

We thank the reviewer for the review and constructive comments. Below we address each comment point by point. Reviewer comments are marked as black, our response as blue and corrections to the changes to the manuscript as red.

This paper attempts to describe a semi-empirical model to simulate the evolution of gas-phase and particle phase measurements of aging emissions from wood combustion in the ILMARI atmospheric simulation chamber. The authors attempt to describe the performance of their model by employing different techniques (e.g. adding noise to their data, smoothing in different ways, filtering the data in different ways).

I find several troublesome aspects of the manuscript. The language/grammar is not clear and is often confusing. It made it difficult to evaluate portions of the manuscript. Further, details regarding the modelling aspects were often introduced with little to no explanation (or background) and in ambiguous terms. Rather than concrete examples of how the model was treating the data. The tables in the text were not clear nor adequately explained making it difficult to assess what data was included and the parameters varied. Honestly, it appeared as if the modelling output was directly placed into a table with no thought to whether or not the information presented was considered useful or not.

Overall, I find the text challenging to disentangle and is not suitable to be published in the current form. It requires significant grammatical polishing and a more extensive discussion regarding the details of the model so that it could be useful for others. I also find it difficult to assess its usefulness to the chamber community writ large. Minor comments / questions can be found in the supplement.

To clarify the methods section, we decided to remove chapters 2.2-2.4 and focused more on connecting causal discovery algorithms and differential equations. Due these changes, the terminology is now somewhat simplified and thus it should be easier to understand for readers applying these types of models.

All tables are necessary for model evaluation and all variables presented in tables are introduced in section 2.3 in the revised manuscript. We have clarified the tables form to be easier to interpret (see detailed comment below).

Other comments:

Line 14 page 2: “to double to triple” this is a bit of a colloquialism.

Changed to “...enhance the organic aerosol concentration between a factor of two to three...”

Line 16 page 2: PAHs

Corrected

Line 29 page 2: ... are important and are needed to ...

Corrected

Line 1 page 3: if a few attempts have been made it might be nice to cite them here.

We added some references to this (Hartikainen et al., 2018, 2020; Isaacman-Vanwertz et al., 2018)

Line 3 page 3: the V in Volatility doesn't need to be capitalized

Corrected

Lines 3 – 6 page 3: this sentence needs considerable work.

Perhaps: In the VBS approach, the evolution of the constituent phases (gas and particle) are modelled based on the volatilities of the compounds, ...

Corrected as suggested

Lines 6 – 11 page 3: I think there needs to be a link between SOA and gas phase oxidation when discussing MCM. An approach to model SOA is to utilize MCM for the production of oxidized molecules with a parameterization based molecular formula / function group analysis to estimate saturation vapor concentrations, etc... This is what you do when talking about the SOM, but MCM itself is not a way to model SOA.

This was now corrected as

“Another approach to model SOA and especially its precursors in the gas-phase is the family of explicit chemical modeling. There exists several chemical models such as Master Chemical Mechanism (MCM) (Jenkin et al., 1997; Saunders et al., 2003) and GECKO-A (Aumont et al., 2005), which comprise large amounts of chemical reactions and pre-determined reaction coefficients to replicate the evolution of the system. MCM has been recently applied to wood burning emissions by running the model with most important primary emission species to model the evolution of gas-phase species using

smaller selection of reactions from the whole system (Coggon et al., 2019). These can be used to parametrize SOA production. ...”

Line 14 page 3: “All approaches differential equation approaches.”
Consider rewording

Reworded as “All approaches, volatility-based, SOM, and explicit chemical modeling, are based on differential equations.”

Line 16 page 3: remove: “here the amount of SOA” or reword. The emphasis on here the amount of SOA is not clear the context. Is this the point of the current paper or the current topic you are introducing (SOA models)?

Removed

Line 18 page 3: “In this kind of system” Please describe what you mean here. System was meant to be one of the approaches mentioned above. This is now clarified as “In the approaches mentioned above ...”

Line 21 page 3: “Initial compounds cause the increase in products and decrease in their own concentrations” maybe add at the beginning “If a reaction is favorable, the initial compounds result in an increase in the products and a decrease in their own concentrations.”

Corrected as suggested

Page 4: it is mentioned that O₃ is put into the chamber to simulate dark aging, where dark aging represents both O₃ and NO₃ chemistry. It is not clear what concentrations of NO_x are in the chamber and why NO₃ chemistry would be taking place. It could be helpful to have an experimental table listing the types of experiments taking place and concentrations of relevant oxidants / trace gases.

Although NO₃ radicals had not been measured directly, the high concentrations of NO₂, which was previously converted from NO by adding ozone, and excess ozone should lead to NO₃ radical formation. In addition, during dark aging (absence of OH-radicals) an extensive decay of phenolic and furanoic VOCs was observed. Since the reaction rates of phenolic and furanoic compounds with ozone are low, it can be concluded that NO₃ radicals were present (Hartikainen et al., 2018). Further, extensive formation of nitrophenols was observed as a result of reactions between NO₃ and phenolic precursors (Hartikainen et al., 2018).

