

1 **Modelling winter organic aerosol at the European scale**
2 **with CAMx: evaluation and source apportionment with a**
3 **VBS parameterization based on novel wood burning smog**
4 **chamber experiments**

5 **Giancarlo Ciarelli¹, Sebnem Aksoyoglu¹, Imad El Haddad¹, Emily A. Bruns¹,**
6 **Monica Crippa², Laurent Poulain³, Mikko Äijälä⁴, Samara Carbone⁵, Evelyn**
7 **Freney⁶, Colin O'Dowd⁷, Urs Baltensperger¹ and André S. H. Prévôt¹**

8 [1]{Paul Scherrer Institute, Laboratory of Atmospheric Chemistry, 5232 Villigen PSI,
9 Switzerland}

10 [2]{European Commission, Joint Research Centre (JRC), Directorate for Energy, Transport
11 and Climate, Air and Climate Unit, Via E. Fermi 2749, I-21027 Ispra (VA), Italy}

12 [3]{Leibniz-Institute for Tropospheric Research (TROPOS), Permoserstr. 15, 04318 Leipzig,
13 Germany}

14 [4]{University of Helsinki, Department of Physics, Helsinki, Finland}

15 [5]{Institute of Physics, University of São Paulo, Rua do Matão Travessa R, 187, 05508-090
16 São Paulo, S.P., Brazil}

17 [6]{Laboratoire de Météorologie Physique (LaMP), CNRS/Université Blaise Pascal,
18 Clermont-Ferrand, France}

19 [7]{School of Physics and Centre for Climate & Air Pollution Studies, Ryan Institute,
20 National University of Ireland Galway, University Road, Galway, Ireland}

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23 Correspondence to: S. Aksoyoglu (sebnem.aksoyoglu@psi.ch)

24 **Abstract**

25 We evaluated a modified VBS (Volatility Basis Set) scheme to treat biomass burning-like
26 organic aerosol (BBOA) implemented in CAMx (Comprehensive Air Quality Model with
27 extensions). The updated scheme was parameterized with novel wood combustion smog
28 chamber experiments using a hybrid VBS framework that accounts for a mixture of wood

29 burning organic aerosol precursors and their further functionalization and fragmentation in the
30 atmosphere. The new scheme was evaluated for one of the winter EMEP intensive campaigns
31 (February-March 2009) against aerosol mass spectrometer (AMS) measurements performed
32 at 11 sites in Europe. We found a considerable improvement for the modelled organic aerosol
33 (OA) mass compared to our previous model application with the mean fractional bias (MFB)
34 reduced from -61% to -29%.

35 We performed model-based source apportionment studies and compared results against
36 positive matrix factorization (PMF) analysis performed on OA AMS data. Both model and
37 observations suggest that OA was mainly of secondary origin at almost all sites. Modelled
38 secondary organic aerosol (SOA) contributions to total OA varied from 32 to 88% (with an
39 average contribution of 62%) and absolute concentrations were generally under-predicted.
40 Modelled primary hydrocarbon-like organic aerosol (HOA) and primary biomass burning-like
41 aerosol (BBPOA) fractions contributed to a lesser extent (HOA from 3 to 30%, and BBPOA
42 from 1 to 39%) with average contributions of 13 and 25%, respectively. Modelled BBPOA
43 fractions was found to represent 12 to 64% of the total residential heating related OA, with
44 increasing contributions at stations located in the northern part of the domain.

45 Source apportionment studies were performed to assess the contribution of residential and
46 non-residential combustion precursors to the total SOA. Non-residential combustion and road
47 transportation sector contributed about 30-40% to SOA formation (with increasing
48 contributions at urban and near industrialized sites) whereas residential combustion (mainly
49 related to wood burning) contributed to a larger extent, around 60-70%. Contributions to OA
50 from residential combustion precursors in different volatility ranges were also assessed: our
51 results indicate that residential combustion gas-phase precursors in the semivolatile range
52 (SVOC) contributed from 6 to 30%, with higher contributions predicted at stations located in
53 the southern part of the domain. On the other hand, the oxidation products of higher volatility
54 precursors (the sum of IVOCs and VOCs) contribute from 15 to 38% with no specific
55 gradient among the stations.

56 Although the new parameterization leads to a better agreement between model results and
57 observations, it still under-predicts the SOA fraction suggesting that uncertainties in the new
58 scheme and other sources and/or formation mechanisms remain to be elucidated. Moreover, a
59 more detailed characterization of the semivolatile components of the emissions is needed.

60 1 Introduction

61 Organic aerosol (OA) comprises the main fraction of fine particulate matter (PM_{10}) (Jimenez et
62 al., 2009). Even though the sources of its primary fraction (primary organic aerosol, POA) are
63 nominally known, uncertainties remain in terms of the total emission fluxes annually released
64 into the troposphere (Kuenen et al., 2014). Moreover, the measured OA load largely exceeds
65 the emitted POA fractions at most measurement sites around the world. A secondary fraction
66 (SOA), formed from the condensation of oxidized gases with low-volatility on pre-existing
67 particles, is found to be the dominant fraction of OA (Crippa et al., 2014; Huang et al., 2014;
68 Jimenez et al., 2009). Such low-volatility products are produced in the atmosphere when
69 higher volatility organic gases are oxidized by ozone (O_3), hydroxyl (OH) radical and/or
70 nitrate (NO_3) radical. The physical and chemical processes leading to the formation of SOA
71 are numerous, e.g. oxidation and condensation, oligomerization or aqueous-phase formation,
72 and they are very uncertain and currently under debate (Hallquist et al., 2009; Tsigaridis et
73 al., 2014; Fuzzi et al., 2015; Woody et al., 2016). Moreover, the solubility of organic
74 compounds in water is also a crucial parameter affecting the life time of organic particles and
75 gases in the atmosphere (Hodzic et al., 2016).

76 Available long-term measurements might help in elucidating the composition and origin of
77 OA in different seasons. Canonaco et al. (2015) presented direct evidence for significant
78 changes in the SOA fingerprint between summer and winter from 13 months of OA
79 measurements conducted in Zürich using the aerosol chemical speciation monitor (ACSM).
80 Their results indicate that summer oxygenated OA mainly arises from biogenic precursors
81 whereas winter oxygenated OA is more strongly influenced by wood burning emissions.
82 Moreover, numerous ambient studies with aircraft of open biomass burning plumes do not
83 show a net increase in OA, despite observed oxidation (Cubison et al., 2011; Jolleys et al.,
84 2012). It is therefore necessary that the chemical transport models (CTMs) correctly
85 reproduce OA concentrations by taking into account all the uncertainties and variability of
86 observations.

87 Most of the CTMs today account for SOA formation from biogenic and anthropogenic high
88 volatility precursors such as terpenes, isoprene, xylene and toluene which have a saturation
89 concentration (C^*) higher than $10^6 \mu\text{g m}^{-3}$ (Aksoyoglu et al., 2011; Ciarelli et al., 2016a). A
90 few models also include intermediate volatility organic compounds (IVOCs) with a C^* of 10^3
91 - $10^6 \mu\text{g m}^{-3}$ and semivolatile organic compounds (SVOCs) with a C^* of $0.1 - 10^3 \mu\text{g m}^{-3}$ co-

92 emitted with POA (Bergström et al., 2012; Ciarelli et al., 2016a; Denier van der Gon et al.,
93 2015; Fountoukis et al., 2014; Tsimpidi et al., 2010; Woody et al., 2016). In these
94 applications, the volatility distributions of POA and IVOCs emissions are based on the study
95 of Robinson et al. (2007), where the IVOC mass is assumed to be 1.5 times the total organic
96 mass available in the semivolatile range.

97 The standard gridded emission inventories do not yet include SVOCs and their emissions are
98 still highly uncertain as their measurement is strongly affected by the method used (Lipsky
99 and Robinson, 2006). A recent study by Denier van der Gon et al. (2015) reported a new
100 residential wood burning emission inventory including SVOCs, where emissions are higher
101 by a factor of 2-3 on average than those in the EUCAARI inventory (Kulmala et al., 2011).
102 The new emission inventory was used in two CTMs (EMEP and PMCAMx) and it improved
103 the model performance for the total OA (Denier van der Gon et al., 2015). Ciarelli et al.
104 (2016a) showed that allowing for evaporation of primary organic particles as available in the
105 European emission inventories degraded the model performance for the total OA mass
106 (further under-predicted OA but the POA to SOA ratio in a better agreement with
107 measurements). In the same study, on the other hand, model performance improved when
108 volatility distribution that implicitly accounts for missing semivolatile material (increasing
109 POA emissions by a factor of 3) was deployed.

110 Various modelling studies were performed by increasing POA emissions by a factor of 3 to
111 compensate for the missing gaseous emissions based on partitioning theory predictions
112 (Ciarelli et al., 2016a; Fountoukis et al., 2014; Shrivastava et al., 2011; Tsimpidi et al., 2010).
113 Fig. S1 shows the partitioning of $\sim 1 \mu\text{g m}^{-3}$ of POA at different temperatures using the latest
114 available volatility distribution for biomass burning (May et al., 2013). The ratio between the
115 available gas and particle phase material in the semivolatile range is predicted to be roughly 3.
116 This implies that, in these applications, the new emitted organic mass (POA + SVOCs +
117 IVOCs) is 7.5 times higher than in original emissions (i.e., $\text{OM} = (3*\text{POA}) + (1.5*(3*\text{POA}))$)
118 which could be used as an indirect method to account for missing organic material in the
119 absence of more detailed gridded emission inventories.

120 Along with ambient measurement studies, novel wood burning smog chamber studies provide
121 more insight into wood burning SOA formation and the nature of its precursors. Bruns et al.
122 (2016) performed several wood-burning aging experiments in a $\sim 7 \text{ m}^3$ smog chamber. Using
123 proton-transfer-reaction mass spectrometry (PTR-MS) they characterized SOA precursors at

124 the beginning of each aging experiment and found that up to 80% of the observed SOA could
125 be explained with a collection of a few SOA precursors that are usually not accounted in
126 regional CTMs (e.g. cresol, phenol, naphthalene). Recently, we used those chamber data to
127 parameterize a hybrid volatility basis set (Ciarelli et al., 2016b). The results provided new
128 direct information regarding the amount of wood burning SOA precursors which could be
129 directly used in CTM applications in the absence of more refined wood burning emissions in
130 gridded inventories. The box-model application reproduced the chamber data with an error of
131 approximately 25% on the OA mass and 15% on the O:C ratio (Ciarelli et al., 2016b).

132 In the current study, the updated volatility basis set (VBS) parameterization was implemented
133 in the comprehensive air quality model with extensions (CAMx) model, and simulations were
134 performed in Europe for a winter period in February-March 2009. Results are compared with
135 previous simulations using the original VBS framework (Ciarelli et al., 2016a) and with
136 source apportionment data at eleven sites with different exposure characteristics, obtained
137 using PMF applied to AMS measurements (Crippa et al., 2014).

138 **2 Method**

139 **2.1 Regional modelling with CAMx**

140 The CAMx version 5.41 with VBS scheme (ENVIRON, 2011; Koo et al., 2014) was used in this
141 study to simulate an EMEP measurement campaign between 25 February and 26 March 2009
142 in Europe. The modelling method and input data were the same as those used in the
143 EURODELTA III (ED III) project, described in detail in Ciarelli et al. (2016a). The model
144 domain covers Europe with a horizontal resolution of $0.25^\circ \times 0.25^\circ$. Meteorological
145 parameters were calculated from ECMWF IFS (Integrated Forecast System) data at 0.2°
146 resolution. There were 33 terrain-following σ -levels from ~20 m above ground level (first
147 layer) up to about 350 hPa, as in the original IFS data. For the gas phase chemistry, the
148 Carbon Bond (CB05) mechanism (Yarwood, 2005). The ISORROPIA thermodynamic model
149 (Nenes et al., 1998) was used for the partitioning of inorganic aerosols (sulfate, nitrate,
150 ammonium, sodium and chloride). Aqueous sulfate and nitrate formation in cloud water was
151 calculated using the RADM algorithm (Chang et al., 1987). Formation and evolution of OA is
152 treated with a hybrid volatility basis set (VBS) that accounts for changes in volatility and O:C
153 ratio (Koo et al., 2014) with dilution and aging. Particle size distributions were treated with a
154 two static mode scheme (fine and coarse). The results presented in this study refer to the fine

155 fraction (PM_{2.5}). We parameterized the biomass burning sets based on chamber data as
156 described in Ciarelli et al. (2016b).

157 The anthropogenic emission inventory was made available for the ED III community team by
158 the National Institute for Industrial Environment and Risks (INERIS) at 0.25° x 0.25°
159 horizontal resolution. More information regarding the anthropogenic emission inventories are
160 available in Bessagnet et al. (2014, 2016) and Ciarelli et al. (2016a). Hourly emissions of
161 biogenic VOCs, such as monoterpenes, isoprene, sesquiterpenes, xylene and toluene, were
162 calculated using the Model of Emissions of Gases and Aerosols from Nature MEGANv2.1
163 (Guenther et al., 2012) for each grid cell in the model domain.

164 **2.2 Organic aerosol scheme**

165 The biomass burning organic aerosol scheme was constrained using recently available wood
166 burning smog chamber data (Bruns et al., 2016) as described in Ciarelli et al. (2016b). The
167 model deploys three different basis sets (Donahue et al., 2011) to simulate the emissions of
168 organics from biomass burning and their evolution in the atmosphere. The first set allocates
169 fresh emissions into five volatility bins with saturation concentrations ranging between 10⁻¹
170 and 10³ µg m⁻³ following the volatility distribution and enthalpy of vaporization proposed by
171 May et al. (2013). In order to include gas-phase organics in the semivolatile range in the
172 absence of more detailed inventory data, we used the approach of increasing the standard
173 emissions by a factor of 3 proposed by previous studies (Shrivastava et al., 2011; Tsimpidi et
174 al., 2010) which is also in line with the recent European study on the revision of the
175 residential wood combustion emissions (Denier van der Gon et al., 2015). This approach of
176 including the semivolatile compounds can be used until detailed emission inventories with
177 more realistic inter-country distribution of the emissions become available (e.g. Denier van
178 der Gon et al., 2015). The second set allocates oxidation products from SVOCs after shifting
179 the volatility by one order of magnitude. The third set allocates oxidation products from the
180 traditional VOCs and biogenic precursors (xylene, toluene, isoprene, monoterpenes and
181 sesquiterpenes) and from non-traditional SOA precursors retrieved from chamber data (~4.75
182 times the amount of organic material in the semivolatile range, Ciarelli et al., 2016b). Primary
183 and secondary semivolatile compounds react with OH in the gas-phase with a rate constant of
184 4×10⁻¹¹ cm³ molec⁻¹ s⁻¹ (Donahue et al., 2013), which decreases their saturation concentration
185 by one order of magnitude. This implies that also aging of biogenic products is implicitly
186 taken into account.

187 A reaction rate of $4 \times 10^{-11} \text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$ was also applied to the rest of the anthropogenic
188 sources (referred to as HOA) in order to be consistent among all the other anthropogenic
189 sources as already proposed by more recent studies for the range of saturation concentrations
190 used here (Donahue et al., 2013). No heterogeneous oxidation of organic particles or
191 oligomerization processes is included in the model. The new model parameterization
192 described in this study is referred to as VBS_BC_NEW throughout the paper to distinguish it
193 from the previous base case called VBS_BC as given in Ciarelli et al. (2016a). All the VBS
194 sets are listed in Table 1. More detailed on the VBS scheme can be found in Ciarelli et al.
195 (2016b) and Koo et al. (2014).

196 **2.3 Model evaluation**

197 The model results for the period between 25 February and 26 March 2009 were compared
198 with OA concentrations measured by AMS at 11 European sites. Modelled BBPOA, HOA
199 and SOA concentrations were compared with multi-linear engine 2 (ME-2) analysis
200 performed on AMS data (Paatero, 1999) using source finder (SoFi) (Canonaco et al., 2013;
201 Crippa et al., 2014). Elevated sites such as Montseny and Puy de Dôme were also included in
202 the analysis and modelled concentrations for these two sites were extracted from higher layers
203 in order to minimize the artefacts due to topography in a terrain-following coordinate system.
204 This was not the case in our previous application, where model OA concentrations were
205 extracted from the surface layer (Ciarelli et al., 2016a). We assumed OA emissions from
206 SNAP2 (emissions from non-industrial combustion plants in the Selected Nomenclature for
207 Air Pollution) and SNAP10 (emissions from agriculture, about 6% of POA in SNAP2), to be
208 representative of biomass burning emissions and thus comparable to the BBPOA PMF factor.
209 OA from all other SNAP categories were compared against HOA-like PMF factors.
210 Unfortunately, gridded emissions for SNAP2 include other emission sources (i.e., coal
211 burning which might be important in eastern European countries like Poland). We could not
212 resolve our emission inventory with sufficient detail to separate the contribution of coal for
213 these European sites (Crippa et al., 2014). Finally, the SOA fraction was compared to the
214 PMF-resolved oxygenated organic aerosol (OOA) fraction.

