be viewed as a parameter fitting exercise to prove that there are multiple sets of 2D-VBS parameters that can result in predictions consistent with the measurements. This is now discussed in the end of the paper.

(7) It's confusing in general how many cases were used and how the averaging was done with the model and measurements, especially between ground based and zeppelin measurements, since many of these didn't match in time/date. This should be made clear throughout the manuscript.
Regarding the specifics of the optimization, the fragmentation probability was varied from 0 to 1 for all cases examined. Examples are shown in Figure S5 in the Supplementary Information. The optimum value was selected minimizing the error for the predicted OA mass concentration. Please note that all model predictions discussed in the paper were matched in time with the measurements (either ground or aloft). The details of the fitting are discussed in more detail in the revised manuscript.

(8) It would be good to include a brief discussion of uncertainty related to model emission inventories, if any details of this are known (e.g. other model-measurement validation studies).
This is always a tricky issue. We have performed detailed evaluation of the three-dimensional chemical transport model PMCAMx using the same pan-European emissions inventory for other periods, stations, and chemical species (Fountoukis et al., 2011). However, especially for organic aerosol, it is difficult to determine if discrepancies between measurements and model predictions are due to the emissions, the chemical transport model itself or the meteorological inputs. Even worse, assessment of the uncertainties of highly resolved (in space and time) emission inventories is non-trivial. We have added citations to the evaluation of the 3D PMCAMx in the same domain using the same inventory.

(9) Ultimately, aging schemes are tuned to fit the measurements and 7 different aging schemes are found to well-reproduce the measurements. However, this paper did not provide any or enough discussion about measurement uncertainty, number of measurements, or the other uncertainties I brought up above (emissions, rate constants) to allow the reader to firmly conclude anything about the validity or transferability of these tuned best-fit schemes.

The uncertainties of the AMS measurements used in this study are the typical AMS measurement uncertainty due to a large part to the estimated collection efficiency (for absolute concentrations) and the fragmentation table for the O:C. We have added citations to papers discussing these AMS uncertainties. We have added also information about the number of measurements performed and used in the model evaluation. We agree that the degree of transferability of the schemes that worked well in this study will need to be determined in future applications using them in other areas and periods and we now clarify this in the Conclusions section in the end of the paper.

(10) I feel that it would be of interest to the community to provide a brief discussion about the pros/cons of the different aging parameterizations used in this study. E.g. the simple functionalization scheme could be implemented into a more computationally intense model (e.g. a global CTM) but potential could have biases from leaving out Y; the detailed functionalization scheme provides X extra information but is likely unrealistic in Z, and so forth.

We have followed the suggestion of the referee and added some discussion of the positive and negative computations features of the different parameterizations. For example, the simple parameterization scheme has the advantage that it can also be implemented in the 1D-VBS reducing a lot the computational cost. In that case, the predictions of OA mass concentrations and the volatility distributions remain the same, but one loses the ability to predict the O:C. The other schemes can be simplified for the 1D-VBS without introductions of errors.

Figures/Tables:

(11) Figure 5: is the average OA from the ground measurements or does it include the Zeppelin measurements? Caption and text should state this clearly.

This is the average OA from the ground measurements. We added the missing information in the caption.

(12) Figure S3: it would be helpful to each SOA type (ASOA-v, bSOA, etc) and the case types redefined either in the caption or in a brief section before the figures redefining both the SOA types and the case types. The case types are defined nicely in Figure S5 but that doesn't help out Figure S3.

We added the information about the seven aging cases under the caption of Figure S3 and more information redefining the OA types in the corresponding sections.

Technical comments

(13) Line 233: what is Figure C.4?

This was a typo. We changed Figure C.4 to Figure S5 in Section 2.3.

(14) Line 272: no comma after "predictions"

Corrected.

(15) Line 311: no comma after “scheme”
Corrected.

(16) Line 400: finish parenthesis
Done.

Simulation of Atmospheric Organic Aerosol using its Volatility-Oxygen Content Distribution during the PEGASOS 2012 campaign

Eleni Karnezi[a], Benjamin N. Murphy[b], Laurent Poulain[c], Hartmut Herrmann[c], Alfred Wiedensohler[c], Florian Rubach[c,d,e], Astrid Kiendler-Scharr[d], Thomas F. Mentel[d] and Spyros N. Pandis[a,f,g*]

[a] *Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, USA*

[b] *National Exposure Research Laboratory, United States Environmental Protection Agency, Research Triangle Park, North Carolina, USA*

[c] *Leibniz Institute for Tropospheric Research, Permoserstr 15, 04318 Leipzig, Germany*

[d] *Institut fur Chemie und Dynamik der Geosphare, ICG, Forschungszentrum Julich, Julich, Germany*

[e] *Max Planck Institute for Chemistry, 55128 Mainz, Germany*

[f] *Department of Chemical Engineering, University of Patras, Patra, Greece*

[g] *Inst. of Chemical Engineering Sciences, FORTH/ ICEHT, Patra, Greece*

Abstract

A lot of effort has been made to understand and constrain the atmospheric aging of the organic aerosol (OA). Different parameterizations of the organic aerosol formation and evolution in the two-dimensional Volatility Basis Set (2D-VBS) framework are evaluated using ground and airborne measurements collected in the 2012 Pan-European Gas AeroSOls-climate-interaction Study (PEGASOS) field campaign in the Po Valley (Italy). A number of chemical aging schemes are examined, taking into account various functionalization and fragmentation pathways for biogenic and anthropogenic OA components. Model predictions and measurements, both at the ground and aloft, indicate a relatively oxidized OA with little average diurnal variation. Total OA concentration and O:C ratios ~~were~~are reproduced within experimental error by a number of chemical aging schemes. Anthropogenic secondary OA (SOA) is predicted to contribute 15-25% of the total OA, while SOA from intermediate volatility compounds oxidation another 20-35%. Biogenic SOA contributions varied from 15 to 45% depending on the modeling scheme. Primary OA ~~contributed to~~contributed around 5% for all schemes and was comparable to the hydrocarbon like OA (HOA) concentrations ~~of~~derived from the Positive Matrix Factorization of~~from~~ the Aerosol Mass Spectrometer (PMF-AMS) ground measurements. The average OA and O:C diurnal

variation and their vertical profiles showed a surprisingly modest sensitivity to the assumed vaporization enthalpy for all aging schemes. This can be explained by the ~~intricate~~ interplay between the ~~changes in~~~~processes of~~ partitioning of the semi-volatile compounds and their gas-phase chemical aging reactions.

1. Introduction

Atmospheric aerosol plays an important role in the Earth's energy balance by absorbing and scattering solar radiation (direct effect) and influencing the properties and lifetime of clouds (indirect effects) (IPCC, ~~2014~~2013). At the same time, certain particles may have significant negative effects on human health, including premature death, increases in respiratory illnesses and cardiopulmonary mortality (Pope et al., 2009; Caiazzo et al., 2013).

Aerosol particles contain a wide variety of inorganic and organic compounds, with organics representing about 50% of the fine (< 1 μm) aerosol particle mass concentration, on average (Zhang et al., 2007). OA originates from many different natural and anthropogenic sources and processes. It can be emitted directly from fossil fuel and biomass combustion (so-called primary organic aerosol, POA) or can be formed by the atmospheric oxidation of organic vapors (secondary organic aerosol, SOA). The oxidation pathways of organic compounds are complex and the corresponding reactions lead to hundreds or even thousands of mostly unknown oxygenated products. As a result, our understanding of OA formation mechanisms and its chemical and physical properties remains incomplete.

The use of lumped species is a computationally efficient approach for the representation of OA in atmospheric chemical transport models (Pandis et al., 1992). The volatility basis set framework (VBS, Donahue et al., 2006) lumps these compounds into surrogates along an axis of volatility. This approach typically employs species with effective saturation concentrations at 298 K separated by one order of magnitude, with values ranging from, say, 0.01 to 10^6 μg m^{-3}. By quantifying the volatility distributions of primary and secondary OA, a physically reasonable, yet suitable for large-scale chemical transport models (CTMs), description of semi-volatile organics can be obtained (Lane et al., 2008).

The VBS framework was extended by Donahue et al. (2011; 2012a) adding another dimension, the oxygen content (expressed as the ratio of oxygen to carbon atoms; O:C), for the description of the OA chemical aging reactions. In the first application of this framework in a

CTM, Murphy et al. (2011) used 12 logarithmically spaced volatility bins (effective saturation concentration C^* varying from 10^{-5} to 10^6 μg m^{-3} at 298 K) and 13 bins of O:C (from 0 to 1.2 with a step of 0.1). In this way, 156 surrogate species were included in the model for each OA type. Five organic aerosol types were simulated separately: anthropogenic secondary organic aerosol (aSOA-v) produced during the oxidation of anthropogenic VOCs~~,~~ (aromatics, alkenes and alkanes), biogenic secondary organic aerosol (bSOA) formed by the~~from~~ oxidation ~~products~~ of biogenic VOCs (isoprene, monoterpenes and sesquiterpenes), fresh primary organic aerosol (POA~~),~~) ~~is fresh emitted OA~~ which may evaporate and recondense during its atmospheric lifetime, but once it reacts with OH it becomes secondary OA, secondary organic aerosol (SOA-sv) from the oxidation of semivolatile ~~OA (SOA-sv)~~organic compounds, that is primary ~~P~~OA that has evaporated and reacted and SOA from the oxidation of intermediate volatility compounds (SOA-iv) ~~as analytically described in Murphy et al.~~ (2014).~~(2014)~~ with saturation concentrations larger than 1000 μg m^{-3}. Details about this terminology can be found in Murphy et al. (2014).

Murphy et al. (2011; 2012) used a one-dimensional Lagrangian CTM (PMCAMx-Trj~~),~~) as the host model for the simulations. PMCAMx-Trj simulates the chemical evolution of a column of air as it travels towards a user-selected receptor site. Three alternative parameterizations of the OA formation and chemical aging were evaluated using measurements of O:C and OA in three European sites (Murphy et al., 2011; 2012). The simplest approach parameterizing the chemical aging of anthropogenic compounds, assuming a net reduction of volatility by one bin during every aging reaction step accompanied by an increase of one or two oxygen atoms with an equal probability was the most successful. A more complex formulation of the chemical aging~~,~~ assumed that functionalization was the only process taking place, and overpredicted the OA concentration while it underpredicted O:C in most cases. Adding fragmentation reactions together with the functionalization gave promising results, but it was clear that the various parameters of the scheme were not well constrained leading to large uncertainties in the simulation results, especially during summertime. Murphy et al. (2012) concluded that the 2D-VBS scheme that was used needs additional testing before it is ready for application in three-dimensional CTMs.

