

Interactive comment on “Modelling organic aerosol concentrations and properties during ChArMEx summer campaigns of 2012 and 2013 in the western Mediterranean region” by Mounir Chrit et al.

Anonymous Referee #1

Review of Chrit et al. This paper models the organic aerosol concentration and properties during the ChArMEx summer campaigns of 2012 and 2013 using a surrogate approach for SOA formation. Although I agree with the importance of this topic and its novelty, the modeling approaches need to be clearly explained. Also, the caveats of these approaches need to be better acknowledged. Below are my specific comments that should be addressed before the paper is accepted for publication.

1. The abstract mentions that surrogate species for monoterpenes are α -pinene and limonene. But on page 5, the authors mention three precursors: α -pinene, β -pinene and limonene. This needs to be clarified. Also, why were these 2 particular species chosen as surrogates for monoterpenes?

Three surrogate species are indeed chosen for monoterpenes: α -pinene, β -pinene and limonene, as detailed in the presentation of the model of this paper and in Pun et al. (2006) and Couvidat et al. (2012). These species are chosen as surrogates for monoterpenes as they are the most abundant monoterpene species emitted, and their abilities to form SOA are different. As the list of monoterpene surrogates is not necessary in the abstract, it is removed, and the sentence “Biogenic precursors are isoprene, monoterpenes (with α -pinene and limonene as surrogate species) and sesquiterpenes.” is replaced by “Biogenic precursors are isoprene, monoterpenes and sesquiterpenes.”

2. Page 3: Why was IEPOX not observed during ChArMEx campaign? Did the instruments measure gas-phase IEPOX or particle phase ievox components? Was the aerosol acidic or neutral?

IEPOX was not measured in the gas phase during the ChArMEx campaign. In Freney et al. (2017), it was estimated in the particle phase using m/z 53 and m/z 82 of AMS measurements. The aerosol is probably acidic over the western Mediterranean region as mentioned by Nicolas José (Thesis), and Couvidat et al. (2013). As postulated in Freney et al. (2017), IEPOX may have reacted to form organosulfates. For clarity, the sentence of the introduction “However, IEPOX was not observed during the ChArMEx campaign over an isoprene-emitting forest in the South of France (Freney et al., 2017).” was replaced by “However, using aerosol mass spectrometer measurements, particle-phase IEPOX was not observed during the ChArMEx campaign over an isoprene-emitting forest in the South of France, suggesting it might have formed organo-sulfates (Freney et al., 2017).”

3. The authors mention the importance of organosulfates in this study. But IEPOX chemistry also makes organosulfates. If these are not coming from isoprene or IEPOX chemistry, what are alternate mechanisms for organosulfates from monoterpenes or sesquiterpenes? Adding some discussions and references regarding this point would be helpful.

Yes, IEPOX may form organo-sulfates. They may also be formed from the oxidation of monoterpenes. A discussion about the formation of organo-sulfates is in section 4.3: “In laboratory, the formation of organosulfate was observed from the uptake of monoterpene

oxidation products (pinonaldehyde) on acidic sulfate aerosols (Liggio and Li, 2006; Surratt et al., 2008), from the uptake of ELVOC (Mutzel et al., 2015), and from the uptake of isoprene oxidation products (Liggio et al., 2005; Nguyen et al., 2014). Isoprene SOA may be formed via the reactive uptake of isoprene-epoxydiol (IEPOX), a second generation oxidation product of isoprene, in the presence of hydrated sulfate (Surratt et al., 2010; Couvidat et al., 2013b; Nguyen et al., 2014). Using aerosol mass spectrometer measurements, Hu et al. (2015) estimated that IEPOX-OA makes a large fraction of the OA (between 17 to 36% in the U.S.) outside urban areas, in agreement with Budisulistiorini et al. (2015). In regions where aerosols are acidic, IEPOX-derived OA may be strongly dependent on the sulfate concentration, which acts as nucleophile and facilitates the ring-opening reaction of IEPOX and organosulfate formation (Nguyen et al., 2014; Xu et al., 2015).

In order to take into account the influence of the formation of organo-sulfates on OA properties, the surrogate products of the model are modified. As Mediterranean aerosol composition displays large concentrations of sulfate, isoprene oxidation products may lead to the formation of organo-sulfate.”.