We added the following text to the revised manuscript line 19-22 page 4:

“The conditions in the chamber simulate polluted atmospheric boundary-layer conditions with an OH concentration of $(0.5\text{--}5) \times 10^6 \text{ molec cm}^{-3}$, ozone concentrations of 20–90 ppb and NO_x concentrations of 40–120 ppb (Tiitta et al., 2016) with a lower VOC-to-NO_x ratio (fast ignition: ratio ≈ 3) yielded smaller total emissions including SOA than the slow ignition cases (ratio ≈ 5).”

Line 26 page 4: “intensive” should be ‘the intense’
Corrected

Line 28 page 4: “their formation products” the formation of what products?
HNO₃? Molecules making up SOA?

Differences in dark and light ageing has been mentioned in lines 12-23 page 4 in revised manuscript. Text has been also clarified by removing one sentence.

Line 1 page 5: can you clarify how it impacts the composition? Just one line.

The first sentence is reworded and second sentence was added as
“The ignition type, i.e. how fast the logwood ignites change influence the emission factors of POA and VOC emission from wood combustion, in particular carbonyls, aromatic hydrocarbons, furanoic and phenolic compounds (Hartikainen et al., 2018; Tiitta et al., 2016). During aging furanoic and phenolic compounds decreased and nitrogen-containing organic compounds in both gas and particulate phase were produced. Photochemical aging increased especially the concentrations of certain gaseous carbonyls, particularly acid anhydrides (Hartikainen et al., 2018).”

Lines 18 – 24 page 5: how are the factors determined?

More detailed description on the factor determination will be given in revised manuscript lines 15-33, page 6.

Line 8 page 6: “ but EFA was selected for further analysis”
Corrected

Line 2 page 7: “OH radical has an ...” should be: “OH radicals have an ...”
Corrected

Section 2.1.2 within Barmet et al. the OH concentration needs to be determine with reference to another VOC with a known rate constant. For instance:

What was the other VOC chosen for comparison?

d9-butanol

Line 29 page 9: “evolvment” should be evolution

Corrected

Lines 30 – 31 page 10: is it reasonable that OH chemistry is not allowed to occur during dark aging? If there is ozonolysis of alkenes taking place, then there will be OH radicals produced. Even if it is a small pathway it shouldn't be ruled out unless there was negligible dark aging in the presence of O₃ alone (without NO₃ chemistry taking place), or if you could model NO₃ production to show there is negligible ozonolysis occurring.

Only minor or no decrease of butanol-d9 was observed during dark aging which indicates that OH-radicals were not produced to any significant extent.

Line 15 Page 11: I believe it should say “physical properties” because I don't understand how physical reactions would be what is meant.

Sentence was reformulated as:

“Evolution of physical properties of particles and many chemical reactions involve more than just one compound, particles of the same size, or phase state, but there are exceptions. As an example, particles of the same size can coagulate during evolution and form larger particles.”

Line 32 Page 11 / Line 1 Page 12: should read “ which assessed the measurement error...” omit was.

Corrected

Line 8 page 12: replace “much” with many

Corrected

Line 8 page 12: omit the sentence starting with “Additionally” either talk about how it was interesting or remove the sentence.

Removed

Line 10/11 page 12: what is “correct structure”?

Correct structure = correct information of dependencies.

We added a sentence to chapter 2.3. of the revised manuscript after first sentence:

“As causal discovery algorithm attempts to search dependencies based on data, there might be incorrect dependencies in the structure formed by an algorithm.”

and to the third sentence

“... dataset, but in a situation where we know the correct structure resulting the aging process”.

Line 18 page 12: “which” should be replaced with ‘whose’
Corrected

Line 20 page 12: what are Mass Action Kinetics system?
This was changed to Laws of Mass Action. In addition, references and the name of used R-package added. We found that episode-package has been removed from CRAN on December 2019. The code was modified to take this into account (download the package from Github instead of CRAN). Sentence was reformulated as

“In smaller datasets, differential equations are following the Laws of Mass Action, applied in R-package *episode* (Mikkelsen, 2017; Seinfeld and Pandis, 2016).”

Line 31 page 12: RMSE is not defined. (I presume root mean square error, and will assume that is what is meant)

RMSE is indeed Root Mean Square Error. This was already defined in chapter 2.5.4 in original manuscript (2.2.4 in revised manuscript).

Lines 33 – 34 page 12: Why is this weighting required? Why would some time series not have a standard deviation (standard deviation of what)? This is not explained adequately.

Weighting was used to better equalize effects of each time series in RMSE. If weighting is not done, time series with larger absolute values would generally have larger effect on RMSE. The sentence is now reformulated, to clarify that each time series was divided with its own standard deviation.

“To equally weight each time series when calculating RMSE, each time series were scaled by dividing those with its standard deviation before calculating RMSE. In further text, we refer to this scaled version as RMSE.”