There is significant second and later generation production of SOA from anthropogenic precursors (Hildebrandt-Ruiz et al., 2015) while the corresponding later production of SOA from biogenic precursors may be a ~~lot~~ smaller (Ng et al., 2006; Tritscher et al., 2011; Szidat et al., 2006; Gilardoni et al., 2011; Yttri et al., 2011; Zhao et al., 2015). In Murphy and Pandis (2009; 2010) and Murphy et al. (2012~~)~~), formation of significant bSOA during second and later generation aging reactions led to overestimation of OA concentration at both urban and rural sites. However, the first generation products of the oxidation of biogenic VOCs do continue to react in the atmosphere. ~~(Ng et al., 2006; Tritscher et al., 2011; Zhao et al., 2015; Szidat et al., 2006; Gilardoni et al., 2011; Yttri et al., 2011)).~~ The net effect on ambient bSOA levels of these chemical aging reactions remains uncertain.

Fragmentation of organic compounds during chemical aging is an important reaction pathway (Chacon-Madrid and Donahue, 2011; Murphy et al., 2011; Hermansson et al., 2014). During fragmentation reactions carbon bonds break, resulting in smaller compounds, which are more volatile than their precursors. A fragmentation probability, depending on O:C, has been used in the 2D-VBS framework (Donahue et al. 2011; 2012). A fragmentation probability, ranging from 0-0.4, has been used in the statistical oxidation model (SOM) that uses the carbon (C) and oxygen (O) atoms per compound as the independent variables (Cappa and Wilson, 2012). While the fragmentation pathways are clearly important for the OA levels, their parameterizations in existing models remain quite uncertain (Murphy et al., 2012).

The effect of temperature on the partitioning of OA components between the gas and particulate phases represents another source of uncertainty. Sheehan and Bowman (2001), focusing on the first generation of SOA production, concluded that a 10 ^{o}C decrease in temperature can result in an increase of SOA by as much as 150% depending on the assumed vaporization enthalpy. This effect can theoretically lead to significant OA vertical gradients. ~~Applying~~Simulating both the first and later generation of reactions in the system while applying the 2D-VBS to FAME-08 in Finokalia, Greece, Murphy et al. (2011) reported low sensitivity of the OA concentration and O:C ratio measurements to the assumed vaporization enthalpy, with higher values leading to slightly lower O:C.

In this study, we evaluate different chemical aging mechanisms in the 2D-VBS approach focusing on the Po Valley in Italy. Extensive measurements were performed both at the ground and aloft from June 6 until July 8, 2012. The Po Valley has major air quality problems due to both industrial and agricultural sources. A number of alternative chemical aging mechanisms are evaluated by comparing the resulting 2D-VBS predictions against the PEGASOS measurements. The role of bSOA chemical aging is explored. Finally, the sensitivity of the model to the assumed effective vaporization enthalpy is quantified in an effort to constrain this uncertain variable using the measurements aloft.

2. Lagrangian CTM Description

A one–dimensional Lagrangian chemical transport model (PMCAMx-Trj) (Murphy et al., 2011; 2012~~),~~) simulating the air parcels that arrive at the desired receptor location, is used as the host for the 2D-VBS module. The model solves the general dynamic equation taking into account the following relevant atmospheric processes: atmospheric transport, gas and aqueous phase chemistry, dry and wet deposition of gases and aerosols ~~and~~, vertical turbulent dispersion ~~together with~~, and area and point emissions. Ten computational cells are used to cover heights up to 3 km. The lowest cell has a height of 60 m. The SAPRC ~~-99 (Carter, 2000)~~ chemical mechanism is used for the simulation of gas–phase chemistry. ~~The same five sources described earlier in Murphy et al. (2011) are used in this study.~~ The meteorological parameters (horizontal winds, temperature, pressure, vertical dispersion coefficients, water vapor, clouds, rainfall and land use) used as inputs in the model are provided by the Weather Research and Forecasting (WRF) model. The WRF simulation was periodically re-initialized (every 3 days) to ensure the accuracy of the inputs to the CTM. Area and point emissions, both anthropogenic and biogenic, were also provided as hourly inputs for the European domain. The Global and regional Earth-system Monitoring using Satellite and in-situ data (GEMS) dataset (Visschedijk et al., 2007) is used for the emissions of anthropogenic gases. Anthropogenic emissions of organic and elemental carbon are based on the Pan-European Carbonaceous Aerosol Inventory developed during EUCAARI (Kulmala et al., 2009). Biogenic gridded emissions are produced from the combination of three different models. The Model of Emissions of Gases and Aerosols from Nature (MEGAN) provides the emissions from terrestrial ecosystems (Guenther et al., 2006) and the O'Dowd et al. (2008) model provides the marine aerosol emissions~~. Finally,~~, and wildfire emissions are ~~also~~ included ~~(~~following Sofiev et al~~.,~~. (2008a, b). Details of the emission inventory used for Europe can be found in Fountoukis et al. (2011). In order to implement these emissions in our 2D-VBS model, we used the same volatility distribution of the emissions as in the original work (Fountoukis et al., 2011) and used the Murphy et al. (2012) methodology for mapping these to the 2D-VBS. Vertically resolved initial conditions and the top boundary conditions for PMCAMx-Trj were obtained from the corresponding output of the PMCAMx regional scale three-dimensional simulation for the same period.

2.1 Simulated periods

The Hybrid Single Particle Lagrangian Integrated Trajectory HYSPLIT model (Draxler et al., 2009) was used to calculate 72 h back trajectories arriving at the ground site of San Pietro Capofiume~~ as their end point~~. Six air parcels arriving at 3:00, 7:00, 11:00, 15:00, 19:00 and 23:00 local time (UTC+1) in the ground site of San Pietro Capofiume were simulated for a total of 7 days (15, 26, 27, and 28 of June and 4, 5 and 8 of July 2012). The air masses in the simulated trajectories originated all from Europe (mostly Portugal or France) or the Atlantic Ocean. We avoided days during which air masses originated from Africa since emission inventories for Africa are quite uncertain. We chose days for which the trajectories at the different altitudes originated all from the same region. ~~The Hybrid Single Particle Lagrangian Integrated Trajectory HYSPLIT model (Draxler et al., 2009) was used to calculate 72 h back trajectories arriving at the receptor site. For consistency, we used the same WRF meteorological data as input to HYSPLIT to calculate the back trajectories.~~ Following Murphy et al. (2011) we used the ensemble average of 20 trajectories with varied heights from 60 m up to 3 km. For consistency, we used the same WRF meteorological data as input to HYSPLIT to calculate the back trajectories.

The twenty 72 h HYSPLIT back trajectories arriving at San Pietro Capofiume at 3:00 LT on July 8, 2012 are shown in Figure 1 as an example. They all originated from the eastern Atlantic Ocean, passed a day over the ocean and then travelled over Portugal and Spain for another day. The air masses continued over the Mediterranean Sea, Western Italy, and a few hours later arrived in the receptor site of San Pietro Capofiume. The HYSPLIT clustering analysis utility was used to estimate the average trajectory that was used in the simulations (Figure 1).

Zeppelin flights over Po Valley took place on 20, 21, 22 and 24 of June of 2012 and 1, 3 and 4 of July 2012. The HYSPLIT model was once again used to calculate the 72 back trajectories ~~arriving at the receptor site around Po Valley~~. The Zeppelin trajectories were based on the actual Zeppelin position every hour, so that we could use all the measurements from all the flights. All the flights took place between 4:00 LT until 13:00 LT. The flight path of the Zeppelin for June 4, 2012 is shown in Figure S1 as an example. The flight took place between 5:00 LT and 10:00 LT and the measurements took place in the nighttime boundary layer, the residual layer, but also in the mixed layer later in the day. For each trajectory ~~All these 72 hour back trajectories were used and~~and for each hour ~~for each hour and point that the parcels would travel,~~ the corresponding emissions ~~from the emissions inventory files~~ are selected from the gridded emissions inventory files. At the same time, ~~and of course~~ the meteorological parameters (temperature, humidity, rain, etc.) are selected from the WRF meteorological data files for each point and hour of the trajectory. ~~that were previously used for the calculation of the back trajectories with HYSPLIT.~~

2.2 Chemical Aging Schemes

In our simulations, we considered three different functionalization schemes, two bSOA chemical aging parameterizations and explored the use of fragmentation mechanisms. These are summarized below.

2.2.1 Functionalization schemes

(a) Simple scheme

The first functionalization scheme (1-bin) used in our simulations was the simple scheme of Murphy et al. (2012) that had the best performance in the cases simulated in that study. In this scheme, there is one volatility bin reduction for every reaction with a simultaneous increase in oxygen atoms, with a probability of 50% for an increase of 1 oxygen atom and 50% probability for an increase of 2 oxygen atoms. The calculation of the O:C change from the number of added oxygen atoms is based on Donahue et al. (2011). The chemical aging reaction constants that are used for the reactions with OH are the same as in the base case of Murphy et al. (2011) with values equal to $1\text{x}10^{-11}$ cm^3 $molec^{-1}$ s^{-1} for anthropogenic SOA from VOCs (aSOA-v) and biogenic SOA (bSOA) and $4\text{x}10^{-11}$ cm^3 $molec^{-1}$ s^{-1} for SOA from semivolatile OA (SOA-sv) and intermediate volatility compounds (SOA-iv). These values are based on the average size of the corresponding compounds, with higher values for the bigger organic molecules.

The simple functionalization scheme has the advantage that it can also be implemented in the 1D-VBS reducing a lot of computational cost. In this case, the predictions of OA mass concentration and the volatility distributions remain the same, but one loses the ability to predict the O:C.

(b) Two-bin shift simple scheme

In the second functionalization scheme (2-bin), a two-volatility bin reduction is assumed for every reaction with a simultaneous increase in oxygen atoms. A 50% probability for the increase of 1 oxygen atom and 50% probability for the increase of 2 oxygen atoms are used. The calculation of the O:C shift in bins from the number of added oxygen atoms is based again on Donahue et al. (2011). This functionalization scheme assumes a more rapid reduction in volatility for every reaction and uses the same reaction constants for the reactions with OH as in the base case of Murphy et al. (2011).