4. Page 4 and 11: In this study, did the authors use VBS for SVOC/IVOC species? Did they account for fragmentation and non-volatile SOA? Details regarding this approach need to be added. Also, note that the Cholakian et al. (2017) paper is not available online. Was the treatment of fragmentation and non-volatile SOA similar or different than other papers, for example: [M. Shrivastava et al., 2015; M. Shrivastava et al., 2013].

In section 2.1 of the revised paper, a brief description of the approach used for SVOC/IVOC species is added. “As detailed in Couvidat et al. (2012), I/S-VOC emissions are emitted in three volatility classes (characterized by their saturation concentrations c^* : $\log(c^*) = -0.04, 1.93, 3.5$). Their ageing is represented through a single oxidation step, without NO_x -dependence, to produce species of lower volatilities ($\log(c^*) = -2.4, -0.064, 1.5$) but higher molecular weights.” The VBS approach is not used here, and fragmentation is not taken into account. The paper of Cholakian et al. (2017), which uses a VBS scheme with fragmentation and non-volatile SOA, is about to be published in ACPD.

5. Page 11: What are IVOC/POA emissions assumed in this study? Was oxygen added during aging? How was fragmentation treated? Do their aging mechanisms include NO_x -dependence?

IVOCs are considered in our emissions and are included as part of SVOCs. For clarity, the sentences “POA are assumed to be the particle phase of semi-volatile anthropogenic organic emissions (SVOC). Total SVOC emissions are estimated as detailed in Couvidat et al. (2012), by multiplying POA by a fixed value, and by assigning them to species of different volatilities. In this study, the ratio SVOC/POA is set to 2.5 (Kim et al., 2016; Zhu et al., 2016). Setting the ratio SVOC/POA to 1 has little impact on the organic concentrations” are replaced by “POA are assumed to be the particle phase of I/S-VOC. Total I/S-VOC emissions (gas and particle phases) are estimated as detailed in Couvidat et al. (2012), by multiplying POA by a fixed value, and by assigning them to species of different volatilities. In this study, the ratio I/S-VOC/POA is set to 2.5 (Kim et al., 2016; Zhu et al., 2016). Setting the ratio I/S-VOC/POA to 1 has little impact on the organic concentrations, as shown in Figure 2.” As now detailed in section 2.1, the ageing of I/S-VOC is represented through a simple approach: a single oxidation step, without NO_x -dependence, to produce species of lower volatilities but higher molecular weights (oxygen is added). As there is only one single oxidation step, fragmentation is not considered.

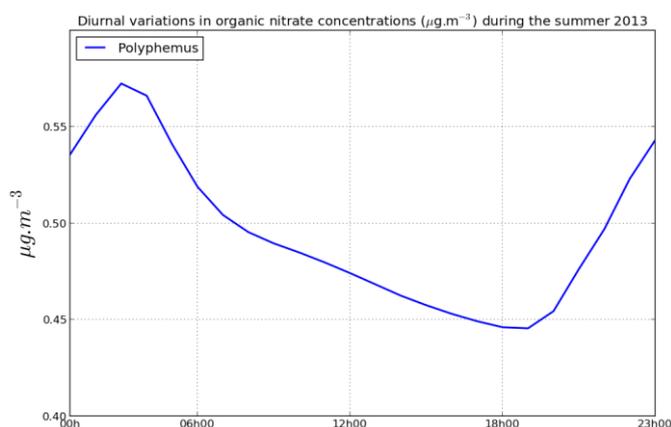
6. Page 6: Organic nitrates: How uncertain are the reaction mechanisms and reaction rates for organic nitrate formation? The authors mention organic nitrates were not measured during ChArMex. But, it would be useful to point out what are the most important routes for organic

nitrate chemistry mechanism: e.g. relative importance of nighttime TERPNRO2 versus daytime TERPRO2 reaction with NO. Also if this mechanism has been validated against other field campaigns in other papers, those references need to be added.