Lines 3-4 page 13: Why is only 30% of the simulated dataset predicted?

30% is the length of the data used for evaluate prediction accuracy. So 100 simulated states were used to fit a model, and then the model was predicting the next 30. Sentence was reformulated as

“Prediction length was 30% of the simulated dataset used to fit a model.”

Section 3.1

Lines 24 – 31 page 14: The problem I have with this paragraph is its order. 1) you show the measurement of error in the Tables. 2) there is good agreement! 3) This isn't surprising. 4) discuss the actual data.

I would suggest rearranging the content so you first say this table shows what you want to show. Then discuss those results, then talk about the goodness of agreement and the overall conclusion.

Corrected

Tables 3-5 and not intuitive and are not adequately described. For instance, what is "unc_fraction"? or what is nObs? This information is not included in the Table headings. Maybe the tables should be adapted so they don't appear as if they were just directly taken from a code output. For example: corMean.mean does not convey helpful information. Purely call the column title "Correlation Mean"

For each table headings, the following has been added:

"Variable nObs is a number of observations in each time series. Variable unc_frac is a standard deviation of random noise added to each time series (sd of each time series is adjusted to 1). "

For tables 6 and 7, unc_frac 0.1 was used. This is added to the table headings.

corMean.mean is mean of the mean correlation in each replication (that's why there was double mean.

Text ".mean" in every table column heading is now replaced with overline.

Line 31 page 15, what is fittingness?

Changed to goodness of fit. Additionally, added "structure" before accuracy.

Figure 5: are there not background measurements? The Figures should all start at 0 on the y-axis. Why do the figures not start at 0 mass loading? What is going on before the initiating of dark aging, are the concentrations stable? Why is the agreement so poor for 3B SOA 1?

Chamber background aerosol concentrations were below 0.3 ug/m³ measured using AMS (Tiitta et al., (2016), Fig. 2). Only very little aerosol off-gassing from the chamber walls is observed (Leskinen et al., 2015). PTR background measurements are listed in Hartikainen et al., (2018), Table S6.

Figures 6 and 8 are now corrected so that y-axis starts from 0.

Before each experiment, there has been a stabilization period. This is mentioned in the first paragraph of chapter 2.

Starting point of Figure 6 is when the chamber is filled and stabilized, thus the concentrations are not zero. In order to clarify this, we added a sentence to the first paragraph of chapter 2 in the revised manuscript:

“The end of the stabilization period is considered as the starting point of our analysis.”

The poor agreement for 3B SOA1 is probably due to the fact that 2B and 3B were both used to find dependence structure for the experiments. Formation process of SOA1 seem to be somewhat different in the two experiments. Our model has not been able to find such a structure that could represent the evolution of SOA1 in both.

Lines 13-14 page 16, why would NO_3 radicals change SOA1 to SOA2? If nitrate is important in this process, then it would be condensed phase process where N_2O_5 could be uptaken into the particle phase.

NO_3 refers here particle-phase measured concentrations. This is now clarified in figure captions and in line 28 page 4:

“The AMS was used to characterize the chemical signatures of particulate chemical species (Org, NO_3 , SO_4 , NH_4 , and Chl) of which organic species as PMF factors (details below) and NO_3 were used in this study.”

Gas-phase NO_3 has to be modeled to answer this question, which is out of scope of this study, in for example (Geyer et al., 2001) the necessary reactions are compiled. It is true that N_2O_5 and subsequent reaction with water is the major sink for NO_3 radicals, i.e. NO_x , but we can expect some influence of NO_3 on SOA formation.

Based on PMF2 modelling SOA1 didn't change to SOA2 (see Tiitta et al., 2016, Fig. 5) but SOA1 concentration was quite stable after relatively fast SOA1 formation process. The species in the SOA1 are expected to be formed via ozonolysis of unsaturated compounds such as alkenes, dienes and terpenes.

It might also be that SOA1 is correlated to some other variable that is affecting SOA2. As causal discovery algorithm is based on observed dependencies, all connections might not be causal.

Line 14 page 16: why is NO₂ attributed here and not NO₃ radicals? Because in the gas-phase that is when NO₃ chemistry would be important.

Based on Tiitta et al. (2016), the formation of secondary organic nitrate factor occur via two channels: one is through the NO₃ radical oxidation in case of excessive NO_x and O₃ in the dark ageing experiments (as described in previous chapter) and the another channel is through photochemistry via reactions of peroxy radical (RO₂/ with NO (Atkinson, 2000)). This most likely explains why we are seeing the formation of SOA₂ also after UV lights were switched on in presence of high NO in the experiment 4B (Fig. 5c, Tiitta et al., 2016).”

Hence, in UV ageing NO should be positively correlated with SOA₂. In dark ageing, the higher the initial NO₂ concentration the more SOA₂ we should obtain, however, considering the timeline of one individual (dark) ageing experiment, SOA₂ and NO₂ should be inversely correlated because NO₂ is consumed to produce SOA₂ (and even more consumed to particulate nitrate).

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