This simple functionalization scheme has again the advantage that it can also be implemented in the 1D-VBS reducing a lot of computational cost but without ~~. Once again though we would lose~~ the ability to predict the O:C.

(c) Detailed scheme

The third aging scheme is the detailed functionalization scheme (DET) introduced by Donahue et al. (2011). This is a more rigorous scheme compared to the previous two conservative aging parameterizations. Following Murphy et al. (2012), there is a 30% probability of adding one O atom, 50% probability of adding two O atoms, and 20% probability of adding three O atoms. Each addition of O atoms results in a different distribution of volatility reductions, with an average reduction of -1.75 in $\log_{10}C^*$ per oxygen group added. These additions of O atoms are translated to changes of O:C ratios following Murphy et al. (2012). The functionalization kernel is applied to all species in the 2D-VBS upon OH reaction. Again the chemical aging reaction constants that are used for the reaction with OH are the same as the two functionalization schemes described above.

~~In~~ Murphy et al. (2011) investigated the sensitivity of the results of the model to the various assumed reaction constants and concluded that their effect on the results was low to moderate. ~~there was also some sensitivity study about these reaction constants values but small to moderate differences were found. This is why we did not continue with similar assumptions.~~

2.2.2 bSOA aging parameterizations

~~Two different parameterizations of bSOA aging are explored.~~ Since the net effect of chemical aging reactions with OH radicals on ambient bSOA levels ~~of chemical aging reactions with OH radicals~~ remains uncertain ~~until now~~, two different parameterizations of bSOA aging are explored. While the fundamentals of the aging scheme are the same for all compounds and it is assumed that homogeneous reactions with OH radicals are the main chemical pathway, the effect of these reactions on the volatility distribution of the secondary organic compounds is allowed to differ between biogenic and anthropogenic SOA components ~~with two different schemes~~. In the first scheme, the chemical aging of biogenic SOA is assumed to result in a negligible net change in volatility but an increase in O:C (Murphy et al., 2011). This scheme is consistent with the lack of bSOA aging that has been used in PMCAMx (Murphy and Pandis, 2009; 2010) and is called in the rest of the paper no-bSOA aging even if the O:C of bSOA does change.

In the second scheme, bSOA components are assumed to age similarly to aSOA, with their processing leading not only to changes in O:C, but also to a net reduction of their volatility. We explore all three functionalization schemes, the simple scheme (1-bin), the faster functionalization (2-bin) and the detailed functionalization scheme (DET) together with the two bSOA aging parameterizations.

2.2.3 Fragmentation parameterizations

Fragmentation parameterizations will be examined that lead to products with lower carbon numbers than the precursor. As in Murphy et al. (2012) the bond cleavage is assumed to happen randomly and to be uniformly distributed throughout the carbon backbone. For these fragmented compounds, the functionalization kernel is applied and this will lead to increases in volatility. ~~The~~In all tests described in this work a constant fragmentation probability ~~in our simulations is~~was assumed during the full corresponding simulation. This value was ~~and~~ allowed to range from zero (for no fragmentation) to unity. In principle, this probability should depend on O:C. However, we have ~~chose to~~ assumed a constant value in order to avoid introducing more free parameters in our schemes.

2.3 Combination of parameterizations

In our simulations, we used all combinations of the three functionalization schemes (1-bin, 2-bin or DET), the two bSOA aging schemes and simulated fragmentation assuming fragmentation probability *b* ranging from zero to 1. In Table 1, we summarize the parameterizations that were finally chosen for the simulations. For each of the six combinations of functionalization and bSOA aging, we assumed zero fragmentation probability (6 cases) plus we determined the fragmentation probability *b* that resulted in the minimum error for the average OA concentration. The determination of the “optimum” fragmentation probability for each case is shown in Figure ~~C.4~~S5. For the 1-bin functionalization scheme and considering no bSOA production during aging, the OA was underpredicted for fragmentation probabilities even low as 5% so in this case the optimum *b* was equal to zero and this became the same as the 1-bin simple scheme of Murphy et al. (2012).

2.4 Evaluation of parameterizations

The prediction skill of our simulations is quantified in terms of the fractional error, the fractional bias, the absolute error, the absolute bias and the root mean square error. ~~These are calculated using:~~The definitions of these metrics can be~~are~~ found in the Supplementary Information. We use the hourly predictions from the simulation of each parameterization and the hourly measurements of either the ground, at the receptor site of San Pietro Capofiume or the Zeppelin measurements above the site of the Po Valley for the model evaluation.~~.~~

$$Fractional\ Error = \frac{2}{n}\sum_{i=1}^{n}\frac{\left|P_i - M_i\right|}{\left(P_i + M_i\right)}$$

$$Fractional\ Bias = \frac{2}{n}\sum_{i=1}^{n}\frac{\left(P_i - M_i\right)}{\left(P_i + M_i\right)}$$

$$Absolute\ Error = \frac{1}{n}\sum_{i=1}^{n}\left|P_i - M_i\right|$$

$$Absolute\ Bias = \frac{1}{n}\sum_{i=1}^{n}\left(P_i - M_i\right)$$

$$Root\ Mean\ Square\ Error = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(P_i - M_i\right)^2}$$

~~where P_i represents the model prediction value, M_i is the corresponding measured value from the ground or above the site with the Zeppelin measurements and n is the total number of data points.~~

3. Results

3.1 Simple functionalization (1-bin case)

The first set of simulations used the simple functionalization scheme (1-bin), assuming negligible addition/production of bSOA during aging (no bSOA aging) and neglected fragmentation assuming that the employed functionalization scheme represents the net effect of these pathways. This case is the same as the base case of Murphy et al. (2012). In this scheme, there is a modest volatility reduction as the organic vapors react with OH. The prediction skill metrics of the model 4-hour average O:C and OA concentration against the averaged ground measurements for the seven selected days during PEGASOS 2012 campaign are summarized in Tables 2 and 3 respectively. Here we have to note that the use of 4 hr long time periods~~bins~~ (6 periods~~times~~ per day of simulation) was a compromise between keeping the computational cost of the hundreds of simulations performed low and maintaining most of the variability of OA and O:C. W~~w~~e tried ~~the single hour~~ simulations with hourly resolution for selected schemes and the differences were marginal.

The average predicted diurnal variation of O:C at the ground level~~,~~ is presented in Figure 2. Given the uncertainty introduced by the use of a trajectory model (e.g. a small error in the path of the air parcels can introduce significant error in the predictions), we rely on the average concentrations instead of the predictions of individual hours. Predicted O:C increased during the afternoon due to the production of secondary OA and photochemical processing (evaporation, oxidation in the gas phase and re-condensation) of the primary OA. The model predictions~~,~~ agree within experimental error with the measurements, with some discrepancies in the afternoon where the model tends to overpredict O:C. They both suggest relatively oxidized OA with modest average diurnal O:C variation. The average predicted O:C is 0.64 and the average measured is 0.58 (Table 2). The fractional error and bias for the 4-hour average O:C were less than 10%. The results are encouraging especially if one takes into account the~~we regard the experimental uncertainties that are the~~ typical AMS measurement uncertainties due to a large part to the estimated collection efficiency (for absolute concentrations) and the fragmentation table for the O:C.

The predicted average O:C vertical model profile is compared to the airborne measurements~~,~~ in Figure 3a. Model predictions~~,~~ agree with the measurements within experimental error and both suggest an oxidized aerosol. The average predicted O:C was equal to 0.59, while the average measured O:C was 0.58. The vertical profile for both the predictions and Zeppelin measurements was relatively flat inside the lowest 1 km.

The predicted average diurnal profile of the OA particle mass concentration for the 1-bin case is shown in Figure 4. The average predicted OA is equal to 2.6 μg m^{-3} and is predicted to be higher during the night time for this specific period. The measurements suggest a relatively flat profile; however, the model predicts higher particle mass concentrations during night time due to increased levels of SOA. The average measured particle mass concentration during the same period was 2.8 μg m^{-3}. The absolute error was equal to 0.78 μg m^{-3} and the fractional bias was 12%. The anthropogenic SOA and SOA from IVOC oxidation (SOA-iv) dominate the predicted OA composition, with biogenic SOA increasing during night time. SOA-iv is predicted to contribute 36% to the total OA. Anthropogenic (aSOA-v) and biogenic SOA are predicted to account for 22 and 17% respectively and SOA-sv and POA represent around 10% each (Figure S3). The predicted average diurnal profile of the POA particle mass concentration compared to the HOA concentration from the AMS-PMF results from the ground from Sullivan et al. (2016) are also shown in Figure S4. The particle mass concentrations are always less than 0.25 μg m^{-3} and the diurnal profiles seem to agree satisfactorily. The biomass burning contribution is not present during these summer months.

The average vertical predicted profile for all Zeppelin flights is compared with the corresponding measurements in Figure 3b. The average measured OA for these periods was equal to 4.7 μg m^{-3} while the average predicted 4.2 μg m^{-3}. Model predictions are within experimental error~~,~~ for altitudes lower than 700 m. The three data points at higher altitudes are all from a single flight on June 20, 2012 during which the model underpredicted the OA aloft. Potential problems with the use of data from this flight include the existence of a pollution layer aloft that day that was not captured by the model or some other relatively rare event that took place at that time. ~~However, once again the vertical measurements are reproduced by the model as the ground~~

~~measurements shown before. Finally, we must note that we binned the measurements in exactly the same time base as the model output in all cases (ground and above the site).~~

3.2 Effect of functionalization scheme

Using the 2-bin simple functionalization scheme the fractional error and bias for O:C are around 10%, similar to the 1-bin parameterization. The average predicted OA is equal to 3.4 μg m^{-3} (Table 3) with similar fractional error and bias with the 1-bin case. The average volatility distribution and O:C of OA at the ground level is shown in Figure S2. The OA mass, using this functionalization scheme is distributed towards smaller volatilities, compared to the 1-bin case, almost one bin to the left (Figure S2b), while the OA mass is distributed around similar values for the O:C with a diurnal ground average equal to 0.63 (Table 2), where 0.58 is the average for the measurements.