215 Statistics were reported in terms of mean bias (MB), mean error (ME), mean fractional bias
216 (MFB), mean fractional error (MFE) and coefficient of determination (R^2) (see Table S1 for
217 the definition of statistical parameters).

218 3 Results and discussions

219 3.1 Analysis of the modelled OA

220 Figure 1 shows the average modelled OA concentrations and surface temperature for the
221 period between 25 February and 26 March 2009. Temperatures were below 0°C in the north,
222 ranged 5-10°C in central Europe and were above 10°C in the southern part of the domain.
223 Model performance for surface temperature was evaluated within the ED III exercise and
224 found to be reproduced reasonably well, with a general under-prediction of around 1°C
225 (Bessagnet et al., 2014).

226 A clear spatial variability in the modelled OA concentrations is observed (Fig. 1). Predicted
227 OA concentrations were higher in eastern European countries (especially Romania and
228 southern Poland) as well as over northern Italy (8-10 $\mu\text{g m}^{-3}$ on average) whereas they were
229 lower in the northern part of the domain. A similar spatial distribution of OA concentrations
230 was also reported by Denier van der Gon et al. (2015) using the EMEP model. Relatively high
231 OA concentrations over the Mediterranean Sea are mainly of secondary origin due to
232 enhanced photochemical activity (more details are found in Section 3.2). In addition, the
233 reduced deposition efficiency over water leads to higher OA levels.

234 The scatter plots in Fig. 2 show the modelled (VBS_BC_NEW) versus measured daily
235 average OA concentrations at 11 sites in Europe together with the results from our previous
236 model application (VBS_BC, Ciarelli et al., 2016a) for comparison. The modified VBS
237 scheme (VBS_BC_NEW) predicts higher OA concentrations compared to our previous study
238 using the original scheme (VBS_BC) (~ 60% more OA on average at all sites). Statistical
239 parameters improved significantly (Table 2); the mean fractional bias MFB decreased from -
240 61% in VBS_BC to -29% in VBS_BC_NEW and the model performance criteria were met
241 (Boylan and Russell, 2006). The coefficient of determination remained almost unchanged for
242 OA in the VBS_BC_NEW case ($R^2=0.58$) compared to VBS_BC ($R^2=0.57$) indicating that the
243 original model was able to similarly capture the OA daily variation, but not its magnitude.
244 Improvements in the modelled SOA fraction were also observed using the original VBS
245 approach (Koo et al., 2014) when aging of the biomass burning vapours were taken into
246 account (Fig. S4). The majority of the stations show an $R^2 \geq 0.4$. Lower values were found for
247 the elevated sites of Montseny and Puy de Dome ($R^2=0.17$ and $R^2=0.13$, respectively) and
248 also at the Helsinki site ($R^2=0.06$). In spite of the improvements with respect to earlier studies,

249 modelled OA is still lower than measured (mean bias MB from $-0.1 \mu\text{g m}^{-3}$ up to $-3.1 \mu\text{g m}^{-3}$)
250 at most of the sites, with only a slight overestimation at a few locations (MB from $0.3 \mu\text{g m}^{-3}$
251 up to $0.9 \mu\text{g m}^{-3}$).

252 The observed OA gradient among the 11 sites was reproduced very well ($R^2 = 0.72$) (Fig. 3).
253 Both measured and modelled OA concentrations were highest in Barcelona. Other sites with
254 concentrations greater than $2 \mu\text{g m}^{-3}$ were Payerne, Helsinki, Vavihill and Montseny.
255 Barcelona and Helsinki are both classified as urban stations, which justifies the higher OA
256 loads due to the anthropogenic activities (e.g. traffic, cooking and heating). Anthropogenic
257 activities in the area of Barcelona could also affect OA concentrations at Montseny which is
258 about 40 km away. In the case of Payerne and Vavihill, the relatively high OA concentrations
259 might be due to residential heating, where wood is largely used as a combustion fuel during
260 cold periods (Denier van der Gon et al., 2015). For Chilbolton, located not far from London,
261 this might not be the case: the fuel wood usage in the UK is the lowest in Europe (Denier van
262 der Gon et al., 2015). Ots et al. (2016) suggested the possibility of missing diesel-related
263 IVOCs emissions, which might be an important source of SOA in those regions. However,
264 other studies reported substantial contribution from solid fuel combustion to OA (Young et
265 al., 2015). In this case, it might be that difficulties in reproducing the OA concentration are
266 mainly related to the relatively complex area of the site (i.e., close to the English Channel).
267 An evaluation of diurnal variations of HOA and SOA concentrations for this site showed a
268 consistent under-prediction of both components (Fig. S2).

269 **3.2 Analysis of the OA components**

270 The predicted POA spatial distribution (Fig. 4) resembles the residential heating emission
271 pattern of different countries (Bergström et al., 2012). The highest POA concentrations were
272 predicted in east European countries, France, Portugal and in northern Italy ($\sim 3\text{-}5 \mu\text{g m}^{-3}$)
273 whereas they were less than $1 \mu\text{g m}^{-3}$ in the rest of the model domain. Very low OA
274 concentrations in Sweden were already shown by previous European studies. Bergström et al.
275 (2012) reported that emissions of organic carbon (OC) from the residential heating sector in
276 Sweden were lower than those in Norway by a factor of 14 in spite of its higher wood usage
277 by 60%. This indicates an underestimation of emissions from residential heating in the
278 emission inventory. The spatial distribution of SOA concentrations, on the other hand, is more
279 widespread with a visible north to south gradient (Fig. 4). Higher SOA concentration were
280 predicted close to primary emission sources (e.g. Poland, Romania, Po Valley and Portugal)

281 but also in most of the countries below 50° latitude and over the Mediterranean Sea where
282 higher OH concentration, reduced deposition efficiency and high contribution from long-
283 range transport are expected (average concentrations around 3-4 $\mu\text{g m}^{-3}$).

284 Comparison of results from this study (VBS_BC_NEW) with the earlier one (VBS_BC,
285 Ciarelli et al., 2016a) suggests that the new VBS scheme predicts higher SOA concentrations
286 by about a factor of 3 (Fig. 5) and improves the model performance when comparing assessed
287 OOA from measurements with modelled SOA (Table 4). POA concentrations, on the other
288 hand, are clustered below 1 $\mu\text{g m}^{-3}$ except in Barcelona (Fig. 5), showing an $R^2=0.36$ (Table
289 3). Although predicted POA concentrations at Barcelona were lower than the measurements,
290 MFB=-47% and MFE=69% were still in the range for acceptable performance criteria (MFE
291 $\leq +75\%$ and $-60 < \text{MFB} < +60\%$, Boylan and Russell, 2006). On the other hand, the model
292 over-predicted the POA concentrations at Hyytiälä (MFB=131% and MFE=131%), Helsinki
293 (MFB=95% and MFE=100%) and Cabauw (MFB=76% and MFE=86%) mainly due to the
294 overestimated BBPOA fraction as seen in Fig. 6.

295 At most of the sites, OA was dominated by SOA (Fig. 6 and Fig. 7) which was
296 underestimated in particular at Chilbolton, Melpitz and Vavihill (Table 4). As already
297 mentioned, the under-prediction of SOA concentrations might be attributed to missing SOA
298 precursors or uncertainties in SOA formation mechanisms and removal processes. On the
299 other hand, the remote station of Mace Head showed a positive bias for SOA (MFB = 30%),
300 even though model and measurement concentrations were very similar (0.54 and 0.35 $\mu\text{g m}^{-3}$,
301 respectively), which could be attributed to an overestimated contribution from the boundaries.
302 The relatively small positive bias at the two elevated sites, Montseny and Puy de Dome (MFB
303 = 4% and 17%, respectively), is most likely the result of difficulties in capturing the inversion
304 layer, as confirmed by the over-prediction of other PM species at these sites (Fig. S3).

305 Mostly traffic-related HOA was underestimated at the urban site Barcelona (Table S2, Fig. 6),
306 with the model not able to reproduce the diurnal variation of HOA at this urban site likely due
307 to poorly reproduced meteorological conditions or too much dilution during day time in the
308 model (Fig. S2). The under-prediction of the HOA fraction is consistent with our previous
309 study where model evaluation for NO_2 revealed a systematic under-estimation of the
310 modelled concentration (Ciarelli et al., 2016a). The coarse resolution of the domain (0.25° x
311 0.25°) may result in too low emissions especially at urban sites. In addition, the gridded
312 emission inventories still represent a large source of uncertainties for CTM applications. The

313 majority of the NO_x (NO+NO₂) emissions in Europe arises from the transportation sector
314 (SNAP7), which might have much larger uncertainties than previously thought (Vaughan et
315 al., 2016). An evaluation of planetary boundary layer height (PBLH) within the EDIII shows
316 that although the PBLH was quite well represented in general in the ECMWF IFS
317 meteorological fields, CAMx tends to underestimate the night-time minima and to
318 overestimate some daytime peaks. The other urban site considered in this study is Helsinki. In
319 this case, HOA concentrations were over-predicted, as seen in Figs. 6 and S2, which might
320 indicate missing dispersion processes in the model or under-estimated dilution.

321 The modelled BBPOA fraction on the other hand was generally overpredicted as in our
322 previous application (Table S4), with an average MFB of 50% (Table S3, Figs. 6-7), which
323 might arise from various factors: 1) In the model, POA emissions from SNAP2 and SNAP10
324 are assumed to be representative of BBPOA emissions which might not be the case for all
325 European countries (other non-wood fuels such as coal, which is allocated to SNAP2 category
326 and could not be separated in this study), 2) The under-prediction of the modelled surface
327 temperature (Bessagnet et al., 2014) will directly influence the partitioning of organic material
328 in the semivolatile range, favouring freshly emitted organic material to condense more to the
329 particle phase, 3) Uncertainties in the adopted volatility distributions and/or in the oxidation
330 processes of semivolatile organic vapours, 4) The simplistic way of accounting for the
331 semivolatile part of primary emissions might lead, in some areas, to the double counting of
332 such compounds 5) Uncertainties in the retrieved BBPOA fraction from PMF analysis.

333 The temporal variability of OA concentrations was reproduced quite well (Fig. 8); the
334 magnitudes of only a few (Vavihill, Chilbolton and Barcelona) were underestimated. Diurnal
335 variations of HOA, BBPOA and SOA components at the rural-background sites suggest that
336 the model was able to reproduce the relatively flat profile of the measured SOA and the
337 increased BBPOA concentrations at night (Fig. 9). On the other hand, there was a slight
338 underestimation of HOA during the day, especially around noon, possibly as a result of too
339 much dilution in the model.

340 In our previous application, we performed a sensitivity study with increased biogenic and
341 residential heating emissions by a factor of two (Ciarelli et al., 2016a). While the model was
342 rather insensitive to the increased biogenic emissions during winter periods, a substantial
343 increase in the OA concentrations was observed when emissions from residential heating
344 were doubled. The model with doubled emissions from residential heating

345 (VBC_BC_2xBBOA), overestimated the POA fraction at most of the sites (Fig. 10) with
346 smaller effects on SOA, even though a better closure was achieved between modelled and
347 observed OA. The results of the simulations using the new parameterization
348 (VBC_BC_NEW), on the other hand, were closer to the measurement data especially for the
349 SOA fraction (Fig. 10).

350 **3.3 Residential versus non-residential combustion precursors**

351 More detailed source apportionment studies were performed in order to assess the importance
352 of residential and non-residential combustion precursors for OA and SOA. The upper panel in
353 Fig. 11 shows the relative contributions to SOA from residential and non-residential
354 combustion precursors. The model results indicate that non-residential combustion and
355 transportation precursors contribute to about 30-40 % of the SOA formation (with increasing
356 contribution at urban and near-industrialized sites) whereas residential combustion (mainly
357 related to wood burning) contributes to a larger extent, i.e., around 60-70%. The residential
358 combustion precursors were further apportioned to semivolatile and higher volatility
359 precursors (Fig. 11, lower panel). In particular, SVOC precursors exhibit a south-to-north
360 gradient with increasing contribution to the residential heating related OA for stations located
361 in the southern part of the domain (maximum and minimum contributions of 42 and 17% in
362 Montseny and Hyytiälä, respectively). Such a gradient also reflects the effect of temperature
363 on the partitioning of semivolatile organic material: the lower temperatures in the northern
364 part of the domain will reduce the saturation concentration of the organic compounds
365 allowing primary organic material to favour the particle phase and reducing the amount of
366 SVOCs available that could act as SOA precursors. In the southern part of the domain, where
367 more OH is available, the higher temperature will favour more organic material in the
368 semivolatile range to reside in the gas-phase, rendering it available for oxidation. On the other
369 hand, no south-to-north gradient was predicted for the SOA formed from the higher volatility
370 class of precursors. Source apportionment for different volatilities classes of the non-
371 residential and transportation sectors is currently not implemented for this model application.
372 Since biogenic SOA is included in the same set as the biomass burning (set3) for this model
373 application, we performed a sensitivity test with no SOA formation from biogenic precursors
374 (where the reactions of isoprene, monoterpene and sesquiterpene with OH, O₃ and NO₃ were
375 turned off). Our results indicated that for this period, biogenic precursors contribute to SOA to
376 a lesser extent (5-20%) than the anthropogenic ones, with higher contributions at southern

377 stations consistent with higher temperatures, and consequently more biogenic emissions
378 compared to the northern stations (Fig. S5). The most predominant source was still predicted
379 to be anthropogenic. Snow cover for March 2009 as retrieved from the TERRA/MODIS
380 revealed that larger parts of the Scandinavian countries were almost completely covered with
381 snow (Fig. S6), partially suppressing the emission of biogenic precursors and in line with very
382 low contribution predicted from biogenic sources in Helsinki and Hyytiälä. Comparison of
383 SOA from VBS_BC_NEW and the sensitivity test with no biogenic SOA formation showed
384 similar improvement with respect to VBS_BC, with differences occurring mainly in the
385 southern stations of Barcelona and Montseny (Fig. S7).

386 A comprehensive summary of the contribution to the total OA from all the sources (i.e. HOA,
387 BBPOA, residential combustion semivolatile precursors, residential combustion higher
388 volatility precursors and non-residential combustion precursors) is shown in Fig. 12 at each of
389 the measurement sites. Residential combustion precursors in the semivolatile range
390 contributed from 6 to 30% whereas higher volatility compounds contributed to a larger extent,
391 i.e. from 15 to 38%. SOA from non-residential combustion precursors contributed from 10 to
392 37% to the total OA. The primary sources HOA and BBPOA contributed from 3 to 30% and
393 1-39%, respectively. These results lead to the conclusion that the overall contribution of
394 residential combustion to OA concentrations in Europe varies between 52% at stations in the
395 UK and 75-76% at stations in Scandinavia.

396 **Conclusion**

397 This study aims to evaluate recent VBS parameterizations in commonly used CTMs and to
398 underline the importance of taking into account updated and more detailed SOA schemes as
399 new ambient and chamber measurements elucidate the high complexity and strong variability
400 of OA. In this context, a new VBS parameterization (based on recent wood burning
401 experiments) implemented in CAMx was evaluated against high-resolution AMS
402 measurements at 11 sites in Europe during February-March 2009, one of the winter EMEP
403 intensive measurement campaigns. Results obtained from this study were compared with
404 those from our earlier work in which the original VBS scheme in CAMx was applied. A
405 detailed source apportionment for the organic aerosol (OA) fraction was discussed. This study
406 provided the following outcome:

- 407 - A considerable improvement was found for the modelled OA concentrations
408 compared to our previous studies mainly due to the improved secondary organic

409 aerosol (SOA) performance. The average bias for the 11 AMS sites decreased by
410 about 60% although the model still underestimates the SOA fraction.