In the organic nitrate formation mechanism developed by Pye et al. (2015), the rate constants are from saprc07 (Carter et al. (2010), Hutzell et al. (2012)) except for the reaction with HO₂ which is calculated based on MCM for a species with 10 carbons (Jenkin et al. (1997), Saunders et al. (2003)). The yields of the reactions are taken from SAPRC07 (Carter et al. (2010)). The yields through the TERPNRO2 + NO and NO₃ pathways were calculated from estimates of the extent to which the radicals decompose to release NO₂ versus retain the nitrate group (Carter et al. (2010)). The yield from the reaction with HO₂ produced 100% hydroperoxide (consistent with MCM, (Jenkin et al. (1997), Saunders et al. (2003)). Therefore, it is not easy to determine lower and upper bounds of the rate constants and yields of the reactions. However, as pointed out to in Pye et al., (2015), there is a critical need for additional laboratory data when it comes to the organic nitrate sources (ozonolysis, photooxidation and chemical pathways that do not contain nitrogen). Besides, structure-dependant and pH-dependant hydrolysis rate constants and the resulting product volatility for a range of organic nitrates from biogenic VOCs oxidation.

Moreover, Pye et al. (2015) studied the formation of the organic nitrate within the framework of the Southern Oxidant and Aerosol Study (SOAS) campaign during the summer 2013 over the south-eastern region of the United States (a representative rural site (“Brent”, Centreville) in Alabaman using CMAQ model). In Pye et al. (2015), the monoterpene nitrate OA was predicted to be the highest in the south-eastern United States (>95%) and a good agreement was found between the simulated and observed OC and the gas-phase organic nitrates with a bias of -30% and 30% respectively.

The diurnal variation of the organic nitrate is shown in the figure below indicating that the night-time NO₃-oxidation might be the most relevant.



The point about the importance of night-time chemistry governing the organic nitrate formation is underlined in section 4.2 of the revised paper by adding:

“The route to organic particulate nitrate may essentially (but not exclusively) be active during the night as NO₃ efficiently photolyzes during the day and the production yields are more important during the night, and higher organic-nitrate concentrations are observed at night (Figure 5).”

7. Figure 4: What is contribution of SVOC/IVOC to evolution of OM:OC ratio and O:C ratio? I/S-VOC have very little impact on SOA concentrations and properties in summer. A

sensitivity study with a different I/S-VOC/POA ratio was performed and the Figure below is added to the paper to show the impact of different I/S-VOC emissions on OM concentrations.

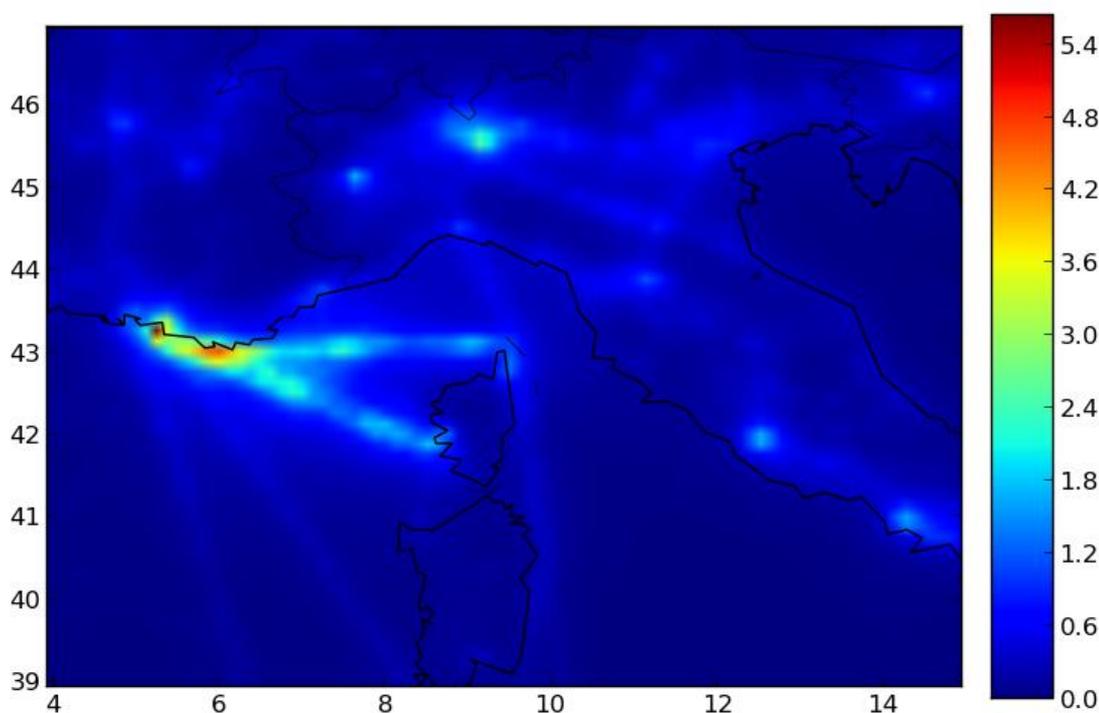


Figure 2. Relative difference (%) of OM1 concentrations simulated using the emission ratio I/S-VOC/POA = 2.5 and 1.