The detailed functionalization scheme~~,~~ underpredicted the O:C, with fractional bias equal to 34% and an average O:C equal to 0.41 (Table 2), when the average measured was 0.58. This is consistent with the conclusions of Murphy et al. (2011; 2012~~),~~) about the tendency of this aggressive functionalization scheme to seriously underpredict O:C. Specifically, the high reduction of the volatility of the organic compounds in this parameterization moves them rapidly to the particulate phase where they cannot be oxidized further. Thus, the scheme moves the compounds to the left of the 2D-VBS but with a small slope, so the final predicted O:C is low and actually lower than observed. The performance of this scheme, was better for the OA mass concentration with an average predicted value equal to 3.2 μg m^{-3} (Table 3) close to the average measured value (2.8 μg m^{-3}). The OA particle mass concentration fractional bias was equal to 11% while the fractional error was 21%. In this functionalization scheme, the predicted OA has a wider distribution in the 2D space than the 2 previous schemes and lower O:C and volatilities. (Figure S2c).

3.3 Effect of bSOA production during aging

The average predicted O:C for the ground level using the 1-bin/bSOA parameterization is 0.55, which is consistent with the measured 0.58 (Table 2). The fractional error and bias of O:C are less than 10%. However, the OA concentration is overpredicted with an average value of 3.8 μg m^{-3}, compared to the measured 2.8 μg m^{-3} (Table 2). The OA particle mass concentration fractional bias and error were 26% and 30% respectively. This is consistent with the conclusions of Hermansson et al. (2014), Lane et al. (2008) and Murphy and Pandis (2009) that treating only the functionalization of bSOA while neglecting fragmentation leads to overpredictions of OA concentrations.

The same behavior was observed in the 2-bin/bSOA simulation in which PMCAMx-Trj predicted an average ground O:C equal to 0.53 with fractional bias less than 10% but overpredicted OA with an average equal to 5 μg m^{-3} and a high fractional bias of 54%. Finally, in the DET/bSOA case, the model seriously underpredicted O:C with an average value equal to 0.35 and fractional bias equal to 50% and overpredicted OA concentration with an average equal to 5.4 μg m^{-3} and a high fractional bias of 60%. In all of these cases, addition of significant later generation bSOA production leads to significant errors in the model predictions.

3.4 The role of fragmentation

To explore the role of fragmentation the 1-bin simple functionalization scheme was first used, assuming additional production of bSOA during aging combined with the fragmentation parameterization varying the fragmentation probability from zero to one. An optimum fragmentation probability equal to 0.15 was estimated (Figure S5b~~).~~) by~~when~~ minimizating~~ion~~ the absolute error for the predicted OA mass concentrations.~~ between the simulations and the ground measurements~~. All model predictions discussed in the paper were matched in time and space with the measurements. The average predicted O:C for this model configuration (1-bin/bSOA/b=0.15) was equal to 0.56 in good agreement with the measurements and a fractional bias of 4% (Table 2). The average predicted OA was equal to 2.9 μg m^{-3} with a fractional bias of just 2%.

The second functionalization scheme (2-bin case) was also tested without and with bSOA aging, (2-bin and 2-bin/bSOA cases respectively). In the first case, the optimum *b*~~ was~~, after minimizing the absolute OA mass concentration~~e~~ error was estimated to be equal to 0.1 and in the second case, assuming bSOA aging, it was equal to 0.4 (Figures S5c and S5d) For both model configurations, the performance was satisfactory (fractional biases less than 10% and fractional errors less than 25%) for both O:C and OA mass (Table 2 and 3).

In the last test, the detailed functionalization scheme (DET case) was used. In the previous simulations, the DET and DET/bSOA parameterizations resulted in high underpredictions of the

O:C and overprediction of the OA concentration for DET/bSOA case. In the DET parameterization, the optimum *b* was estimated to be equal to 0.3 and in the second case, assuming bSOA aging, it was equal to 0.7 (Figures S5e and S5f). These schemes performed well with fractional biases less than 10% and fractional errors less than 25% for OA and less than 10% for O:C.

For all three aging schemes, including suitable fragmentation schemes, resulted in satisfactory results compared to the measurements at the ground level. In Figure S4 all the parameterizations had similar POA concentrations compared to the HOA concentrations from the ground PMF-AMS measurements. The situation was similar for the Zeppelin measurements as shown in Figure S6 in the Supplementary Information. All these parameterizations resulted in similar vertical profiles of O:C and OA with similar agreement with the measurements.

The range of fragmentation probabilities from all cases was high (from 0.1 to 0.7) and the model appeared to use it as a correction factor to reduce the SOA produced by the most aggressive schemes. However, both the low and high values of this range are reasonable for lightly and highly substituted organic compounds (Donahue et al., 2012a). There have been a number of studies that have tried to constrain this process for selected systems like squalene particles (Kroll et al., 2009) and a series of alkanes, ketones, aldehydes and acids (Chacon-Madrid et al., 2010; Chacon-Madrid and Donahue, 2011). While these studies have provided useful insights we are far from constraining this parameter. Additional emphasis on the production of volatile organic compounds (including small organic molecules) during the aging process will clearly help.

3.5 Synthesis of results

The previous results suggest that there are seven aging parameterizations from those examined that reproduce well both the ground and Zeppelin measurements. These are:

- the simple functionalization scheme and assuming negligible bSOA aging (1-bin case) corresponding to the base case in Murphy et al. (2011),
- the 1-bin shift with bSOA aging and a fragmentation probability equal to 15% (1-bin/bSOA/b=0.15),
- the 2-bin shift without bSOA aging (2-bin),
- the 2-bin shift without bSOA aging and a fragmentation probability equal to 10% (2-bin/b=0.1),

- the 2-bin shift with bSOA aging and a fragmentation probability equal to 40% (2-bin/bSOA/b=0.4),
- the detailed functionalization scheme, without bSOA aging and a fragmentation probability equal to 30% (DET/b=0.3),
- the detailed functionalization scheme with bSOA aging and fragmentation probability equal to 70% (DET/bSOA/b=0.7).

Parameterizations that appear to be inconsistent with the measurements are the ones that use the detailed functionalization scheme, without any fragmentation schemes, leading to underprediction of the O:C. Parameterizations including net bSOA production during the chemical aging reactions and neglecting fragmentation were also inconsistent with the measurements resulting in overprediction of the OA levels.

These seven aging schemes predict different OA composition (Figure 5), while all perform well enough compared to the measurements. Considering the modeling uncertainty introduced by the use of a 1-D trajectory model and the corresponding measurement uncertainties, all models perform satisfactorily. While statistically, the performance of the 2-bin/bSOA/b=0.4 scheme is a little better than the others, this difference is clearly within experimental/modeling error. Anthropogenic SOA from VOCs (aSOA-v) is predicted to contribute between 14 and 27% of the total OA (Figure S3a). It is a high contributor for the simulations assuming negligible additional production of bSOA during chemical aging. The parameterization using the faster functionalization scheme (2-bin) predicts the highest percentage of 27% while the scheme with the detailed functionalization, additional bSOA production and rapid fragmentation (DET/bSOA/b=0.7) predicts the lowest (14%).

The predicted contribution of biogenic SOA (bSOA) was the most variable ranging from 16 to 45% of the total OA depending on the scheme (Figure S3b). The highest contribution, as expected, was predicted by the schemes assuming production of bSOA during aging. The highest fraction (45%) was predicted using the 2-bin shift functionalization parameterization and fragmentation by 40% (2-bin/bSOA/b=0.4~~.~~). The lower bSOA mass concentrations were predicted by the four schemes assuming negligible net bSOA production during aging.

SOA from the oxidation of intermediate volatility compounds (SOA-iv) varied between 19 and 36% depending on the model (Figure S3c). The lowest contributions were predicted by the simulations in which the bSOA mass concentration was high. The primary OA (FPOA) varied from 5 to 6%, the OA from long range transport from 6 to 8%, and the SOA from evaporation of the primary and subsequent oxidation (SOA-sv) from 7 to 11%.

These results are encouraging because the various parameterizations even if they are quite different they give a rather consistent picture (with exception of the picture of the bSOA maybe) about the various pathways contributing to the OA levels in this area. Additional constraining of these schemes will require applications of the corresponding models in other areas, additional measurements, and probably additional laboratory studies.

3.6 The role of vaporization enthalpy

The vaporization enthalpy is a physical property that has always been assumed in chemical transport models with values ranging from very low as 20 to even 200 kJ mol^{-1} that have been suggested after constraining these values with experimental data (Stanier et al., 2007; Offenberg et al., 2017). In our model, three different effective vaporization enthalpies equal to 30, 75 and 150 kJ mol^{-1} were assumed and used together with the simple functionalization scheme (1-bin case). All three simulations, predicted the same flat diurnal profile for both the O:C and OA concentration, with differences less than 20%, mostly in the first hours of the day (Figure 6a and b). The predictions of the scheme with the higher vaporization enthalpy tend to be a little closer to the ground measurements of O:C. As vaporization enthalpy increased, the predicted O:C decreased and OA concentration increased (Table S1) However, the differences were small with the average O:C ranging from 0.59 for the 150 kJ mol^{-1} case to 0.64 for the 30 kJ mol^{-1} case, while the measured average value was 0.58. The fractional biases for O:C were similar ranging from 2% for a vaporization enthalpy equal to 150 kJ mol^{-1} to 10% for 30 kJ mol^{-1}. The results for the OA concentration were similar.

The comparison of the model predictions with the vertical profiles from the Zeppelin measurements showed similar results (Figure 6c and d). The predicted vertical profiles of O:C and OA particle mass concentration were once more not that sensitive to the assumed effective vaporization enthalpy. This lack of sensitivity can be explained by the intricate interplay between the ~~changes in~~ two processes (first generation production/partitioning ~~of the semi-volatile compounds~~ and ~~their gas-phase~~ chemical aging). Specifically, when a high evaporation enthalpy was used, the first generation SOA evaporated more at high temperatures and its concentration was reduced. However, now there were more semivolatile vapors available for the aging reactions~~.~~ with the OH. So, these reactions produced more later-generation SOA. The reduction of first generation SOA (due to evaporation) was offset by the higher SOA from the chemical aging reactions, so the total SOA did not change much. The opposite happened when a lower enthalpy was used. T~~Finally, t~~he sensitivity to~~of~~ the vaporization enthalpy was examined for different ~~with all~~ aging mechanisms and the conclusions were the same.

~~For values of ΔH_{vap} that favor the partitioning of the OA components to the gas phase the resulting decrease in OA concentrations is partially offset by an acceleration of the gas-phase chemical aging reactions and the additional SOA production. Vice-versa for ΔH_{vap} values that favor the partitioning to the particulate phase the resulting OA increase is balanced by a reduction in the aging rate.~~

4. Conclusions

The effects of the parameterization of the chemical aging processes of atmospheric organic compounds on organic aerosol (OA) particle mass concentration and chemical composition were investigated by using different formulations of the two-dimensional Volatility Basis Set (2D-VBS) together with ground and airborne measurements in the Po Valley in Italy.