411 - Both model and PMF source apportionment based on measurements suggested that
412 OA was mainly of secondary origin with smaller primary contribution, with primary
413 contribution of 13 and 25% for HOA and BBPOA, respectively. Predicted HOA
414 concentrations were in the range of those retrieved from the PMF analysis at most of
415 the sites except at the urban Barcelona site which could be related to the uncertainties
416 in emissions or too much dilution in the model. On the other hand, the modelled
417 BBPOA was higher than the measurements at several stations indicating the need for
418 further studies on residential heating emissions, their volatility distribution and
419 oxidation pathway of the semivolatile organic gases. In addition, more detailed
420 emission inventories are needed to characterize the semivolatile components better, as
421 proposed by Denier van der Gon et al. (2015).

422 - Emissions from the residential heating sector (SNAP2) largely influenced the OA
423 composition. The modeled primary BBPOA fraction contributed from 46% to 77% of
424 the total primary organic fraction (POA), with an average contribution of 65%. Non-
425 residential combustion and transportation precursors contributed about 30-40% to
426 SOA (with increasing contribution at urban and near-industrialized sites) whereas
427 residential combustion (mainly related to wood burning) contributes to a larger extent,
428 ~ 60-70%. Moreover, the contribution to OA from residential combustion precursors
429 in different range of volatilities was also investigated: residential combustion gas-
430 phase precursors in the semivolatile range contributed from 6 to 30% with a positive
431 south-to-north gradient. On the other hand, higher volatility residential combustion
432 precursors contributed from 15 to 38% showing no specific gradient among the
433 stations.

434 - Model simulations performed with and without biogenic SOA formation revealed that,
435 for this period, biogenic SOA contributed only to a small extent to the total SOA (5-
436 20%), with an increasing gradient from north to south.

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468 **References**

469 Aksoyoglu, S., Keller, J., Barmadimos, I., Oderbolz, D., Lanz, V. A., Prévôt, A. S. H. and
470 Baltensperger, U.: Aerosol modelling in Europe with a focus on Switzerland during summer
471 and winter episodes, *Atmos. Chem. Phys.*, 11 (14), 7355–7373, doi:10.5194/acp-11-7355-
472 2011, 2011.

473 Bergström, R., Denier van der Gon, H. A. C., Prévôt, A. S. H., Yttri, K. E. and Simpson, D.:
474 Modelling of organic aerosols over Europe (2002–2007) using a volatility basis set (VBS)
475 framework: application of different assumptions regarding the formation of secondary organic
476 aerosol, *Atmos. Chem. Phys.*, 12 (18), 8499–8527, doi:10.5194/acp-12-8499-2012, 2012.

477 Bessagnet, B., Colette, A., Meleux, F., Rouïl, L., Ung, A., Favez, O., Cuvelier, C., Thunis, P.,
478 Tsyro, S., Stern, R., Manders, A., Kranenburg, R., Aulinger, A., Bieser, J., Mircea, M.,
479 Briganti, A., Cappelletti, A., Calori, G., Finardi, S., Silibello, C., Ciarelli, G., Aksoyoglu, S.,
480 Prévôt, A., Pay, M. T., Baldasano, J. M., García Vivanco, M., Garrido, J. L., Palomino, I.,
481 Martín, F., Pirovano, G., Roberts, P., Gonzalez, L., White, L., Menut, L., Dupont, J. C.,
482 Carnevale, C. and Pederzoli, A.: The EURODELTA III exercise – Model evaluation with
483 observations issued from the 2009 EMEP intensive period and standard measurements in
484 Feb/Mar 2009, 2014.

485 Boylan, J. W. and Russell, A. G.: PM and light extinction model performance metrics, goals,
486 and criteria for three-dimensional air quality models, *Atmos. Environ.*, 40 (26), 4946–4959,
487 doi:10.1016/j.atmosenv.2005.09.087, 2006.

488 Bruns, E. A., El Haddad, I., Slowik, J. G., Kilic, D., Klein, F., Baltensperger, U. and Prévôt,
489 A. S. H.: Identification of significant precursor gases of secondary organic aerosols from
490 residential wood combustion, *Sci. Rep.*, 6, 27881, doi:10.1038/srep27881, 2016.

491 Canonaco, F., Crippa, M., Slowik, J. G., Baltensperger, U. and Prévôt, A. S. H.: SoFi, an
492 IGOR-based interface for the efficient use of the generalized multilinear engine (ME-2) for
493 the source apportionment: ME-2 application to aerosol mass spectrometer data, *Atmos. Meas.*
494 *Tech.*, 6 (12), 3649–3661, doi:10.5194/amt-6-3649-2013, 2013.

495 Canonaco, F., Slowik, J. G., Baltensperger, U. and Prévôt, A. S. H.: Seasonal differences in
496 oxygenated organic aerosol composition: implications for emissions sources and factor
497 analysis, *Atmos. Chem. Phys.*, 15 (12), 6993–7002, doi:10.5194/acp-15-6993-2015, 2015.

498 Chang, J. S., Brost, R. A., Isaksen, I. S. A., Madronich, S., Middleton, P., Stockwell, W. R.
499 and Walcek, C. J.: A three-dimensional Eulerian acid deposition model: Physical concepts

500 and formulation, *J. Geophys. Res. Atmospheres*, 92 (D12), 14681–14700,
501 doi:10.1029/JD092iD12p14681, 1987.

502 Ciarelli, G., Aksoyoglu, S., Crippa, M., Jimenez, J.-L., Nemitz, E., Sellegri, K., Äijälä, M.,
503 Carbone, S., Mohr, C., O'Dowd, C., Poulain, L., Baltensperger, U. and Prévôt, A. S. H.:
504 Evaluation of European air quality modelled by CAMx including the volatility basis set
505 scheme, *Atmos. Chem. Phys.*, 16 (16), 10313–10332, doi:10.5194/acp-16-10313-2016,
506 2016a.

507 Ciarelli, G., El Haddad, I., Bruns, E., Aksoyoglu, S., Möhler, O., Baltensperger, U. and
508 Prévôt, A. S. H.: Constraining a hybrid volatility basis set model for aging of wood burning
509 emissions using smog chamber experiments, *Geosci. Model Dev.*, accepted, 2016b.

510 Crippa, M., Canonaco, F., Lanz, V. A., Äijälä, M., Allan, J. D., Carbone, S., Capes, G.,
511 Ceburnis, D., Dall'Osto, M., Day, D. A., DeCarlo, P. F., Ehn, M., Eriksson, A., Freney, E.,
512 Hildebrandt Ruiz, L., Hillamo, R., Jimenez, J. L., Junninen, H., Kiendler-Scharr, A.,
513 Kortelainen, A.-M., Kulmala, M., Laaksonen, A., Mensah, A. A., Mohr, C., Nemitz, E.,
514 O'Dowd, C., Ovadnevaite, J., Pandis, S. N., Petäjä, T., Poulain, L., Saarikoski, S., Sellegri,
515 K., Swietlicki, E., Tiitta, P., Worsnop, D. R., Baltensperger, U. and Prévôt, A. S. H.: Organic
516 aerosol components derived from 25 AMS data sets across Europe using a consistent ME-2
517 based source apportionment approach, *Atmos. Chem. Phys.*, 14 (12), 6159–6176,
518 doi:10.5194/acp-14-6159-2014, 2014.

519 Cubison, M. J., Ortega, A. M., Hayes, P. L., Farmer, D. K., Day, D., Lechner, M. J., Brune,
520 W. H., Apel, E., Diskin, G. S., Fisher, J. A., Fuelberg, H. E., Hecobian, A., Knapp, D. J.,
521 Mikoviny, T., Riemer, D., Sachse, G. W., Sessions, W., Weber, R. J., Weinheimer, A. J.,
522 Wisthaler, A. and Jimenez, J. L.: Effects of aging on organic aerosol from open biomass
523 burning smoke in aircraft and laboratory studies, *Atmos. Chem. Phys.*, 11 (23), 12049–12064,
524 doi:10.5194/acp-11-12049-2011, 2011.

525 Denier van der Gon, H. A. C., Bergström, R., Fountoukis, C., Johansson, C., Pandis, S. N.,
526 Simpson, D. and Visschedijk, A. J. H.: Particulate emissions from residential wood
527 combustion in Europe – revised estimates and an evaluation, *Atmos. Chem. Phys.*, 15 (11),
528 6503–6519, doi:10.5194/acp-15-6503-2015, 2015.

529 Donahue, N. M., Epstein, S. A., Pandis, S. N. and Robinson, A. L.: A two-dimensional
530 volatility basis set: 1. organic-aerosol mixing thermodynamics, *Atmos. Chem. Phys.*, 11 (7),
531 3303–3318, doi:10.5194/acp-11-3303-2011, 2011.

532 Donahue, N. M., Chuang, W., Epstein, S. A., Kroll, J. H., Worsnop, D. R., Robinson, A. L.,
533 Adams, P. J. and Pandis, S. N.: Why do organic aerosols exist? Understanding aerosol
534 lifetimes using the two-dimensional volatility basis set, *Environ. Chem.*, 10 (3), 151,
535 doi:10.1071/EN13022, 2013.

536 ENVIRON: User's Guide, Comprehensive Air Quality Model with Extensions (CAMx),
537 Version 5.40, Environ International Corporation, California, 2011.

538 Fountoukis, C., Megaritis, A. G., Skyllakou, K., Charalampidis, P. E., Pilinis, C., Denier van
539 der Gon, H. A. C., Crippa, M., Canonaco, F., Mohr, C., Prévôt, A. S. H., Allan, J. D., Poulain,
540 L., Petäjä, T., Tiitta, P., Carbone, S., Kiendler-Scharr, A., Nemitz, E., O'Dowd, C., Swietlicki,
541 E. and Pandis, S. N.: Organic aerosol concentration and composition over Europe: insights
542 from comparison of regional model predictions with aerosol mass spectrometer factor
543 analysis, *Atmos. Chem. Phys.*, 14 (17), 9061–9076, doi:10.5194/acp-14-9061-2014, 2014.

544 Grieshop, A. P., Logue, J. M., Donahue, N. M. and Robinson, A. L.: Laboratory investigation
545 of photochemical oxidation of organic aerosol from wood fires 1: measurement and
546 simulation of organic aerosol evolution, *Atmos. Chem. Phys.*, 9 (4), 1263–1277,
547 doi:10.5194/acp-9-1263-2009, 2009.

548 Guenther, A. B., Jiang, X., Heald, C. L., Sakulyanontvittaya, T., Duhl, T., Emmons, L. K. and
549 Wang, X.: The Model of Emissions of Gases and Aerosols from Nature version 2.1
550 (MEGAN2.1): an extended and updated framework for modeling biogenic emissions, *Geosci.*
551 *Model Dev.*, 5 (6), 1471–1492, doi:10.5194/gmd-5-1471-2012, 2012.

552 Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M.,
553 Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H.,
554 Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A.,
555 Maenhaut, W., McFiggans, G., Mentel, T. F., Monod, A., Prévôt, A. S. H., Seinfeld, J. H.,
556 Surratt, J. D., Szmigielski, R. and Wildt, J.: The formation, properties and impact of
557 secondary organic aerosol: current and emerging issues, *Atmos. Chem. Phys.*, 9 (14), 5155–
558 5236, doi:10.5194/acp-9-5155-2009, 2009.

559 Heald, C. L., Kroll, J. H., Jimenez, J. L., Docherty, K. S., DeCarlo, P. F., Aiken, A. C., Chen,
560 Q., Martin, S. T., Farmer, D. K. and Artaxo, P.: A simplified description of the evolution of
561 organic aerosol composition in the atmosphere, *Geophys. Res. Lett.*, 37 (8), n/a-n/a,
562 doi:10.1029/2010GL042737, 2010.

563 Hodzic, A., Kasibhatla, P. S., Jo, D. S., Cappa, C. D., Jimenez, J. L., Madronich, S., and Park,
564 R. J.: Rethinking the global secondary organic aerosol (SOA) budget: stronger production,
565 faster removal, shorter lifetime, *Atmos. Chem. Phys.*, 16, 7917-7941, doi:10.5194/acp-16-
566 7917-2016, 2016.

567 Huang, R.-J., Zhang, Y., Bozzetti, C., Ho, K.-F., Cao, J.-J., Han, Y., Daellenbach, K. R.,
568 Slowik, J. G., Platt, S. M., Canonaco, F., Zotter, P., Wolf, R., Pieber, S. M., Bruns, E. A.,
569 Crippa, M., Ciarelli, G., Piazzalunga, A., Schwikowski, M., Abbaszade, G., Schnelle-Kreis,
570 J., Zimmermann, R., An, Z., Szidat, S., Baltensperger, U., Haddad, I. E. and Prévôt, A. S. H.:
571 High secondary aerosol contribution to particulate pollution during haze events in China,
572 *Nature*, 514 (7521), 218–222, doi:10.1038/nature13774, 2014.

573 Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prevot, A. S. H., Zhang, Q., Kroll, J. H.,
574 DeCarlo, P. F., Allan, J. D., Coe, H., Ng, N. L., Aiken, A. C., Docherty, K. S., Ulbrich, I. M.,
575 Grieshop, A. P., Robinson, A. L., Duplissy, J., Smith, J. D., Wilson, K. R., Lanz, V. A.,
576 Hueglin, C., Sun, Y. L., Tian, J., Laaksonen, A., Raatikainen, T., Rautiainen, J., Vaattovaara,
577 P., Ehn, M., Kulmala, M., Tomlinson, J. M., Collins, D. R., Cubison, M. J., Dunlea, E. J.,
578 Huffman, J. A., Onasch, T. B., Alfarra, M. R., Williams, P. I., Bower, K., Kondo, Y.,
579 Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Salcedo, D., Cottrell,
580 L., Griffin, R., Takami, A., Miyoshi, T., Hatakeyama, S., Shimono, A., Sun, J. Y., Zhang, Y.
581 M., Dzepina, K., Kimmel, J. R., Sueper, D., Jayne, J. T., Herndon, S. C., Trimborn, A. M.,
582 Williams, L. R., Wood, E. C., Middlebrook, A. M., Kolb, C. E., Baltensperger, U. and
583 Worsnop, D. R.: Evolution of organic aerosols in the atmosphere, *Science*, 326 (5959), 1525–
584 1529, doi:10.1126/science.1180353, 2009.

585 Jolleys, M. D., Coe, H., McFiggans, G., Capes, G., Allan, J. D., Crosier, J., Williams, P. I.,
586 Allen, G., Bower, K. N., Jimenez, J. L., Russell, L. M., Grutter, M. and Baumgardner, D.:
587 Characterizing the Aging of Biomass Burning Organic Aerosol by Use of Mixing Ratios: A
588 Meta-analysis of Four Regions, *Environ. Sci. Technol.*, 46 (24), 13093–13102,
589 doi:10.1021/es302386v, 2012.

590 Koo, B., Knipping, E. and Yarwood, G.: 1.5-Dimensional volatility basis set approach for
591 modeling organic aerosol in CAMx and CMAQ, *Atmos. Environ.*, 95, 158–164,
592 doi:10.1016/j.atmosenv.2014.06.031, 2014.

593 Kuenen, J. J. P., Visschedijk, A. J. H., Jozwicka, M. and Denier van der Gon, H. A. C.: TNO-
594 MACC_II emission inventory; a multi-year (2003–2009) consistent high-resolution European
595 emission inventory for air quality modelling, *Atmos. Chem. Phys.*, 14 (20), 10963–10976,
596 doi:10.5194/acp-14-10963-2014, 2014.