8. Page 14: Discussions on water soluble organics should acknowledge pathways other than organic nitrate to formation of water soluble species. For example, biomass burning sources (if significant), other SOA chemistry e.g. formation of organic salts, aqueous phase and cloud processing etc. See the recent review article on SOA [Shrivastava et al., 2017].

Aqueous processing is taken into account in our model, as the affinity with water of most of the surrogates is considered.

To better understand the aqueous treatment of aerosols, a brief description of the gas/particle partitioning of the surrogates is added in section 2.1 of the revised paper. The sentence “For organic aerosols, the partitioning is computed using SOAP (Couvidat and Sartelet, 2015), and bulk equilibrium is also assumed for SOA partitioning.” is replaced by “For organic aerosols, the gas/phase partitioning of the surrogates is computed using SOAP (Couvidat and Sartelet, 2015), and bulk equilibrium is also assumed for SOA partitioning. The gas/phase partitioning of hydrophobic surrogates is modelled following Pankow (1994), with absorption by the organic phase (hydrophobic surrogates). The gas/phase partitioning of hydrophilic surrogates is computed using the Henry’s law modified to extrapolate infinite dilution conditions to all conditions using an aqueous-phase partitioning coefficient, with absorption by the aqueous phase (hydrophilic organics, inorganics and water). Activity coefficients are computed with the thermodynamic model UNIFAC (UNIversal Functional group, Fredenslund et al., 1975).”

The influence of biomass burning may be low during the periods studied. Organic cloud processing is indeed not considered, although the impact during the summer time over the

Mediterranean domain may be relatively low. Interactions of organics/inorganics are partly considered here (inorganic provide a mass onto which hydrophilic surrogates may condense, but their interactions via activity coefficients are not). In the paper, the discussion shows that the influence of organic nitrate on the hydrophilic properties is high on 16 July compared to 30 July. The hydrophilic properties are indeed influenced by all the surrogates. The following sentences are added in the conclusion to acknowledge pathways that are not considered.

“There are other pathways and mechanisms that are not considered in the model, but that may change the concentrations and hydrophylicity of organics (Shrivastava et al., 2017). For example, salting effects (via activity coefficients) are not considered, although inorganics provide a mass onto which hydrophilic organic surrogates may condense. Furthermore, pathways such as the aging chemistry of VOCs and I/S-VOCs from biomass burning (wildfires) and organic cloud processing are not considered. However, these pathways may be relatively low during the studied periods.”

9. Page 20: Hydrolysis is mostly interpreted as a loss mechanism. But Pye et al. 2015 referred to it as pseudo-hydrolysis of organic nitrates that makes them non-volatile. Please clarify if this is what is being referred to.

Hydrolysis referred here to the pseudo-hydrolysis mechanism detailed in Pye et al. (2015). For clarity, in section 4.4, the sentence “Although this organic nitrate is assumed to be hydrophobic, it may have undergone hydrolysis and formed water soluble compounds.” is replaced by “Although this organic nitrate is assumed to be hydrophobic, it may have undergone hydrolysis resulting in nitric acid and nonvolatile secondary organic aerosol that may change the hydrophylicity of organics and the organic composition, as detailed in Pye et al. (2015).”

10. Hydrophylic properties could change not just due to the hydrophobicity of organic nitrates. It could point to other mechanisms and SOA pathways not considered in the model e.g. aqueous and cloud chemistry, other SOA pathways like organic salts, organic-inorganic interactions etc. It is important to make sure the model is getting the right answers for the right reasons.

Other mechanisms and SOA pathways that are not considered in the model, but may change the hydrophylicity of organics are pointed out to in section 4.4 of the revised paper as mentioned in the response of the comment 8.

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