We applied first~~ly~~ the simple aging mechanism of the base case (Murphy et al., 2012), presented here as the 1-bin case. The advantage of this scheme is that can be ~~is simple scheme is firstly used, because of its advantage to be~~ implemented in the 1D-VBS also, so one can the same performance for OA at a low ~~reducing a lot of~~ computational cost. The predictions of the model were satisfactory, both at the ground and aloft, within experimental variability and with fractional biases for the 4-hour average O:C and OA concentration around 10%. The average diurnal POA concentration was similar to the HOA concentration from the PMF-AMS ground measurements with concentrations less than 0.25 μg m^{-3}. The vertical profile for both predictions of the 1-bin case and Zeppelin measurements was relatively flat inside the lowest 1 km and the diurnal variation in O:C ratio was modest. They both suggested a relatively oxidized OA for the Po Valley, Italy, with an average O:C around 0.6. Anthropogenic SOA and SOA from intermediate volatility compounds oxidation dominated the predicted OA composition based on this parameterization.

Seven aging schemes (out of more than a hundred tested), with different assumed functionalization algorithms, bSOA aging and fragmentation probabilities (ranging from 0.1 to 1) were found to reproduce well the ground and Zeppelin O:C and OA measurements. Anthropogenic SOA from VOCs was predicted to contribute between 15 and 25% of the total OA and SOA from the oxidation of intermediate volatility compounds oxidation between 20 and 35%. The contribution of biogenic SOA varied from 15 to 45%, depending on the parameterization scheme. POA was around 5%, with~~ almost~~ similar average diurnal profiles between the different parameterizations and similar to the HOA concentrations from the PMF-AMS ground measurements. The OA from long range transport varied from 6 to 8% and the SOA from evaporation of the primary OA and subsequent oxidation from 7 to 11%. These results are encouraging because despite the uncertainty introduced by the different schemes, their predictions about source contributions are relatively robust. However, ~~Although~~, the robustness~~validity~~ of these schemes, that were tuned to the measurements in a specific area and period, will need to be tested in future work. For the time being, this work can be viewed as a parameter fitting exercise demonstrating~~to prove~~ that there are multiple sets of 2D-VBS parameters that can result in predictions consistent with the measurements.

Addition of bSOA produced during the corresponding chemical aging reactions in the functionalization-only schemes resulted in overpredictions of the OA mass concentration. Addition of significant fragmentation (fragmentation probabilities ranging from 15 to 70%) was necessary to balance this additional source. This is clearly a topic that deserves additional research both in the laboratory and in the field. The dependence on the fragmentation probability on O:C was neglected in this study and should be better addressed in future work. ~~Also, these fragmentation probabilities were supposed to have constant values and did not depend on O:C. Clearly, in future work this fragmentation probability should be better constrained in all similar schemes.~~

~~There was also~~SOA models rely on the partitioning of the semivolatile organic vapors between the gas and particulate phases. ~~In any simulation of the atmosphere,~~ T~~t~~his process is ~~very~~ sensitive to the evaporation enthalpy and changing temperature. However, i~~I~~n our work, there was surprising low sensitivity of predicted OA particle mass concentration and O:C both at the ground and aloft to enthalpy of vaporization. Using three different vaporization enthalpies equal to 30, 75 and 150 kJ mol^{-1}, the model predictions showed a very similar flat diurnal profile for O:C and OA particle mass concentration at the ground with differences less than 20% and being within experimental variability. Similar were the conclusions for the vertical profiles of the model in comparison to the Zeppelin measurements. ~~The~~This behavior is due to ~~comes from~~ the fact that in the schemes used here, chemical aging cancels to a large extent this sensitivity. ~~SOA model used in this work, there is a quite different process (chemical aging) that cancels to a large extent this sensitivity because of the interplay between the partitioning of the compounds and the chemical aging reactions as well as the .~~ The small temperature ~~sensitivity,~~differences for altitudes ~~until~~up to 600 m might also partially explain this ~~small~~low sensitivity ~~to vaporization enthalpy.~~. There was some weak evidence though that the higher values (~~like~~ 150 kJ mol^{-1}) are in better agreement with the O:C observations at the ground and aloft. Probably this low sensitivity is also a feature of analyzing within the boundary layer during only the summer. The interplay between pa~~o~~rtitioning and chemical aging for example during wintertime would still be present, but the chemical aging should be slower. Future work with three-dimensional models and measurements with high altitude predictions and/or annual simulations with wintertime predictions may be useful.

Acknowledgements

This research was supported by the PEGASOS project funded by the European Commission under the Framework Program 7 (FP7-ENV-2010-265148) and the grant 1455244 from the US National Science Foundation.

References

Caiazzo, F., Ashok, A., Waitz, I. A., Yim, S. H. L. and Barrett, S. R. H.: Air pollution and early deaths in the United States. Part I: Quantifying the impact of major sectors in 2005, Atmospheric Environment, 79, 198–208, 2013.

Cappa, C. D. and Wilson, K. R.: Multi-generation gas-phase oxidation, equilibrium partitioning, and the formation and evolution of secondary organic aerosol, Atmos. Chem. Phys., 12, 9505–9528, 2012.

Cappa, C. D., Zhang, X., Loza, C. L., Craven, J. S., Yee, L. D., and Seinfeld, J. H.: Application of the Statistical Oxidation Model (SOM) to secondary organic aerosol formation from photooxidation of C12 alkanes, Atmos. Chem. Phys., 13, 1591–1606, 2013.

~~Carter, W. P. L.: Programs and files implementing the SAPRC-99 mechanism and its associated emissions processing procedures for Models-3 and other regional models, 31 January, 2000.~~

Chacon-Madrid, H. J., Presto, A. A., and Donahue, N. M.: Functionalization vs. fragmentation: n-aldehyde oxidation mechanisms and secondary organic aerosol formation, Phys. Chem. Chem. Phys., 12, 13975–13982, ~~10.1039/C0cp00200c,~~ 2010.

Chacon-Madrid, H. J. and Donahue, N. M.: Fragmentation vs. functionalization: chemical aging and organic aerosol formation, Atmos. Chem. Phys., 11, 10553–10563, 2011.

Donahue, N. M., Robinson, A. L., Stanier, C. O., and Pandis, S. N.: Coupled partitioning, dilution, and chemical aging of semivolatile organics, Environ. Sci. Technol., 40, 2635-2643, 2006.

Donahue, N. M., Kroll, J. H., Pandis, S. N., and Robinson, A. L.: A two-dimensional volatility basis set: 1. organic-aerosol mixing thermodynamics, Atmos. Chem. Phys., 11, 3303–3318, 10.5194/acp-11-3303-2011, 2011.

Donahue, N. M., Epstein, S. A., Pandis, S. N., and Robinson, A. L.: A two-dimensional volatility basis set – Part 2: Diagnostics of organic-aerosol evolution, Atmos. Chem. Phys., 12, 615–634, 10.5194/acp-12-615-2012, 2012a.

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., Reinnig, M. C., Hoffmann, T., Salo, K., Hallquist, M., Frosch, M., Bilde, M., Tritscher, T., Barmet, P., Baltensperger, U.: Aging of biogenic secondary organic aerosol via gas-phase OH radical reactions, Proc. Natl. Acad. Sci., 109, 13503–13508, 2012b.

Draxler, R., Stunder, B., Rolph, G., Stein, A., and Taylor, A.: HYSPLIT4 User's Guide, NOAA Silver Spring, MD, 231, 2009.

Fountoukis C., Racherla P. N., Denier van der Gon H. A. C., Polymeneas P., Charalampidis P. E., Pilinis C., Wiedensohler A., Dall'Osto M., O'Dowd C., and S. N. Pandis: Evaluation of a three-dimensional chemical transport model (PMCAMx) in the European domain during the EUCAARI May 2008 campaign, Atmos. Chem. Phys., 11, 10331-10347, ~~10.5194/acp-11-10331-2011,~~ 2011.

Gilardoni, S., Vignati, E., Cavalli, F., Putaud, J. P., Larsen, B. R., Karl, M., Stenstrom, K., Genberg, J., Henne, S., and Dentener, F.: Better constraints on sources of carbonaceous aerosols using a combined ^{14}C - macro tracer analysis in a European rural background site, Atmos. Chem. Phys., 11, 5685–5700, 2011.

Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P. I., and Geron, C.: Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature), Atmos. Chem. Phys., 6, 3181–3210, ~~10.5194/acp-6-3181-2006,~~ 2006.

Hermansson, E., Roldin, P., Rusanen, A., Mogensen, D., Kivekäs, N., Väänänen, R., Boy, M., and Swietlicki, E.: Biogenic SOA formation through gas-phase oxidation and gas-to-particle partitioning – a comparison between process models of varying complexity, Atmos. Chem. Phys., 14, 11853–11869, 2014.

Hildebrandt Ruiz, L., Paciga, A. L., Cerully, K. M., Nenes, A., Donahue, N. M., and Pandis, S. N.: Formation and aging of secondary organic aerosol from toluene: changes in chemical composition, volatility, and hygroscopicity, Atmos. Chem. Phys., 15, 8301-8313, ~~10.5194/acp-15-8301-2015~~, 2015.

IPCC (Intergovernmental Panel on Climate Change): Climate Change ~~2014: Mitigation of Climate Change.~~2013: The Physical Science Basis. Contribution of Working Group ~~III~~I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change~~,~~ [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)]. Cambridge University Press, Cambridge, ~~UK~~United Kingdom and New York, ~~2014~~NY, USA, ~~1535 pp, 10.1017/CBO9781107415324,~~ 2013.

Jathar, S. H., Cappa, C. D., Wexler, A. S., Seinfeld, J. H. and Kleeman, M. J.: Multi-generational oxidation model to simulate secondary organic aerosol in a 3-D air quality model, Geosci. Model Dev., 8, 2553-2567, 2015.

Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prévôt, A. S. H., Zhang, Q., Kroll, J. H., DeCarlo, P. F., Allan, J. D., Coe, H., Ng, N. L., Aiken, A. C., Docherty, K., Ulbrich, I., 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., Huffman, J. A., Onasch, T. B., Alfarra, M. R., Williams, P., 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., 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.