597 Kulmala, M., Asmi, A., Lappalainen, H. K., Baltensperger, U., Brenguier, J.-L., Facchini, M.
598 C., Hansson, H.-C., Hov, Ø., O’Dowd, C. D., Pöschl, U., Wiedensohler, A., Boers, R.,
599 Boucher, O., de Leeuw, G., Denier van der Gon, H. A. C., Feichter, J., Krejci, R., Laj, P.,
600 Lihavainen, H., Lohmann, U., McFiggans, G., Mentel, T., Pilinis, C., Riipinen, I., Schulz, M.,
601 Stohl, A., Swietlicki, E., Vignati, E., Alves, C., Amann, M., Ammann, M., Arabas, S., Artaxo,
602 P., Baars, H., Beddows, D. C. S., Bergström, R., Beukes, J. P., Bilde, M., Burkhardt, J. F.,
603 Canonaco, F., Clegg, S. L., Coe, H., Crumeyrolle, S., D’Anna, B., Decesari, S., Gilardoni, S.,
604 Fischer, M., Fjaeraa, A. M., Fountoukis, C., George, C., Gomes, L., Halloran, P., Hamburger,
605 T., Harrison, R. M., Herrmann, H., Hoffmann, T., Hoose, C., Hu, M., Hyvärinen, A., Hörrak,
606 U., Iinuma, Y., Iversen, T., Josipovic, M., Kanakidou, M., Kiendler-Scharr, A., Kirkevåg, A.,
607 Kiss, G., Klimont, Z., Kolmonen, P., Komppula, M., Kristjánsson, J.-E., Laakso, L.,
608 Laaksonen, A., Labonnote, L., Lanz, V. A., Lehtinen, K. E. J., Rizzo, L. V., Makkonen, R.,
609 Manninen, H. E., McMeeking, G., Merikanto, J., Minikin, A., Mirme, S., Morgan, W. T.,
610 Nemitz, E., O’Donnell, D., Panwar, T. S., Pawlowska, H., Petzold, A., Pienaar, J. J., Pio, C.,
611 Plass-Duelmer, C., Prévôt, A. S. H., Pryor, S., Reddington, C. L., Roberts, G., Rosenfeld, D.,
612 Schwarz, J., Seland, Ø., et al.: General overview: European Integrated project on Aerosol
613 Cloud Climate and Air Quality interactions (EUCAARI) – integrating aerosol research from
614 nano to global scales, *Atmos. Chem. Phys.*, 11, 13061–13143, doi:10.5194/acp-11-13061-
615 2011, 2011.

616 Lipsky, E. M. and Robinson, A. L.: Effects of Dilution on Fine Particle Mass and Partitioning
617 of Semivolatile Organics in Diesel Exhaust and Wood Smoke, *Environ. Sci. Technol.*, 40 (1),
618 155–162, doi:10.1021/es050319p, 2006.

619 May, A. A., Levin, E. J. T., Hennigan, C. J., Riipinen, I., Lee, T., Collett, J. L., Jimenez, J. L.,
620 Kreidenweis, S. M. and Robinson, A. L.: Gas-particle partitioning of primary organic aerosol

621 emissions: 3. Biomass burning, *J. Geophys. Res. Atmospheres*, 118 (19), 2013JD020286,
622 doi:10.1002/jgrd.50828, 2013.

623 Nenes, A., Pandis, S. N. and Pilinis, C.: ISORROPIA: a new thermodynamic equilibrium
624 model for multiphase multicomponent inorganic aerosols, *Aquat. Geochem.*, 4, 123–152,
625 1998, *Aquat. Geochem.*, 4, 123–152, 1998.

626 Ots, R., Young, D. E., Vieno, M., Xu, L., Dunmore, R. E., Allan, J. D., Coe, H., Williams, L.
627 R., Herndon, S. C., Ng, N. L., Hamilton, J. F., Bergström, R., Di Marco, C., Nemitz, E.,
628 Mackenzie, I. A., Kuenen, J. J. P., Green, D. C., Reis, S. and Heal, M. R.: Simulating
629 secondary organic aerosol from missing diesel-related intermediate-volatility organic
630 compound emissions during the Clean Air for London (ClearfLo) campaign, *Atmos. Chem.*
631 *Phys.*, 16 (10), 6453–6473, doi:10.5194/acp-16-6453-2016, 2016.

632 Paatero, P.: The Multilinear Engine: A Table-Driven, Least Squares Program for Solving
633 Multilinear Problems, including the n-Way Parallel Factor Analysis Model, *J. Comput.*
634 *Graph. Stat.*, 8 (4), 854, doi:10.2307/1390831, 1999.

635 Robinson, A. L., Donahue, N. M., Shrivastava, M. K., Weitkamp, E. A., Sage, A. M.,
636 Grieshop, A. P., Lane, T. E., Pierce, J. R. and Pandis, S. N.: Rethinking Organic Aerosols:
637 Semivolatile Emissions and Photochemical Aging, *Science*, 315 (5816), 1259–1262,
638 doi:10.1126/science.1133061, 2007.

639 Shrivastava, M., Fast, J., Easter, R., Gustafson Jr., W. I., Zaveri, R. A., Jimenez, J. L., Saide,
640 P. and Hodzic, A.: Modeling organic aerosols in a megacity: comparison of simple and
641 complex representations of the volatility basis set approach, *Atmos. Chem. Phys.*, 11, 6639–
642 6662, 2011.

643 Tsigaridis, K., Daskalakis, N., Kanakidou, M., Adams, P. J., Artaxo, P., Bahadur, R.,
644 Balkanski, Y., Bauer, S. E., Bellouin, N., Benedetti, A., Bergman, T., Berntsen, T. K.,
645 Beukes, J. P., Bian, H., Carslaw, K. S., Chin, M., Curci, G., Diehl, T., Easter, R. C., Ghan, S.
646 J., Gong, S. L., Hodzic, A., Hoyle, C. R., Iversen, T., Jathar, S., Jimenez, J. L., Kaiser, J. W.,
647 Kirkevåg, A., Koch, D., Kokkola, H., Lee, Y. H., Lin, G., Liu, X., Luo, G., Ma, X., Mann, G.
648 W., Mihalopoulos, N., Morcrette, J.-J., Müller, J.-F., Myhre, G., Myriokefalitakis, S., Ng, N.
649 L., O'Donnell, D., Penner, J. E., Pozzoli, L., Pringle, K. J., Russell, L. M., Schulz, M., Sciare,
650 J., Seland, Ø., Shindell, D. T., Sillman, S., Skeie, R. B., Spracklen, D., Stavrakou, T.,
651 Steenrod, S. D., Takemura, T., Tiitta, P., Tilmes, S., Tost, H., van Noije, T., van Zyl, P. G.,

652 von Salzen, K., Yu, F., Wang, Z., Wang, Z., Zaveri, R. A., Zhang, H., Zhang, K., Zhang, Q.
653 and Zhang, X.: The AeroCom evaluation and intercomparison of organic aerosol in global
654 models, *Atmos. Chem. Phys.*, 14 (19), 10845–10895, doi:10.5194/acp-14-10845-2014, 2014.

655 Tsimpidi, A. P., Karydis, V. A., Zavala, M., Lei, W., Molina, L., Ulbrich, I. M., Jimenez, J. L.
656 and Pandis, S. N.: Evaluation of the volatility basis-set approach for the simulation of organic
657 aerosol formation in the Mexico City metropolitan area, *Atmos. Chem. Phys.*, 10, 525–546,
658 2010.

659 Vaughan, A. R., Lee, J. D., Misztal, P. K., Metzger, S., Shaw, M. D., Lewis, A. C., Purvis, R.
660 M., Carslaw, D. C., Goldstein, A. H., Hewitt, C. N., Davison, B., Beevers, S. D. and Karl, T.
661 G.: Spatially resolved flux measurements of NO_x from London suggest significantly higher
662 emissions than predicted by inventories, *Faraday Discuss*, doi:10.1039/C5FD00170F, 2016.

663 Woody, M. C., Baker, K. R., Hayes, P. L., Jimenez, J. L., Koo, B. and Pye, H. O. T.:
664 Understanding sources of organic aerosol during CalNex-2010 using the CMAQ-VBS,
665 *Atmos. Chem. Phys.*, 16 (6), 4081–4100, doi:10.5194/acp-16-4081-2016, 2016.

666 Yarwood, G.: Updates to the Carbon Bond Chemical 852 Mechanism: CB05, 2005.

667 Young, D. E., Allan, J. D., Williams, P. I., Green, D. C., Flynn, M. J., Harrison, R. M., Yin,
668 J., Gallagher, M. W. and Coe, H.: Investigating the annual behaviour of submicron secondary
669 inorganic and organic aerosols in London, *Atmos. Chem. Phys.*, 15 (11), 6351–6366,
670 doi:10.5194/acp-15-6351-2015, 2015.

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673 **4 Tables and Figures**

674 Table 1. Properties of the VBS space. Oxygen numbers for each volatility bin were calculated
 675 using the group-contribution of Donahue et al. (2011). Hydrogen numbers were calculated
 676 from the van Krevelen relation (Heald et al., 2010).

	log (C*)	Oxygen number	Carbon number	Hydrogen number	Molecular weight
POA set1*	-1	4.11	11.00	17.89	216
(BBOA-like)	0	3.43	11.75	20.07	216
Primary biomass	1	2.73	12.50	22.27	216
burning (BBPOA)	2	2.01	13.25	24.49	216
	3	1.27	14.00	26.73	215
SOA set2*	-1	4.53	9.00	13.47	194
(BBOA-like)	0	4.00	9.25	14.50	189
SOA from SVOCs	1	3.40	9.50	15.60	184
biomass burning	2	2.83	9.75	16.67	179
SOA set3*	-1	5.25	5.00	4.75	149
(BBOA-like)	0	4.70	5.25	5.80	144
SOA from	1	4.20	5.50	6.80	140
VOC/IVOCs biomass	2	3.65	5.75	7.85	135
burning and biogenics	3	3.15	6.00	8.85	131
POA set1**	-1	2.69	17.00	31.3	278
(HOA-like)	0	2.02	17.50	33.0	275
Rest of primary	1	1.34	18.00	34.7	272
anthropogenic sources	2	0.63	18.50	36.4	268
	3	0.0	19.00	38.0	266
SOA set1**	-1	4.90	7.00	9.10	172
(HOA-like)	0	4.38	7.25	10.1	167
SOA from rest of all	1	3.84	7.50	11.2	163
anthropogenic in all	2	3.30	7.75	12.2	158

volatility range (SVOCs,IVOCs,VOCs)	3	2.74	8.00	13.3	153
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678 *Based on Ciarelli et al. (2016b).

679 **Molecular structure as in Koo et al. (2014) and Ciarelli et al. (2016a).

680

681 Table 2. Statistics of OA for the VBS_BC_NEW case for February-March 2009 at each AMS
 682 site as well as an average of all sites for both VBS_BC_NEW and VBS_BC. Bold numbers
 683 represent the stations where model performance criteria were met.

Site*	Mean observed OA ($\mu\text{g m}^{-3}$)	Mean modelled OA ($\mu\text{g m}^{-3}$)	MB ($\mu\text{g m}^{-3}$)	ME ($\mu\text{g m}^{-3}$)	MFB [-]	MFE [-]	r	R ²
Barcelona (BCN)	8.3	5.1	-3.1	3.7	-0.4	0.5	0.6	0.4
Cabauw (CBW)	1.2	1.5	0.3	0.7	0.1	0.5	0.7	0.4
Chilbolton (CHL)	2.4	1.0	-1.4	1.5	-0.9	0.9	0.8	0.6
Helsinki (HEL)	2.7	3.6	0.9	1.8	0.3	0.6	0.3	0.1
Hyytiälä (SMR)	1.3	1.7	0.3	0.8	-0.1	0.6	0.8	0.6
Mace Head (MHD)	0.8	0.7	-0.1	0.3	-0.1	0.7	0.7	0.5
Melpitz (MPZ)	1.5	0.8	-0.6	0.9	-0.6	0.7	0.6	0.3
Montseny (MSY)	3.1	3.5	0.4	2.0	0.1	0.6	0.4	0.1
Payenne (PAY)	4.1	2.9	-1.2	1.9	-0.5	0.7	0.7	0.4
Puy de Dôme (PDD)	0.6	1.1	0.4	0.8	0.3	0.8	0.4	0.2
Vavihill (VAV)	3.9	2.1	-1.8	2.0	-0.8	0.8	0.8	0.6
VBS_BC_NEW	3.0	2.3	-0.7	1.6	-0.3	0.7	0.8	0.6
VBS_BC (Ciarelli et al., 2016a)	3.0	1.4	-1.5	1.8	-0.6	0.8	0.8	0.6

684 * Model OA concentrations extracted at surface level except for the stations of Puy de Dôme
 685 and Montseny.

686

687 Table 3. Statistics of POA for the VBS_BC_NEW case for February-March 2009 at each
 688 AMS site as well as an average of all sites for both VBS_BC_NEW and VBS_BC. Bold
 689 numbers represent the stations where model performance criteria were met.

Site	Mean observed POA ($\mu\text{g m}^{-3}$)	Mean modelled POA ($\mu\text{g m}^{-3}$)	MB ($\mu\text{g m}^{-3}$)	ME ($\mu\text{g m}^{-3}$)	MFB [-]	MFE [-]	r	R ²
Barcelona	4.0	2.0	-2.1	2.4	-0.5	0.7	0.4	0.2
Cabauw	0.4	0.9	0.5	0.5	0.8	0.9	0.5	0.2
Chilbolton	1.0	0.5	-0.5	0.5	-0.6	0.7	0.8	0.6
Helsinki	0.8	2.5	1.7	1.7	1.0	1.0	0.2	0.0
Hyytiälä	0.1	0.5	0.4	0.4	1.3	1.3	0.5	0.3
Mace Head	0.2	0.1	-0.1	0.2	0.5	1.0	0.2	0.1
Melpitz	0.3	0.3	0.1	0.2	0.3	0.7	0.5	0.2
Montseny	0.5	0.4	0.0	0.3	0.2	0.7	0.3	0.1
Payerne	0.7	1.1	0.3	0.6	0.5	0.7	0.5	0.3
Puy de Dôme	0.2	0.3	0.1	0.2	0.5	0.9	0.2	0.1
Vavihill	1.1	1.0	-0.1	0.6	-0.3	0.7	0.5	0.2
VBS_BC_NEW	0.9	0.9	-0.1	0.7	0.3	0.8	0.6	0.3
VBS_BC (Ciarelli et al., 2016a)	0.9	0.9	0.0	0.8	0.3	0.8	0.6	0.4

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696 Table 4. Statistics of SOA for the VBS_BC_NEW case for February-March 2009 at each
 697 AMS site as well as an average of all sites for both VBS_BC_NEW and VBS_BC. Bold
 698 number represents the stations where model performance criteria were met.

Site	Mean observed SOA ($\mu\text{g m}^{-3}$)	Mean modelled SOA ($\mu\text{g m}^{-3}$)	MB ($\mu\text{g m}^{-3}$)	ME ($\mu\text{g m}^{-3}$)	MFB [-]	MFE [-]	r	R ²
Barcelona	4.4	3.2	-1.2	1.6	-0.4	0.5	0.7	0.5
Cabauw	1.0	0.6	-0.4	0.6	-0.7	0.9	0.7	0.4
Chilbolton	1.4	0.5	-0.9	1.0	-1.1	1.2	0.7	0.5
Helsinki	1.8	1.1	-0.7	1.1	-0.7	0.9	0.4	0.2
Hyytiälä	1.2	1.1	-0.1	0.7	-0.7	1.0	0.8	0.6
Mace Head	0.4	0.5	0.2	0.6	0.3	1.0	0.4	0.2
Melpitz	1.2	0.5	-0.7	0.8	-1.0	1.1	0.6	0.4
Montseny	2.6	3.1	0.5	1.8	0.0	0.7	0.4	0.1
Payerne	3.7	2.0	-1.7	2.1	-0.8	0.9	0.5	0.3
Puy de Dôme	0.6	0.9	0.3	0.8	0.2	0.9	0.2	0.1
Vavihill	2.8	1.1	-1.7	1.7	-1.2	1.2	0.8	0.7
VBS_BC_NEW	2.1	1.4	-0.6	1.2	-0.6	0.9	0.7	0.5
VBS_BC (Ciarelli et al., 2016a)	2.1	0.5	-1.5	1.6	-1.1	1.3	0.7	0.6

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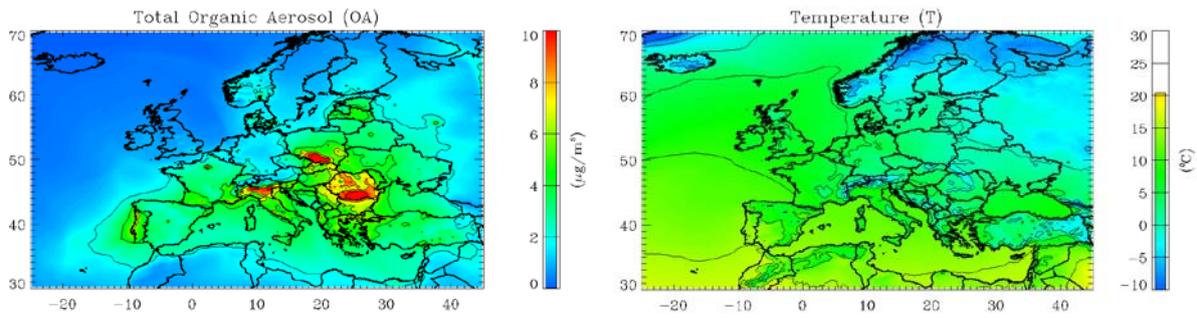
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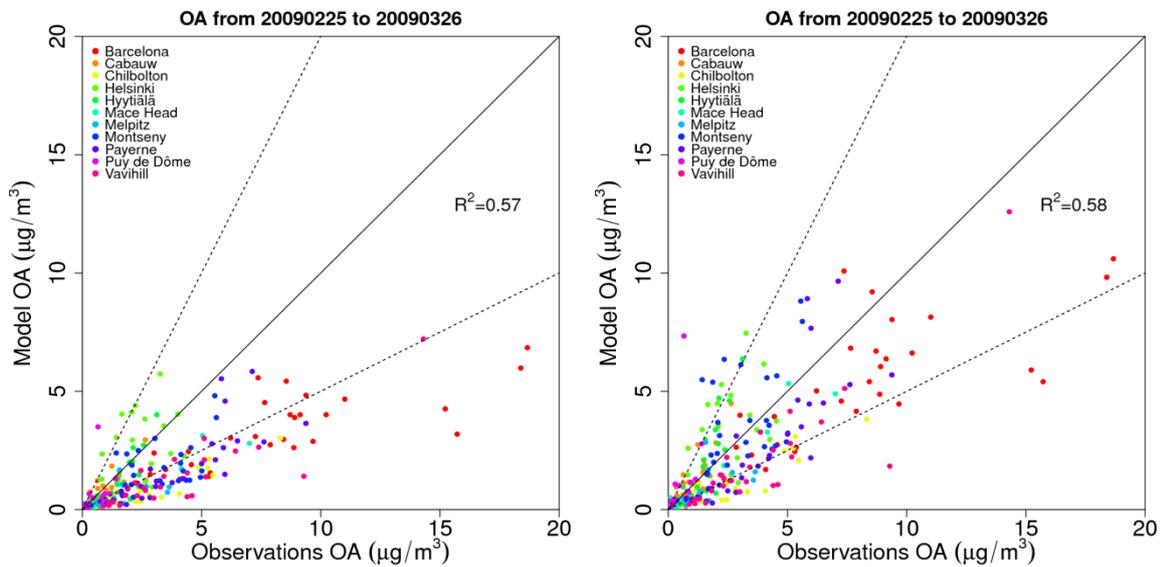


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707 Figure 1. Modelled average total organic aerosol (OA) concentrations (VBC_BC_NEW) and
 708 surface temperature (T) for the period between 25 February and 26 March 2009.

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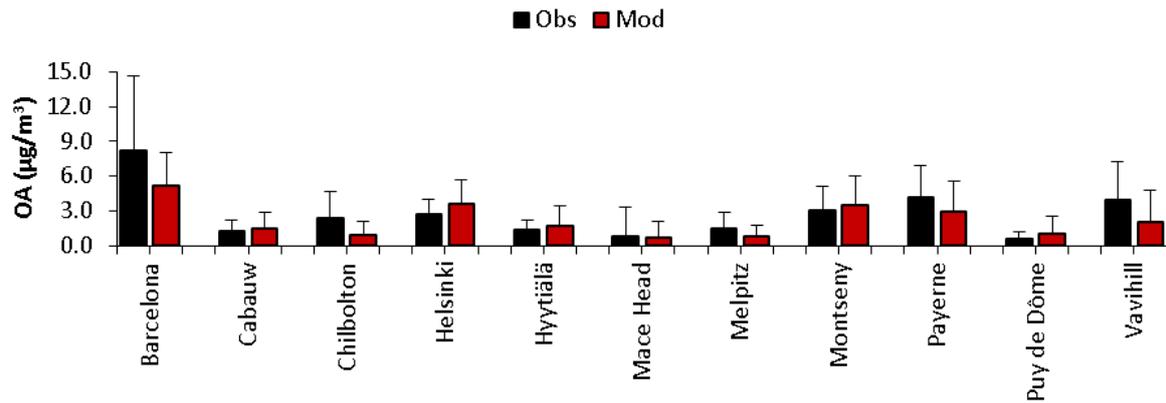


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712 Figure 2. Daily average scatter plots for OA concentrations at 11 AMS sites for the period
 713 between 25 February and 26 March 2009 for VBS_BC (left) and VBS_BC_NEW case (right).
 714 Solid lines indicate the 1:1 line. Dotted lines are the 1:2 and 2:1 lines.

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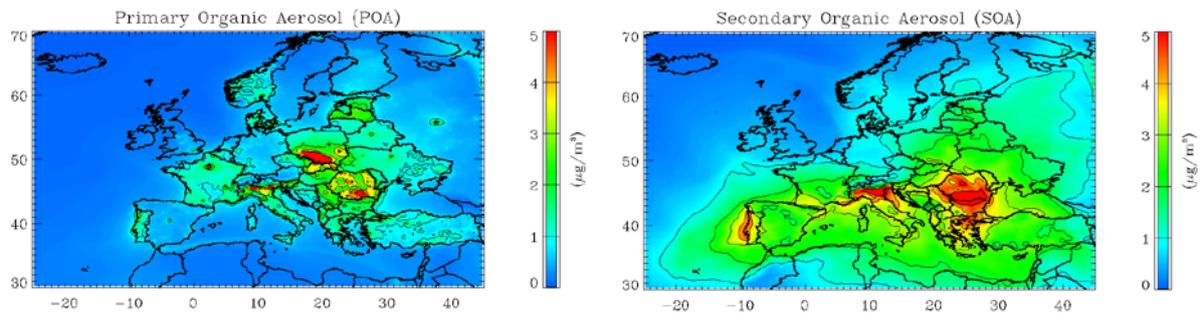
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718 **Figure 3. Observed (black) and modelled (VBS_BC_NEW) (red) average OA mass at AMS**
719 **sites for the period between 25 February and 26 March 2009.**

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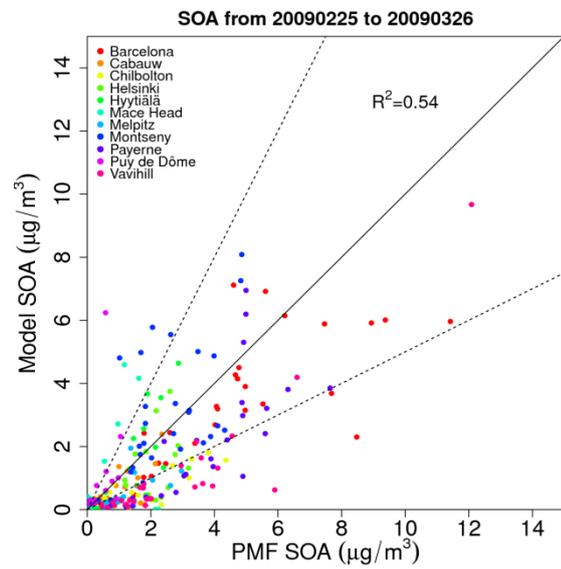
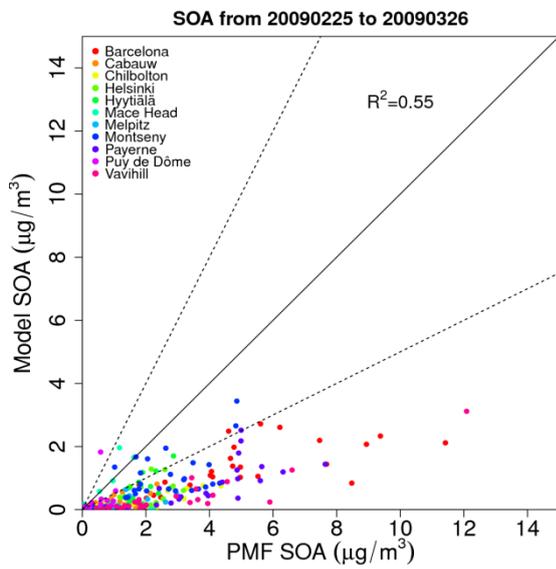
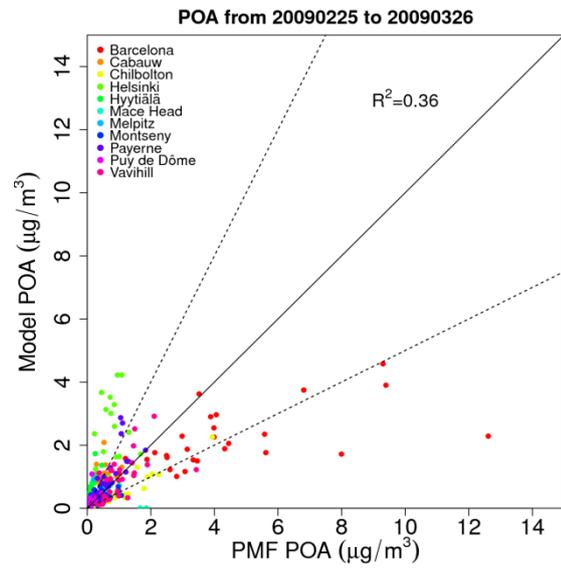
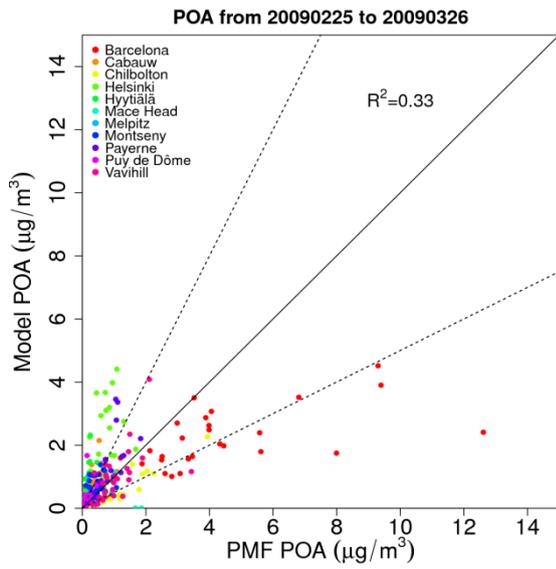
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722 **Figure 4. Modelled average POA (left) and SOA (right) concentrations for the period between**
723 **25 February and 26 March 2009.**

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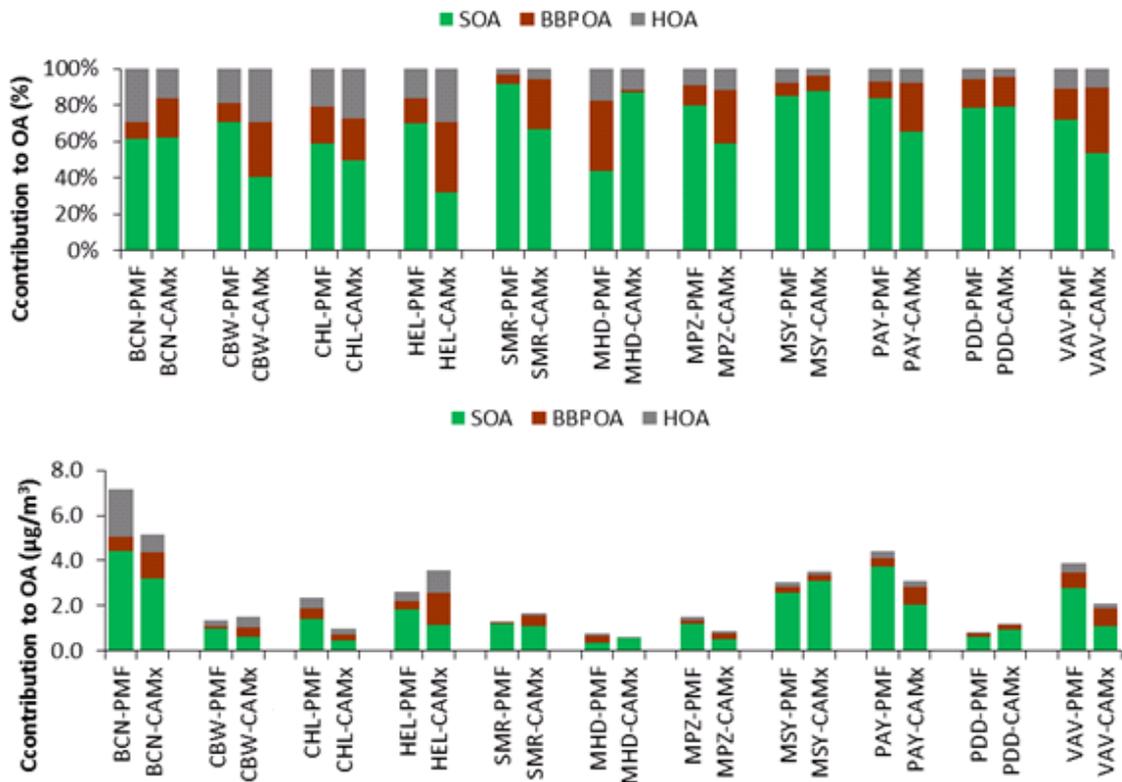
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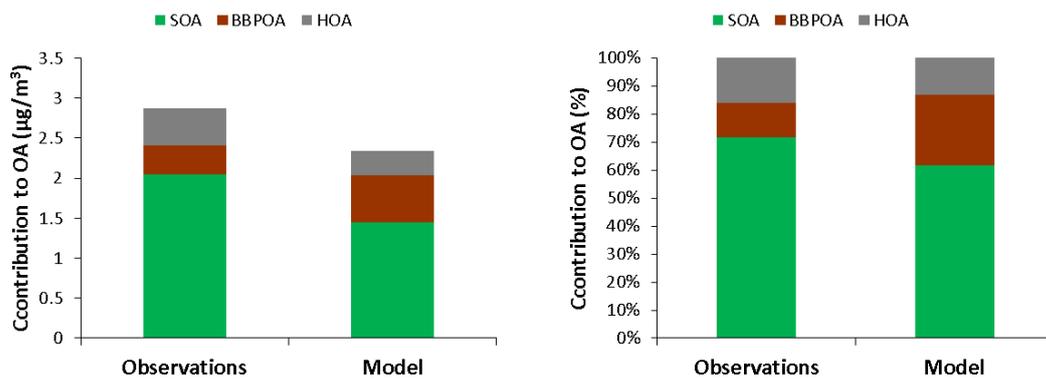
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729 Figure 5. Daily average scatter plots of POA and SOA concentrations at 11 AMS sites for
 730 February-March 2009 in VBS_BC (Ciarelli et al., 2016a) (left) and VBS_BC_NEW (right).
 731 Solid lines indicate the 1:1 line. Dotted lines are the 1:2 and 2:1 lines.