Kroll, J. H., Smith, J. D., Che, D. L., Kessler, S. H., Worsnop, D. R., and Wilson, K. R.: Measurement of fragmentation and functionalization pathways in the heterogeneous oxidation of oxidized organic aerosol, Phys. Chem. Chem. Phys., 11, 8005–8014, ~~10.1039/B905289e,~~ 2009.

Kulmala, M., Asmil, A., Lappalainen, H. K., Carslaw, K. S., Poschl, U., Baltensperger, U., Hoy, O., Brenquier, J.-L., Pandis, S. N., Facchini, M. C., Hansson, H. C., Wiedensohler, A., and O’Dowd, C. D.: Introduction: European Integrated Project on Aerosol Cloud Climate and Air Quality interactions (EUCAARI) – integrating aerosol research from nano to global scales, Atmos. Chem. Phys., 9, 2825–2841, ~~10.5194/acp-9-2825-2009,~~ 2009.

Lane, T. E., Donahue, N. M., and Pandis, S. N.: Simulating secondary organic aerosol formation using the volatility basis-set approach in a chemical transport model, Atmos. Environ., 42, 7439–7451, 2008.

Murphy, B. N. and Pandis, S. N.: Simulating the formation of semivolatile primary and secondary organic aerosol in a regional chemical transport model, Environ. Sci. Technol., 43, 4722–4728, 2009.

Murphy, B. N. and Pandis, S. N.: Exploring summertime organic aerosol formation in the eastern United States using a regional-scale budget approach and ambient measurements, J. Geophys. Res., 115, D24216, 10.1029/2010jd014418, 2010.

Murphy, B. N., Donahue, N. M., Fountoukis, C., and Pandis, S. N.: Simulating the oxygen content of ambient organic aerosol with the 2D volatility basis set, Atmos. Chem. Phys., 11, 7859-7873, ~~10.5194/ acp-11-7859-7873-2011,~~ 2011.

Murphy, B. N., Donahue, N. M., Fountoukis, C., Dall’Osto, M., Dowd, C. O., Kiendler-Scharr, A., and Pandis, S. N.: Functionalization and fragmentation during ambient organic aerosol aging: application of the 2-D volatility basis set to field studies, Atmos. Chem. Phys., 12, 10797-10816,~~10.5194/ acp-12-10797-10816-2012,~~ 2012.

Murphy, B. N., Donahue, N. M., Robinson, A. L., and Pandis, S. N.: A naming convention for atmospheric organic aerosol, Atmos. Chem. Phys., 14, 5825–5839, ~~doi:10.5194/acp-14-5825-2014,~~ 2014.

Ng, N. L., Kroll, J. H., Keywood, M. D., Bahreini, R., Varutbangkul, V., Flagan, R. C., and Seinfeld, J. H.: Contribution of first- versus second-generation products to secondary organic aerosols formed in the oxidation of biogenic hydrocarbons, Environ. Sci. Technol., 40, 2283–2297, 2006.

O’Dowd, C. D., Langmann, B., Varghese, S., Scannell, C., Ceburnis, D., and Facchini, M. C.: A combined organic-inorganic sea spray source function, Geophys. Res. Lett., 35, L01801, 10.1029/2007GL030331, 2008.

Offenberg, J. H., Lewandowski, M., Kleindienst, T. E., Docherty, K. S., Jaoui, M., Krug, J., Riedel, T. P., and Olson D. A.: Predicting Thermal Behavior of Secondary Organic Aerosols, Environ. Sci. Technol., 51, 9911-9919, 2017.

Pandis S. N., Harley R. A., Cass G. R. and Seinfeld J. H.: Secondary o~~O~~rganic a~~A~~erosol f~~F~~ormation and t~~T~~ransport, Atmos. Environ., 26, 2266-2282, 1992.

Pathak, R. K., Presto, A. A., Lane, T. E., Stanier, C. O., Donahue, N. M., and Pandis, S. N.: Ozonolysis of α-pinene: parameterization of secondary organic aerosol mass fraction, Atmos. Chem. Phys., 7, 3811–3821, ~~10.5194/acp-7-3811-2007,~~ 2007.

Pope, C. A., III, Ezzati, M. and Dockery, D. W.: Fine-particulate air pollution and life expectancy in the United States, New England Journal of Medicine, 360, 376–386, 2009.

Sheehan, P. E. and Bowman, F. M.: Estimated effects of temperature on secondary organic aerosol concentrations, Environ. Sci. Technol., 35, 2129–2135, 2001.

Shrivastava, M., Fast, J., Easter, R., Gustafson Jr., W. I., Zaveri, R. A., Jimenez, J. L., Saide, P., and Hodzic, A.: Modeling organic aerosols in a megacity: comparison of simple and complex representations of the volatility basis set approach, Atmos. Chem. Phys., 11, 6639–6662, 2011.

Sofiev, M., Lanne, M., Vankevich, R., Prank, M., Karppinen, A., and Kukkonen, J.: Impact of wild-land fires on European air quality in 2006–2008, Modeling, Monitoring and Management of Forest Fires, WIT Trans. Ecol. Envir., 119, 353–361, 2008a.

Sofiev, M., Vankevich, R., Lanne, M., Koskinen, J., and Kukkonen, J.: On integration of a Fire Assimilation System and a chemical transport model for near-real-time monitoring of the impact of wild-land fires on atmospheric composition and air quality, Modeling, Monitoring and Management of Forest Fires, WIT Trans. Ecol. Envir., 119, 343–351, 2008b.

Stanier, C. O., Pathak, R. K., and Pandis, S. N.: Measurements of the volatility of aerosols from α-pinene ozonolysis, Environ. Sci. Technol., 41, 2756–2763, 2007.

Stanier, C. O., Donahue, N., Pandis, S. N.: Parameterization of secondary organic aerosol mass fractions from smog chamber data, Atmos. Environ., 42, 2276–2299, 2008.

Sullivan, A. P., Hodas, N., Turpin, B. J., Skog, K., Keutsch, F. N., Gilardoni, S., Paglione, M., Rinaldi, M., Decesari, S., Facchini, M. C., Poulain, L., Herrmann, H., Wiedensohler, A., Nemitz, E., Twigg, M. M., and Collett Jr., J. L.: Evidence for ambient dark aqueous SOA formation in the Po Valley, Italy, Atmos. Chem. Phys., 16, 8095-8108, 2016.

Szidat, S., Jenk, T. M., Synal, H.-A., Kalberer, M., Wacker, L., Hajdas, I., Kasper-Giebl, A., and Baltensperger, U.: Contributions of fossil fuel, biomass-burning, and biogenic emissions to carbonaceous aerosols in Zurich as traced by 14C, J. Geophys. Res., 111, D07206, 10.1029/2005JD006590, 2006.

Tritscher, T., Dommen, J., DeCarlo, P. F., Barmet, P. B., Pra-plan, A. P., Weingartner, E., Gysel, M., Prévôt, A. S. H., Riipinen, I., Donahue, N. M., and Baltensperger, U.: Volatility and hygroscopicity of aging secondary organic aerosol in a smog chamber, Atmos. Chem. Phys., 11, 11477-11496, 2011.

Visschedijk, A. J., Zandveld, P., and Denier van der Gon, H. A. C.: TNO Report 2007 A-R0233/B: A high resolution gridded European emission database for the EU integrated project GEMS, Organization for Applied Scientific Research, The Netherlands, 2007.

Yttri, K. E., Simpson, D., Nøjgaard, J. K., Kristensen, K., Genberg, J., Stenström, K., Swietlicki, E., Hillamo, R., Aurela, M., Bauer, H., Offenberg, J. H., Jaoui, M., Dye, C., Eckhardt, S., Burkhart, J. F., Stohl, A., and Glasius, M.: Source apportionment of the summer time carbonaceous aerosol at Nordic rural background sites, Atmos. Chem. Phys., 11, 13339-13357, 2011.

Zhang, Q., Jimenez, J. L., Canagaratna, M. R., Allan, J. D., Coe, H., Ulbrich, I., Alfarra, M. R., Takami, A., Middlebrook, A. M., Sun, Y. L., Dzepina, K., Dunlea, E., Docherty, K., De-

Carlo, P. F., Salcedo, D., Onasch, T., Jayne, J. T., Miyoshi, T., Shimono, A., Hatakeyama, S., Takegawa, N., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Williams, P., Bower, K., Bahreini, R., Cottrell, L., Griffin, R. J., Rautiainen, J., Sun, J. Y., Zhang, Y. M., and Worsnop, D. R.: Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically-influenced Northern Hemisphere midlatitudes, Geophys. Res. Lett., 34, L13801, 10.1029/2007GL029979, 2007.

Zhang, Q. J., Beekmann, M., Drewnick, F., Freutel, F., Schneider, J., Crippa, M., Prévôt, A. S. H., Baltensperger, U., Poulain, L., Wiedensohler, A., Sciare, J., Gros, V., Borbon, A., Colomb, A., Michoud, V., Doussin, J. F., Denier van der Gon, H. A. C., Haeffelin, M., Dupont, J. C., Siour, G., Petetin, H., Bessagnet, B., Pandis, S. N., Hodzic, A., Sanchez, O., Honoré, C., and Perrussel, O.: Formation of organic aerosol in the Paris region during the MEGAPOLI summer campaign: evaluation of the volatility-basis-set approach within the CHIMERE model, Atmos. Chem. Phys., 13, 5767–5790, 2013.

Zhao, B., Wang, S., Donahue, N. M., Chuang, W., Hildebrandt-Ruiz, L., Ng, N. L., Wang, Y., and Hao, J.: Evaluation of one-dimensional and two-dimensional volatility basis sets in simulating the aging of secondary organic aerosol with smog-chamber experiments, Environ. Sci. Technol., 49, 2245–2254, 2015.

Table 1. Characteristics of the different parameterizations used in our simulations.