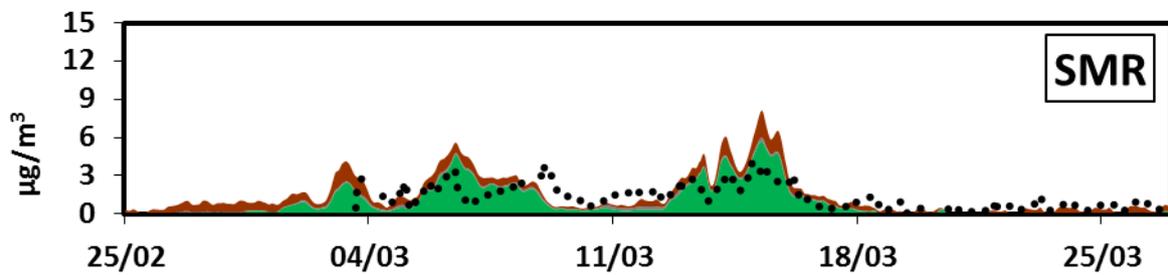
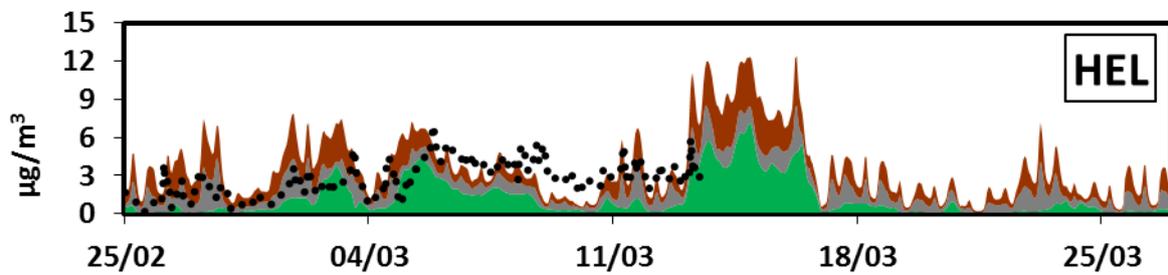
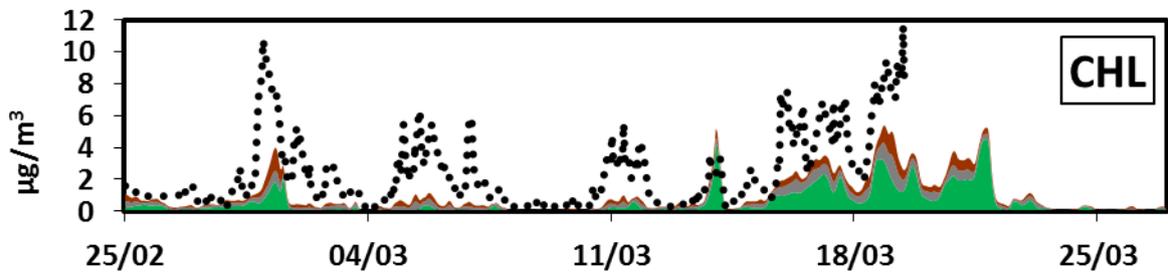
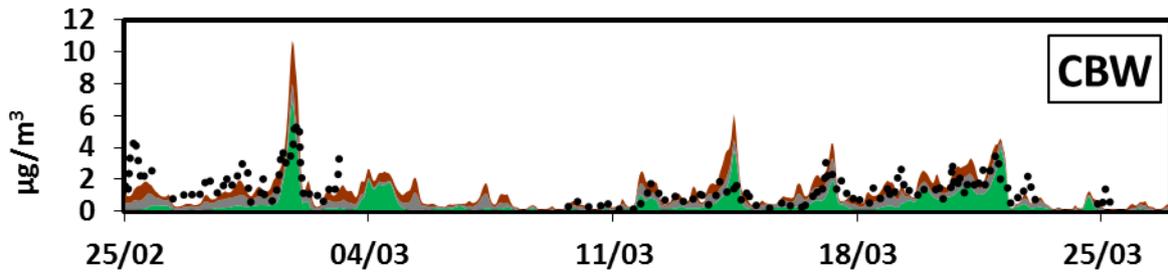
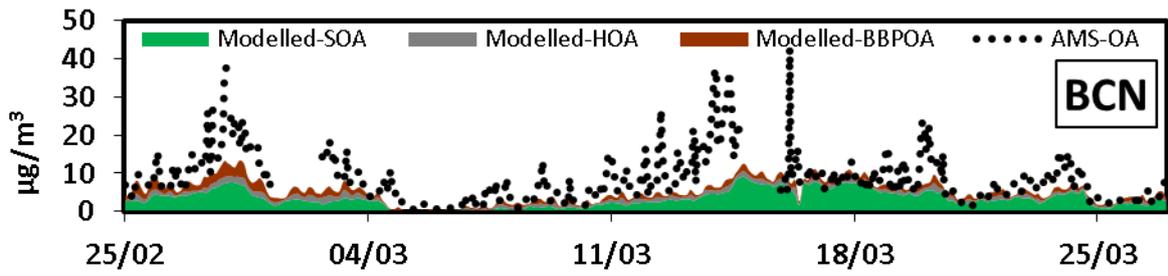
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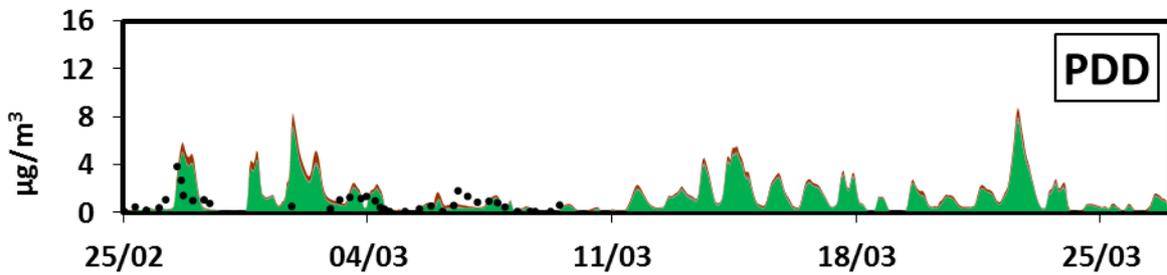
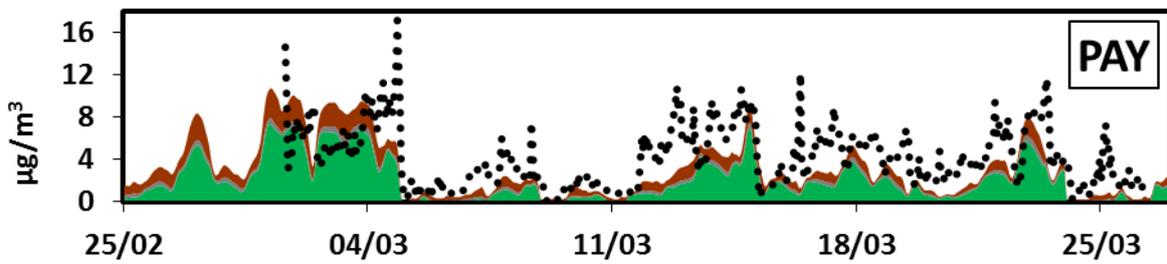
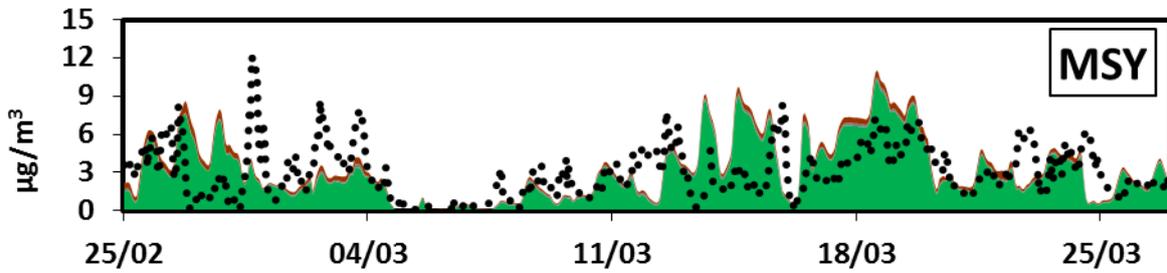
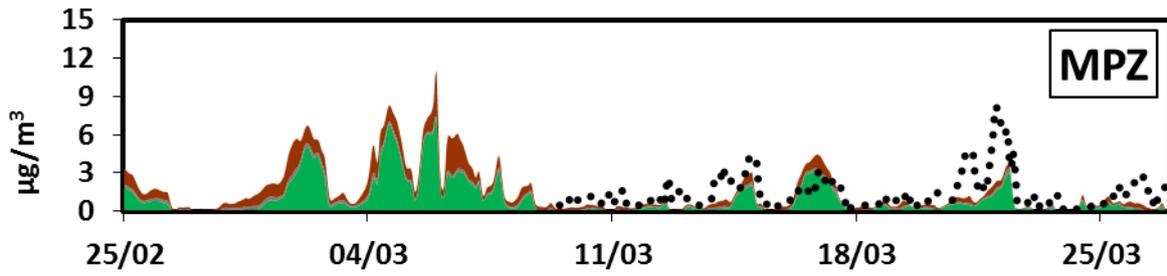
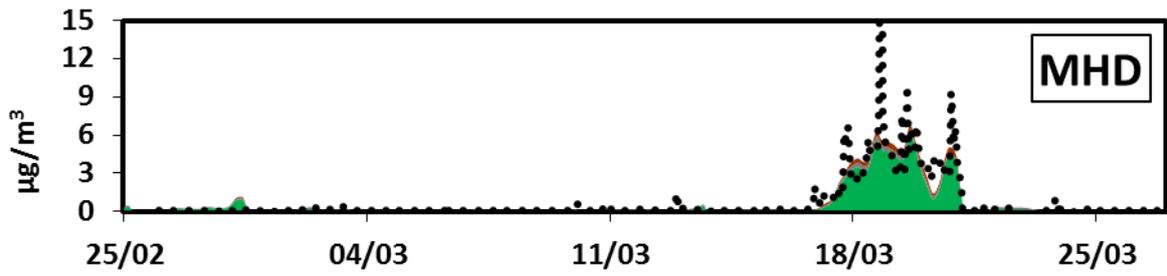
733 Figure 6. Relative (upper panel) and absolute (lower panel) contribution of HOA, BBPOA and
 734 SOA to OA concentrations at 11 sites from PMF analysis of AMS measurements (first bar)
 735 and CAMx VBS_BC_NEW results (second bar) for the period between 25 February and 26
 736 March 2009.

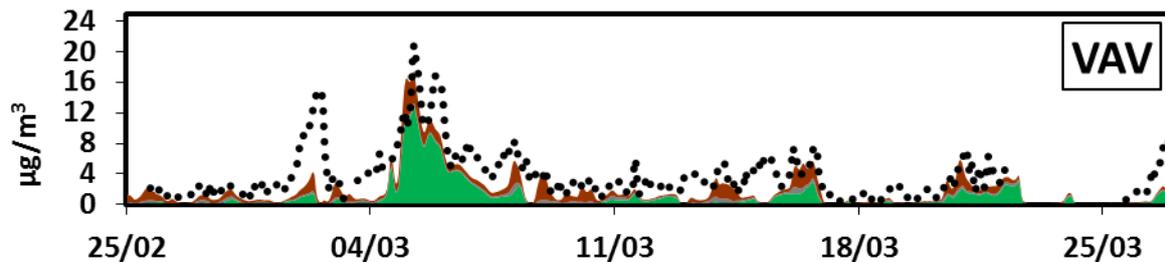


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738 Figure 7. Measured and modelled average absolute (left panel) and relative (right panel)
 739 contributions of HOA, BBPOA and SOA to OA concentrations for all the 11 sites for the
 740 period between 25 February and 26 March 2009.

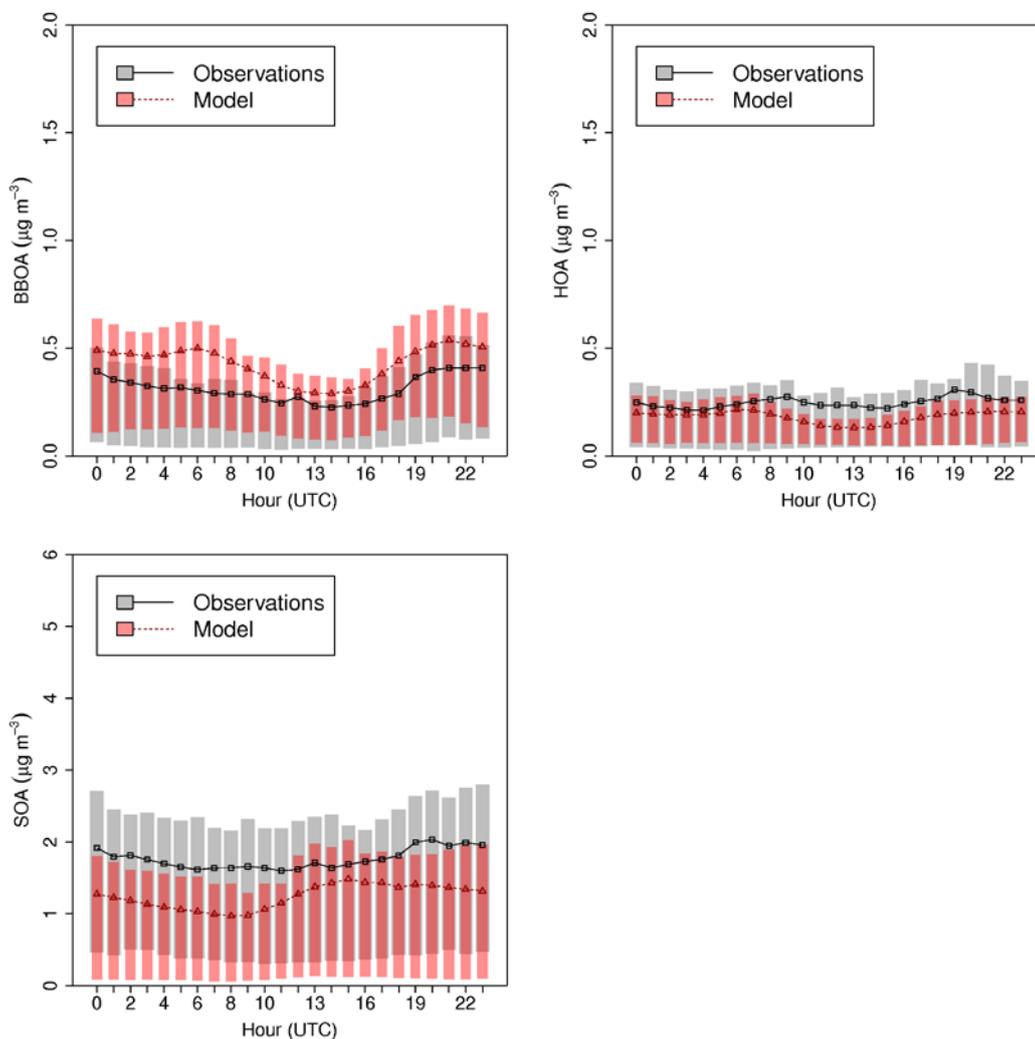




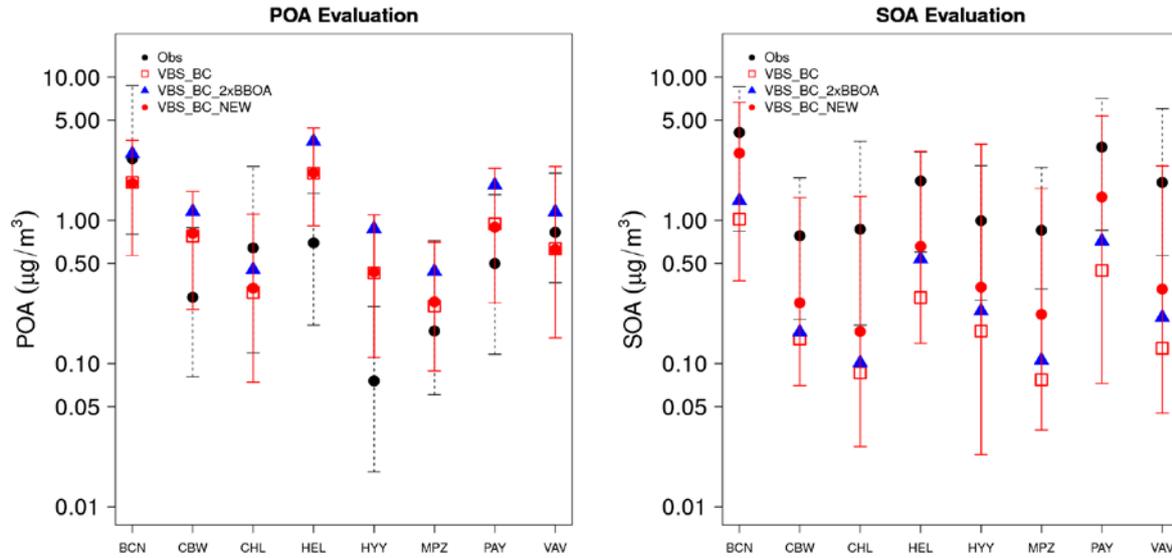


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 752 Figure 8. Comparison of measured hourly OA mass concentrations (AMS-OA dotted line),
 753 with modelled components HOA, BBPOA and SOA.

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 757 Figure 9. Comparison of modelled (red) and measured (grey) BBPOA, HOA and SOA diurnal
 758 profiles at the rural-background sites. The extent of the bars indicates the 25th and 75th
 759 percentiles.



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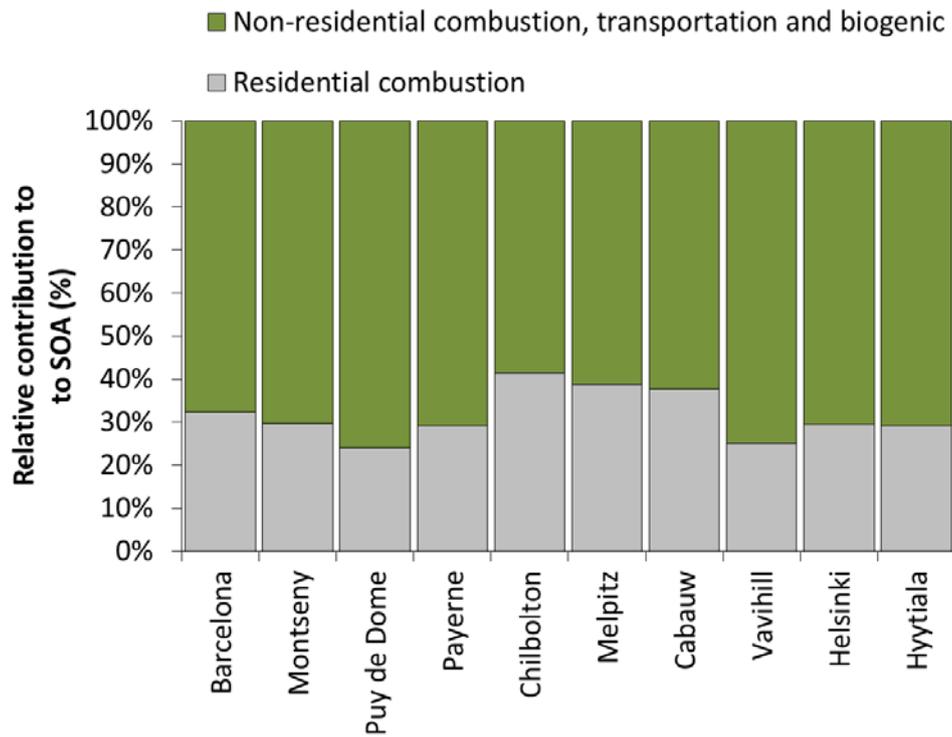
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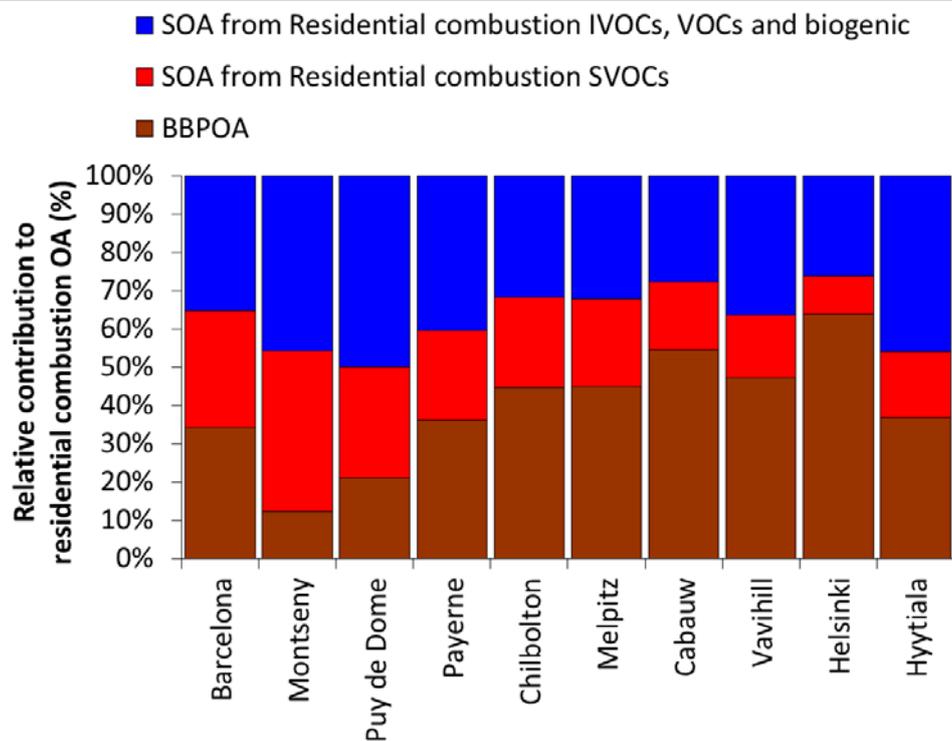
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Figure 10. POA (left) and SOA (right) median concentrations at 8 AMS sites for February-March 2009 in the VBS_BC, VBS_BC_2xBBOA and VBS_BC_NEW cases. Dotted lines indicate the 10th and 90th quartile range (also reported in red for the VBS_BC_NEW case). Data for the Puy de Dôme and Montseny sites at higher layers are not available for the VBS_BC_2xBBOA scenario.

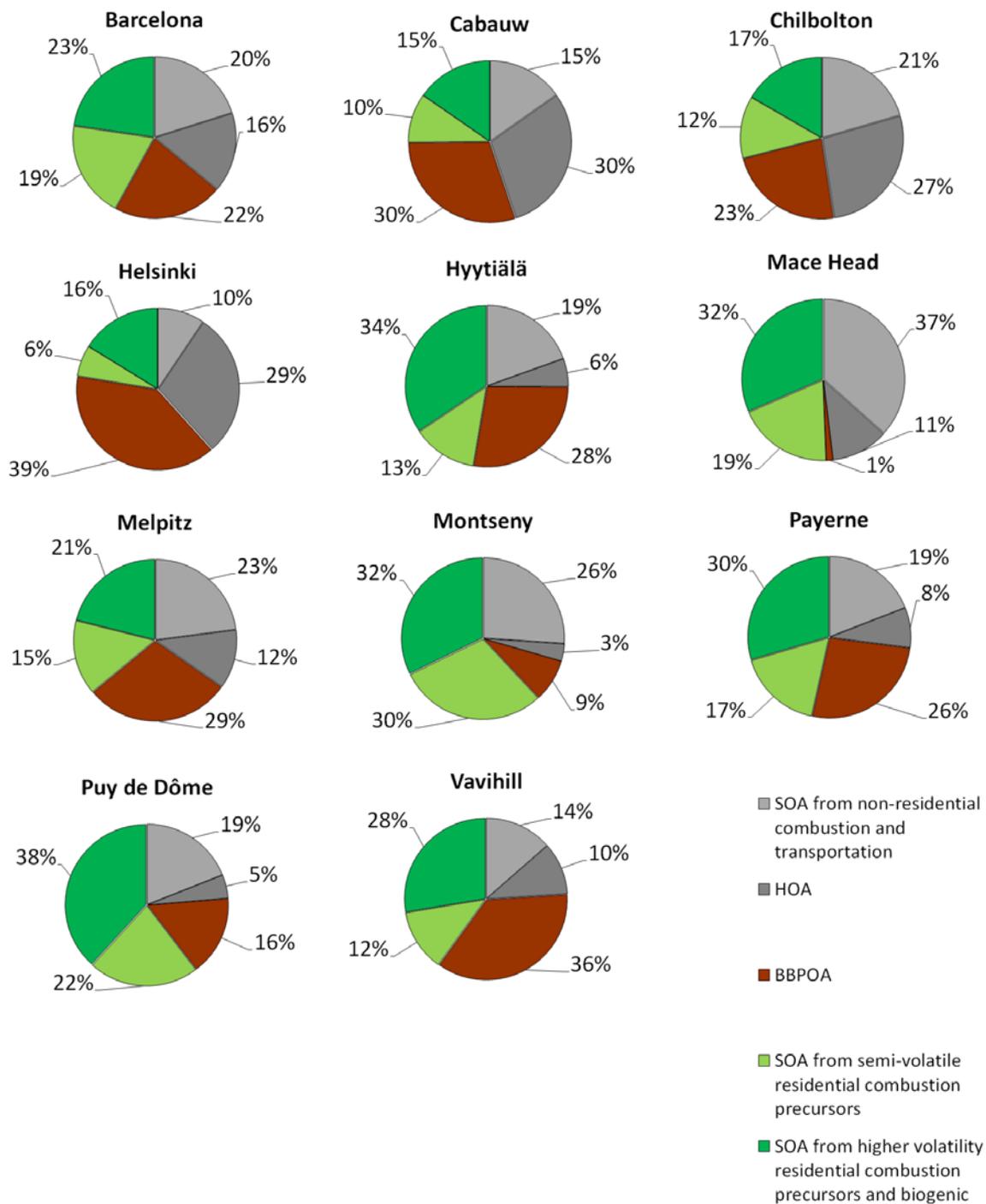


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772 Figure 11. Contribution of residential and non-residential combustion precursors to SOA at
 773 different sites (upper panel). Contribution of BBPOA, SVOCs and higher volatility organic
 774 precursors to residential heating OA (lower panel). Stations are ordered from south to north.



777 Figure 12. Average modelled composition of OA at the 11 AMS sites for the period between
 778 25 February and 26 March 2009.

1 **5 Supplement**

2 Table S1. Statistics for model evaluation. M_i represents the modelled value, O_i the
 3 observations, \bar{O} the mean of the observations and n the total number of data points.

Mean Bias (MB)	$MB = \frac{1}{n} \sum_{i=1}^n (M_i - O_i),$
Mean Error (ME)	$ME = \frac{1}{n} \sum_{i=1}^n (M_i - O_i),$
Mean Fractional Bias (ME)	$MFB = \frac{2}{n} \sum_{i=1}^n \left(\frac{M_i - O_i}{M_i + O_i} \right),$
Mean Fractional Bias (ME)	$MFE = \frac{2}{n} \sum_{i=1}^n \left(\frac{ M_i - O_i }{M_i + O_i} \right),$
Coefficient of determination (R^2)	$R2 = 1 - \frac{\sum_{i=1}^n (O_i - M_i)^2}{\sum_{i=1}^n (O_i - \bar{O})^2}.$

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1 Table S2. Statistical analysis for HOA during February-March 2009 periods at 11 AMS sites.

Site	Mean observed HOA ($\mu\text{g m}^{-3}$)	Mean modelled HOA ($\mu\text{g m}^{-3}$)	MB ($\mu\text{g m}^{-3}$)	ME ($\mu\text{g m}^{-3}$)	MFB [-]	MFE [-]	r	R ²
Barcelona	2.1	0.8	-1.3	1.5	-0.4	0.8	0.4	0.1
Cabauw	0.3	0.4	0.2	0.2	0.6	0.8	0.5	0.2
Chilbolton	0.5	0.3	-0.2	0.3	-0.5	0.7	0.8	0.6
Helsinki	0.4	1.0	0.6	0.7	0.8	0.9	0.2	0.1
Hyytiälä	0.0	0.1	0.1	0.1	0.7	0.8	0.6	0.3
Mace Head	0.1	0.1	-0.1	0.1	0.5	1.1	0.6	0.3
Melpitz	0.1	0.1	0.0	0.1	-0.1	0.6	0.6	0.3
Montseny	0.2	0.1	-0.1	0.2	-0.3	0.8	0.4	0.1
Payerne	0.3	0.3	-0.1	0.2	0.0	0.6	0.4	0.1
Puy de Dôme	0.0	0.1	0.0	0.0	0.3	0.8	0.1	0.0
Vavihill	0.4	0.2	-0.2	0.2	-0.4	0.7	0.5	0.2

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1 Table S3 Statistical analysis for BBPOA during February-March 2009 periods at 11 AMS
 2 sites.

Site	Mean observed BBPOA ($\mu\text{g m}^{-3}$)	Mean modelled BBPOA ($\mu\text{g m}^{-3}$)	MB ($\mu\text{g m}^{-3}$)	ME ($\mu\text{g m}^{-3}$)	MFB [-]	MFE [-]	r	R ²
Barcelona	0.7	1.1	0.5	0.7	0.6	0.8	0.4	0.2
Cabauw	0.1	0.5	0.3	0.3	1.0	1.1	0.5	0.3
Chilbolton	0.5	0.2	-0.3	0.3	-0.6	0.8	0.6	0.4
Helsinki	0.4	1.4	1.0	1.1	1.1	1.1	0.1	0.0
Hyytiälä	0.1	0.5	0.4	0.4	1.5	1.5	0.7	0.5
Mace Head	0.3	0.0	-0.3	0.3	-0.9	1.4	-0.1	0.0
Melpitz	0.2	0.3	0.1	0.2	0.7	0.9	0.4	0.2
Montseny	0.2	0.3	0.1	0.2	0.5	0.8	0.2	0.1
Payerne	0.4	0.8	0.4	0.5	0.8	0.9	0.6	0.3
Puy de Dôme	0.1	0.2	0.1	0.2	0.5	1.0	0.3	0.1
Vavihill	0.7	0.7	0.1	0.5	-0.1	0.7	0.5	0.2

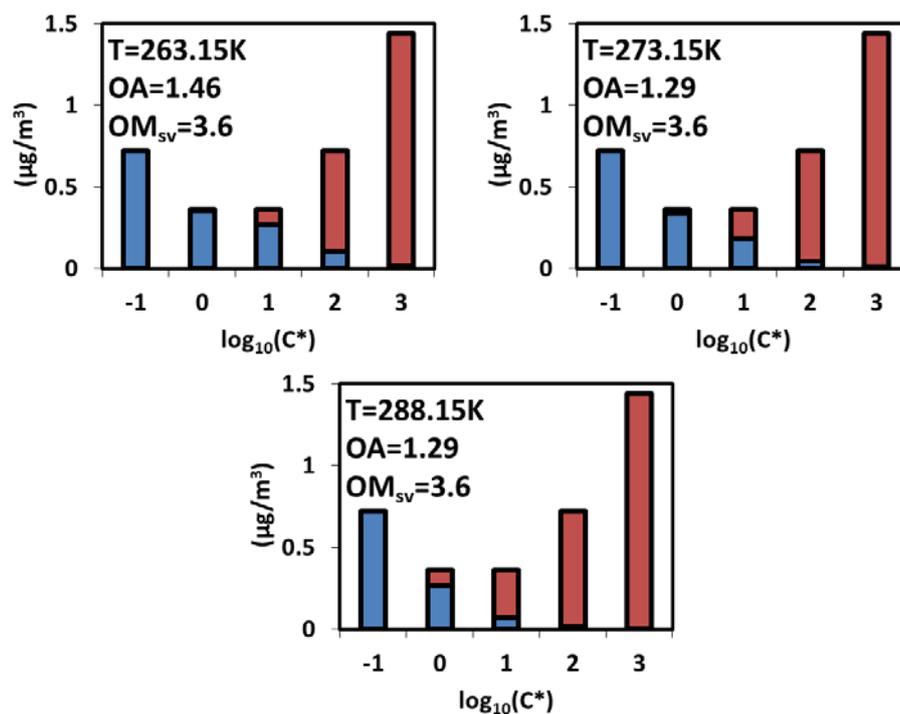
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4 Table S4. Comparison of statistics for BBPOA in VBS_BC_NEW with VBS_BC (average of all sites
 5 in February-March 2009)

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	Mean obs ($\mu\text{g m}^{-3}$)	Mean mod ($\mu\text{g m}^{-3}$)	MB ($\mu\text{g m}^{-3}$)	ME ($\mu\text{g m}^{-3}$)	MFB [-]	MFE [-]
VBS_BC	0.36	0.60	0.24	0.45	0.47	0.98
VBS_BC_NEW	0.36	0.59	0.23	0.43	0.50	0.97

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3 Figure S1. Box-model partitioning of biomass burning POA at about $1 \mu\text{g m}^{-3}$ OA at different
 4 temperatures (263.15, 273.15 and 288.15 K) using volatility distributions proposed by May et
 5 al. (2013). Particle phase is represented blue and gas phase in red. The lowest bin ($\log_{10}C^*=-1$)
 6 is used as a proxy for all non-volatile species which will only reside in the particle phase.