Parameterization Name	**Functionalization scheme**	**bSOA increase during aging**	**Fragmentation probability**	**Comments**
1-bin	1-bin	No	b=0	
1-bin/bSOA	1-bin	Yes	b=0	
1-bin	1-bin	No	b=0-1	Optimum for b=0, same as 1-bin case
1-bin/bSOA/b=0.15	1-bin	Yes	b=0-1	Optimum for b=0.15
2-bin	2-bin	No	b=0	
2-bin/bSOA	2-bin	Yes	b=0	

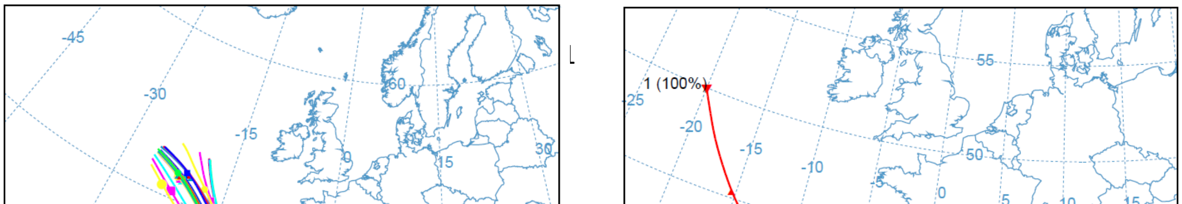
2-bin/b=0.1	2-bin	No	b=0-1	Optimum for b=0.1
2-bin/bSOA/b=0.4	2-bin	Yes	b=0-1	Optimum for b=0.4
DET	DET	No	b=0	
DET/bSOA	DET	Yes	b=0	
DET/b=0.3	DET	No	b=0-1	Optimum for b=0.3
DET/bSOA/b=0.7	DET	Yes	b=0-1	Optimum for b=0.7

Table 2. Performance metrics of different parameterizations during the PEGASOS campaign for ground O:C measurements. The measured average O:C was 0.58.

2D-VBS Parameterization	**Predicted Average**	**Fractional Error**	**Fractional Bias**	**Absolute Error**	**Absolute Bias**	**Root Mean Square Error**
1-bin	0.64	0.1	0.09	0.06	0.06	0.08
1-bin/bSOA	0.55	0.07	-0.06	0.04	-0.03	0.05
1-bin/bSOA/b=0.15	0.56	0.07	-0.04	0.04	-0.02	0.05
2-bin	0.63	0.09	0.08	0.05	0.05	0.06
2-bin/bSOA	0.53	0.10	-0.10	0.05	-0.05	0.06
2-bin/b=0.1	0.65	0.12	0.11	0.07	0.07	0.08
2-bin/bSOA/b=0.4	0.58	0.05	0.0	0.03	0.00	0.04
DET	0.41	0.34	-0.34	0.17	-0.17	0.17
DET/bSOA	0.35	0.49	-0.49	0.23	-0.23	0.23
DET/b=0.3	0.57	0.05	-0.03	0.03	-0.01	0.04
DET/bSOA/b=0.7	0.62	0.08	0.06	0.05	0.04	0.05

Table 3. Performance metrics of different parameterizations during the PEGASOS campaign for ground OA mass measurements. The measured average organic aerosol concentration was 2.8 μg m^{-3}.

2D-VBS Parameterization	**Predicted Average (μg m^{-3})**	**Fractional Error**	**Fractional Bias**	**Absolute Error (μg m^{-3})**	**Absolute Bias (μg m^{-3})**	**Root Mean Square Error (μg m^{-3})**
1-bin	2.6	0.29	-0.12	0.78	-0.25	0.89
1-bin/bSOA	3.8	0.3	0.26	1.09	0.97	1.50
1-bin/bSOA/b=0.15	2.9	0.27	-0.02	0.79	0.05	0.96
2-bin	3.4	0.23	0.16	0.76	0.56	1.06
2-bin/bSOA	5	0.54	0.54	2.21	2.21	2.53
2-bin/b=0.1	2.9	0.22	0.02	0.67	0.11	0.85
2-bin/bSOA/b=0.4	3.1	0.22	0.07	0.71	0.3	0.96
DET	3.2	0.21	0.11	0.67	0.4	0.93
DET/bSOA	5.4	0.6	0.6	2.53	2.53	2.80
DET/b=0.3	2.9	0.22	0.01	0.66	0.1	0.84
DET/bSOA/b=0.7	2.9	0.24	0.02	0.71	0.12	0.87



(a) **(b)**

Figure 1. (a) The ensemble of twenty~~20~~ 72-hour back trajectories calculated by HYSPLIT for air parcels arriving at the San Pietro Capofiume site on 8 July 2012 at 3:00 LT and **(b)** the ensemble average trajectory calculated by the HYSPLIT clustering utility.

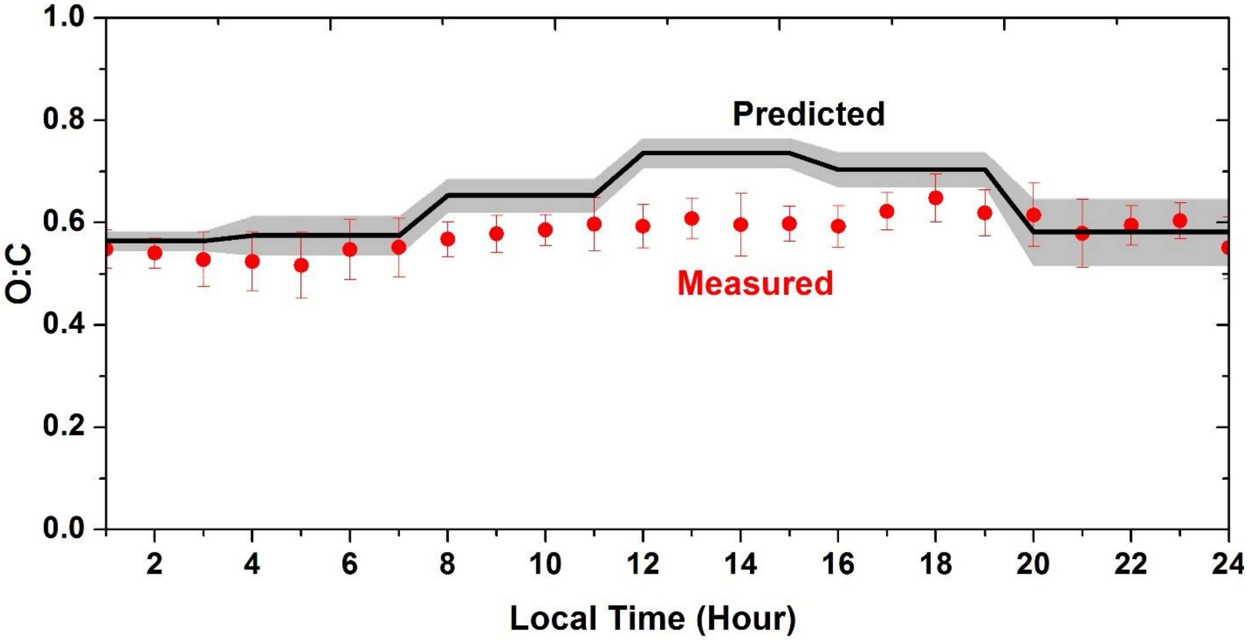


Figure 2. Average O:C diurnal evolution at the ground level in San Pietro Capofiume for the 1-bin simulation~~.~~, ~~-~~as a~~-~~n~~first~~ example. The black line shows the 4-hour model average predictions for all simulated~~representative seven~~ days (6 plateaus from 6 hours of model predictions) and the shaded area corresponds to one standard deviation. The red symbols represent the ground AMS measurements and the error bars correspond to one standard deviation.

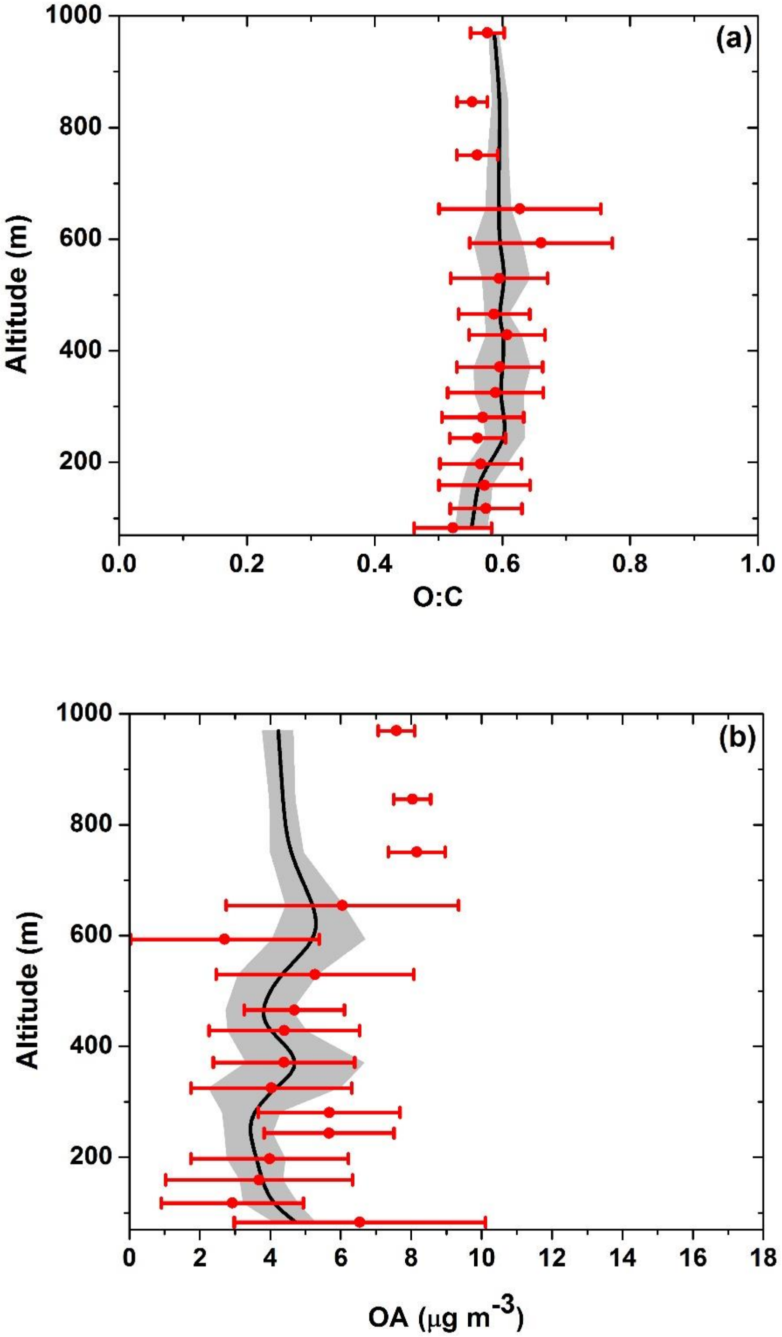


Figure 3. Average vertical predicted and measured (1-bin case, as an example) **(a)** O:C ratio and **(b)** organic aerosol mass concentration for all the Zeppelin measurements over Po Valley. The black line shows the model predictions and the shaded areas the standard deviation. The red

symbols represent the AMS Zeppelin measurements and the error bars correspond to one standard deviation. The discontinuity at~~on~~ the top is due to the results of a single ~~comes from one~~ flight on ~~20~~ June 20, 2012.

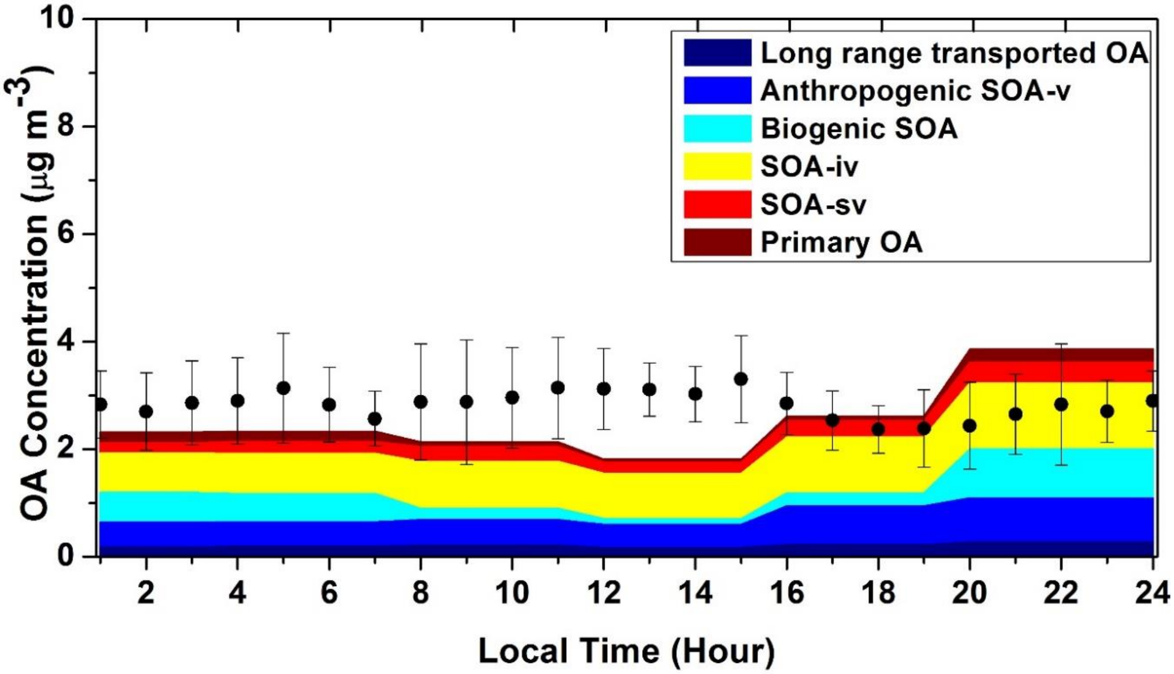


Figure 4. Average diurnal profile at the ground level OA in San Pietro Capofiume (1-bin case, as an example). With dark blue we represent the OA from long range transport, with blue the anthropogenic SOA produced during the oxidation of anthropogenic VOCs (aSOA-v), with cyan the biogenic SOA (bSOA), with yellow the SOA from oxidation of intermediate volatility compounds (SOA-iv), with red the SOA from the oxidation of semivolatile OA (SOA-sv) and finally with dark red the fresh primary organic aerosol (FPOA). The ground AMS measurements are shown with black symbols and the error bars correspond to one standard deviation.

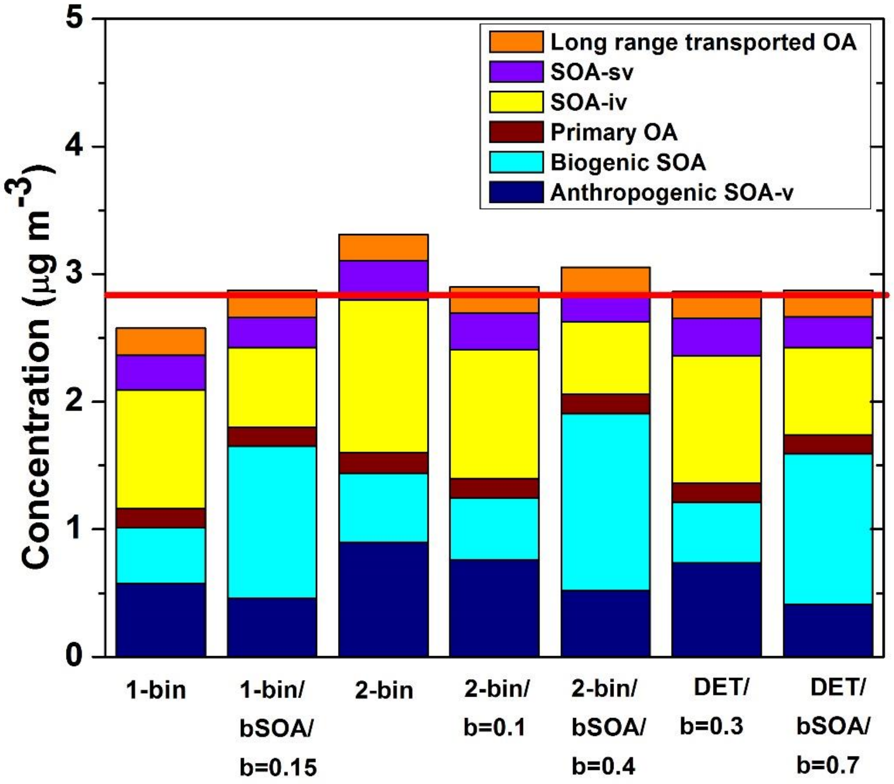


Figure 5. Predicted OA composition for the schemes with good performance for San Pietro Capofiume. The red line indicates the average ground measured OA equal to 2.8 μg m^{-3}.

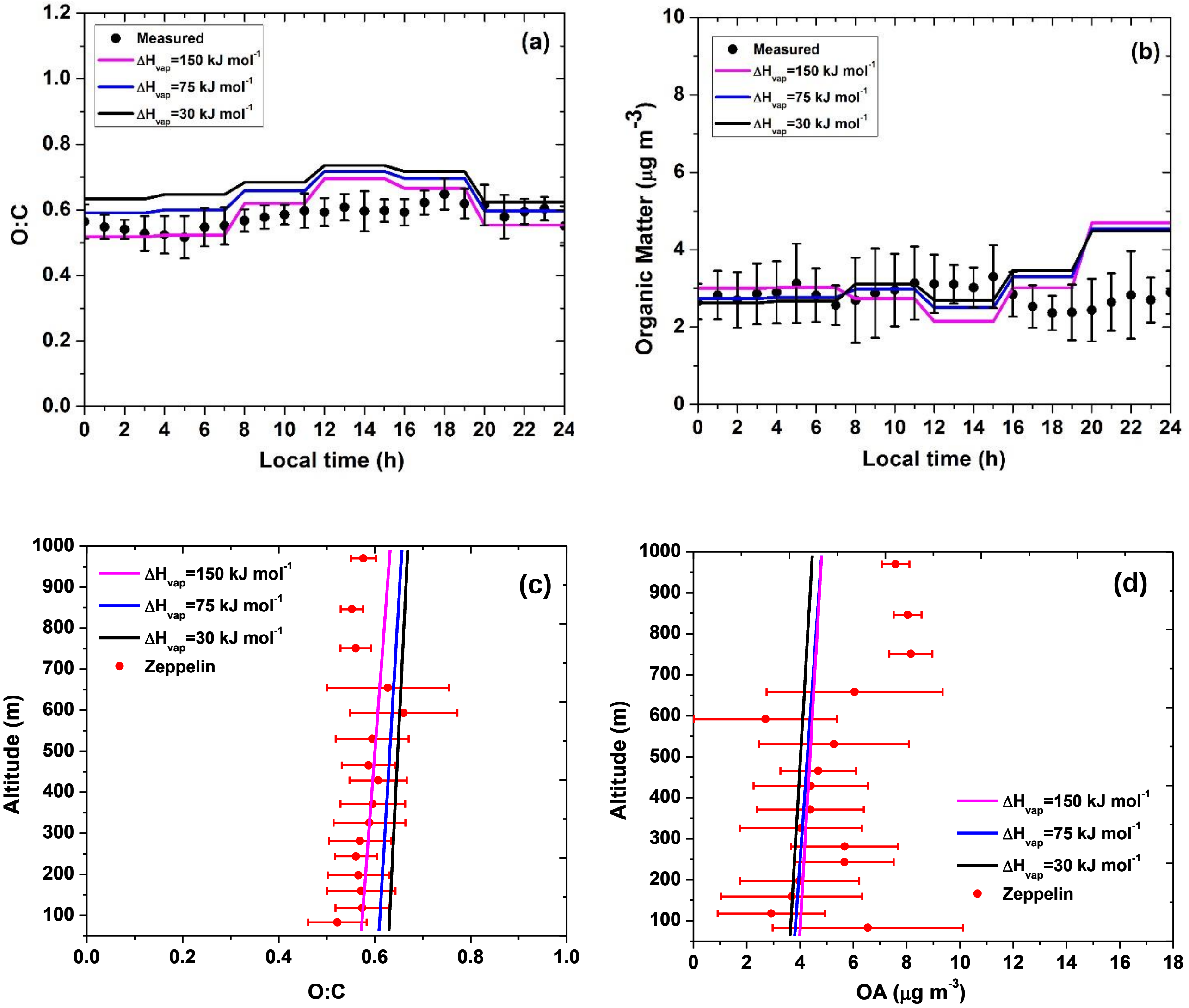


Figure 6. Diurnally ~~average~~averaged (a) O:C ratios and (b) organic aerosol mass concentrations. Average vertical organic aerosol (c) O:C and (d) organic aerosol mass concentrations assuming in the model ΔH_{vap}= 30 kJ mol^{-1} (black line), ΔH_{vap}= 75 kJ mol^{-1} (blue line), and ΔH_{vap}= 150 kJ mol^{-1} (magenta line) for the Po Valley in Italy. The black symbols show the ground AMS measurements. The red symbols show the Zeppelin measurements. The error bars represent one standard deviation.