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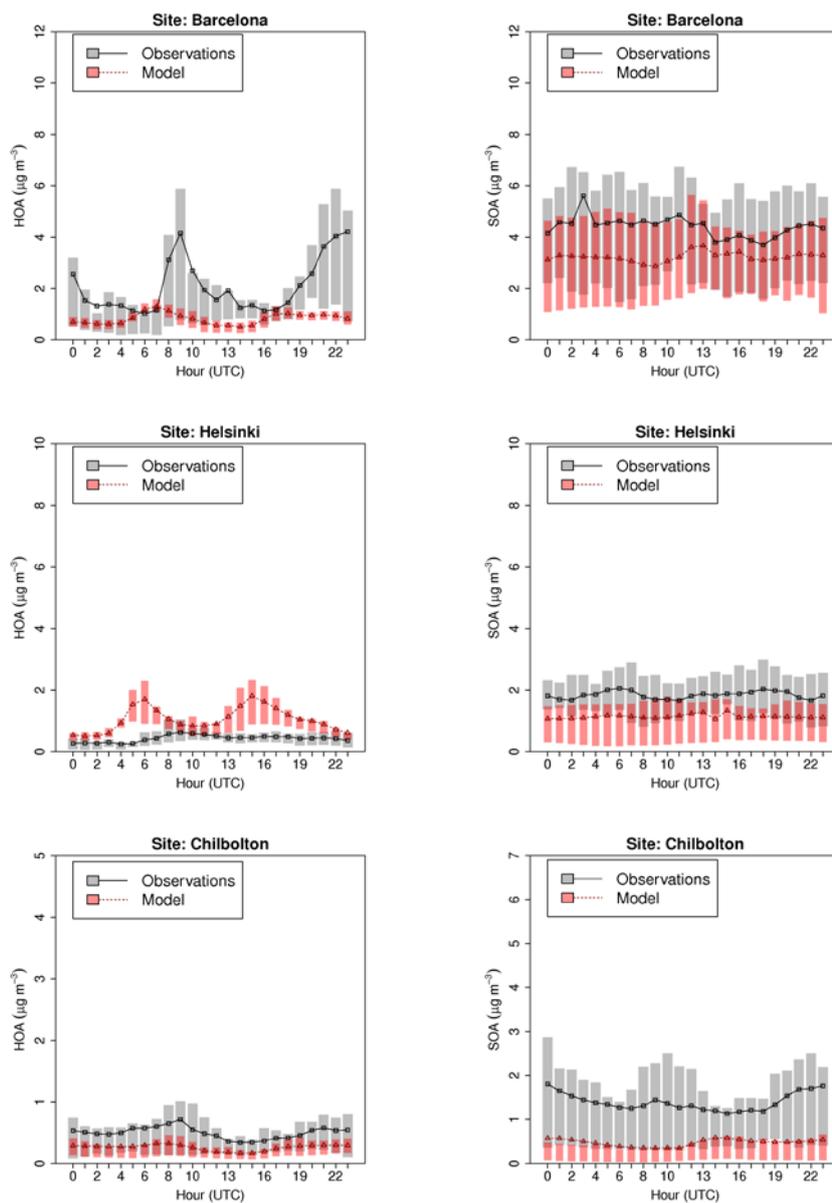
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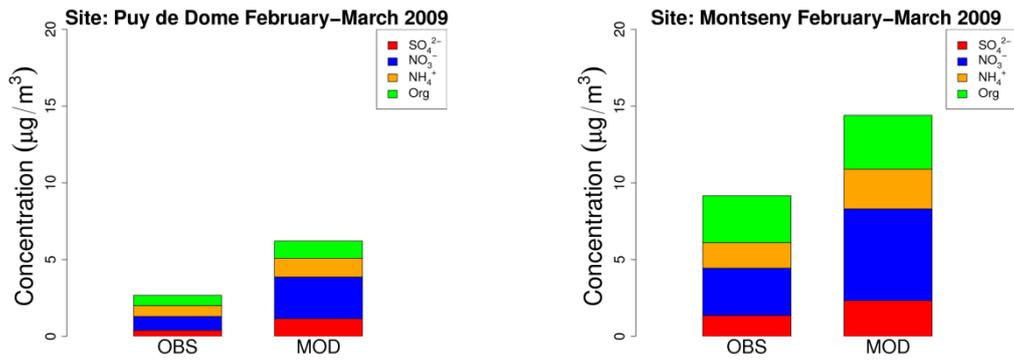
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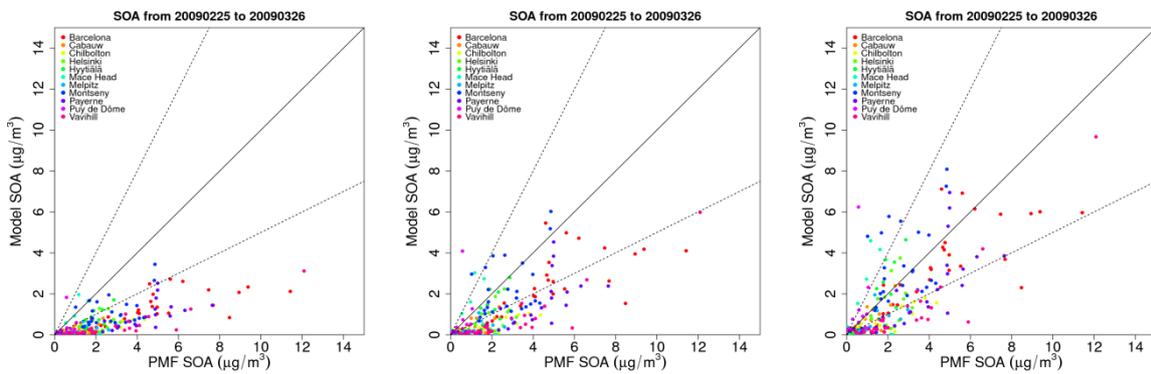
3

4 Figure S2. Comparison of modelled (red) and measured (grey) HOA and SOA diurnal profiles
 5 at the sites of Barcelona, Helsinki and Chilbolton. The extent of the bars indicates the 25th
 6 and 75th percentiles.

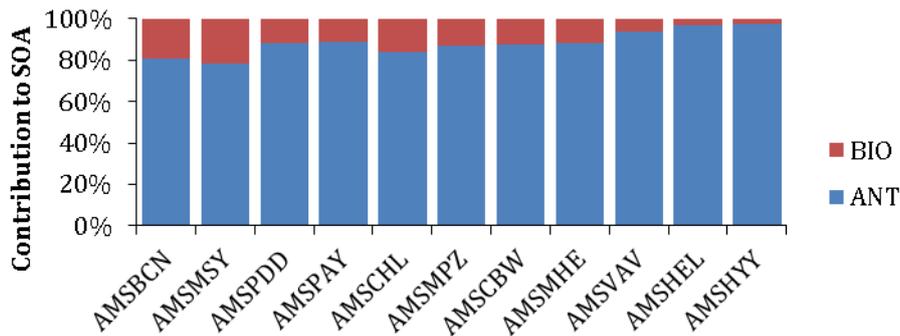
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1
2 **Figure S3. Comparison of modelled non-refractory PM₂₅ components at Puy de Dome and**
3 **Montseny with the AMS measurements in February-March 2009.**

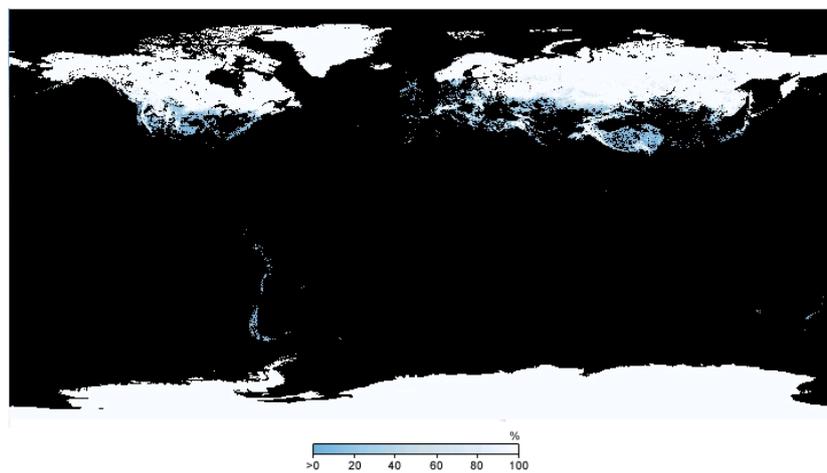


6
7 **Figure S4. Modelled versus PMF SOA; with VBS_BC (Ciarelli et al., 2016a) (left panel),**
8 **with VBS_BC where BBPOA vapours were allowed to be further oxidized (Koo et al. 2014)**
9 **(middle panel), and with VBS_BC_NEW (right panel).**



11
12 **Figure S5. Biogenic and anthropogenic contribution to SOA at stations from south to north**
13 **retrieved as a difference between the predicted SOA in the reference simulation (including**
14 **biogenic) and a sensitivity test with no biogenic SOA formation.**

1

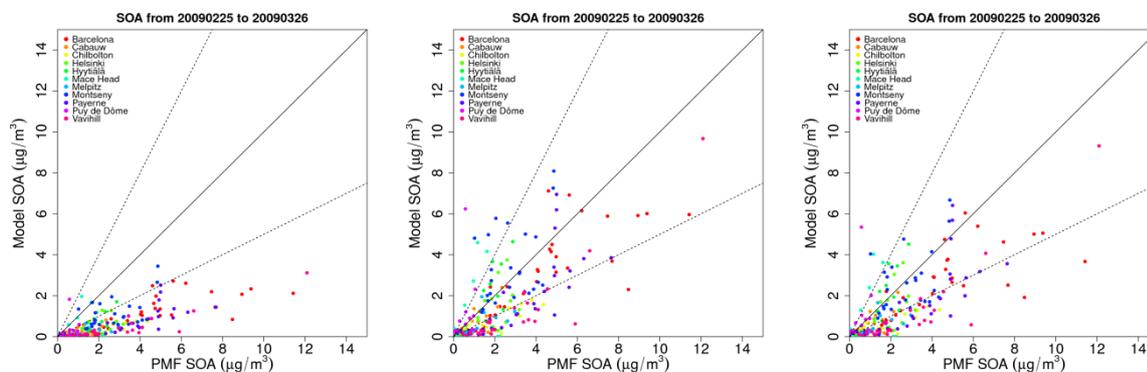


2

3 **Figure S6. Snow cover for March 2009 as retrieved by the TERRA/MODIS instrument.**

4

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7

8 **Figure S7. Modelled versus PMF SOA; with VBS_BC (Ciarelli et al., 2016a) (left panel),**
9 **with VBS_BC_NEW (middle panel), and with VBS_BC_NEW but without biogenic SOA**
10 **(right panel).**

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Responses to the comments of anonymous referee #1

1 Thank you for your comments which helped to improve our manuscript. Please find below your
2 comments in blue, our responses in black and modifications in the revised manuscript in *italic*.

3
4 In the manuscript by Ciarelli et al. a modified VBS scheme for biomass burning-like OA is
5 implemented in the chemistry transport models CAMx. The new VBS scheme was developed by
6 the authors and is described in a paper under review in the GMD (Ciarelli et al., 2016b). CAMx is
7 then used to simulate the wintertime OA mass concentration in Europe in Feb-Mar 2009. The
8 model results are compared with model results from simulations using a different VBS scheme
9 for biomass bring-like OA (Ciarelli et al., 2016a) and with AMS measurements from 11 stations
10 around Europe. The manuscript addresses a very relevant and important topic: the contribution
11 of small-scale residential (mainly wood) combustion to the OA mass loading in Europe during
12 wintertime. My review mainly focuses on the method section, which I partly found quite hard to
13 understand. I have a few critical questions conserving how the different VBS methods was
14 applied which would like to get answered and also explained clearly in the manuscript. If this is
15 done properly and the new VBS parameterization is considered to be scientifically sound by the
16 reviewers of the GMD manuscript Ciarelli et al.,2016b, then I think the manuscript can be
17 suitable for publication in Atmospheric Chemistry and Physics.

18
19
20 More general comments mainly concerning the method:

21
22 1.

23 Is it correct that the only difference between the base case model runs from Ciarelli et al., 2016a
24 and this new study is that you use the new VBS sets (called VBS_BC_NEW) instead of VBS_BC to
25 describe the OA formation from biomass burning emissions? If the answer on this question is
26 Yes, which I hope is the case, then please state this clearly in the manuscript. If e answer is No,
27 you have to clearly explain all differences between the two different model runs.

28
29 The answer to this question is yes; all model input data prepared for Ciarelli et al. (2016a) were
30 kept the same for this new application (VBS_BC_NEW). The model scheme to treat biomass
31 burning like organic aerosol was updated based on Ciarelli et al. (2016b) which was accepted for
32 final publication in GMD.

33
34 2.

35 Is it correct that you in total use 3 VBS sets to describe OA formation from biomass burning, 1 set
36 for fresh HOA from fossil fuel combustion, 1 set for aged oxidized HOA, 1 VBS set for BVOC
37 oxidation products (no ageing considered). Thus in total 6 VBS sets? I think you need to describe
38 this more clearly in the manuscript and how this compares to the VBS sets used in Ciarelli et al.,
39 2016a.

40
41 We agree with the referee that further description of the VBS sets is needed in the manuscript.
42 The model deploys 3 sets to treat biomass burning-like aerosol (as shown in Ciarelli et al.,
43 2016b) and 2 sets to treat HOA-like aerosol, based on Koo et al., (2014). In addition, it assumes
44 that the primary semivolatile vapours from the HOA generate SOA, and not POA, upon oxidation
45 with the OH radical and further condensation in the particle-phase. However, we don't have a
46 separate set to allocate oxidation products from biogenic precursors, and they follow the same
47 oxidation pathways of biomass burning-like aerosol as in the previous case (Ciarelli et al.,
48 2016a), including aging. We are currently working on an updated version of CAMx which
49 includes the separation of biogenic sources. In our reply to comment 8, we present a sensitivity
50 test with no biogenic SOA formation in order to better address the importance of this source.

1 We further clarified this point as follows:

2

3 at line 179 of the revised manuscript

4

5 *The third set allocates oxidation products from the traditional VOCs and biogenic precursors*
6 *(xylene, toluene, isoprene, monoterpenes and sesquiterpenes)*

7

8 and at line 185-186:

9 *This implies that also aging of biogenic products is implicitly taken into account.*

10 Moreover, we added Table 1, as suggested in comment 4, to clarify all the different sets used in
11 the model (as also suggested by referee #2).

12

13 3.

14 In Ciarelli et al. (2016a) for further aging of ASOA and POA vapors from HOA-like emissions you
15 use a reaction rate with OH of $2 \times 10^{-11} \text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$. How about this new study? Was it $4 \times 10^{-11} \text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$ instead or is this only the reaction rate used for BBOA precursors?

16

17 A reaction rate of $4 \times 10^{-11} \text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$ was used to treat aging of biomass semivolatiles SOA
18 which we also applied to the rest of anthropogenic sources (referred to as HOA in the
19 manuscript) in order to be consistent among all the other anthropogenic sources and as already
20 proposed by more recent studies for the range of saturation concentrations used here (Donahue
21 et al., 2013; Jo et al., 2013; Hodzic et al., 2016).

22

23 We added the following information at line 187 of the revised manuscript:

24 *A reaction rate of $4 \times 10^{-11} \text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$ was also applied to the rest of the anthropogenic sources*
25 *(referred to as HOA) in order to be consistent among all the other anthropogenic sources as*
26 *already proposed by more recent studies for the range of saturation concentrations used here*
27 *(Donahue et al., 2013).*

28

29 4.

30 I suggest that you create a table where you list all VBS sets used in the two different model
31 simulations and if they represent SOA or POA, the sources (i.e. BVOCs, biomass burning or fossil
32 fuel burning) and if they represent HOA, BBOA or Biogenic OA. As the manuscript is written now
33 I get very confused about which organic compounds that are POA and SOA, their origin and if
34 they are classified as HOA, BBOA or Biogenic OA. If I understand it correctly the BBOA is only the
35 not atmospheric processed (oxidized) POA emission from biomass burning, and the POA from
36 biomass burning sources that evaporates and then form more oxidized OA is treated as SOA
37 (VBS_BC_NEW set 2) and the VBS_BC_NEW set 3 OA is always treated as SOA. I think you need to
38 more clearly state that BBOA is only referring to the POA from biomass burning but not the SOA
39 formed from biomass burning. I suggest that you change from BBOA to BBPOA. It is only in the
40 abstract L40-41 that you mention that BBOA is referring to primary biomass burning-like OA and
41 HOA primary hydrocarbon-like OA. I missed this and was confused about this when I was
42 reading the manuscript the first time.

43

1
 2 We agree with the referee and added Table1 listing all the sets/sources that we used. We also
 3 changed BBOA to BBPOA throughout the manuscript in order to clarify that BBOA refers only to
 4 the primary fraction.

5
 6 *Table 1. Properties of the VBS space. Oxygen numbers for each volatility bin were calculated using*
 7 *the group-contribution of Donahue et al. (2011). Hydrogen numbers were calculated from the van*
 8 *Krevelen relation (Heald et al., 2010).*

9

	log (C*)	Oxygen number	Carbon number	Hydrogen number	Molecular weight
POA set1*	-1	4.11	11.00	17.89	216
(BBOA-like)	0	3.43	11.75	20.07	216
Primary biomass	1	2.73	12.50	22.27	216
burning (BBPOA)	2	2.01	13.25	24.49	216
	3	1.27	14.00	26.73	215
SOA set2*	-1	4.53	9.00	13.47	194
(BBOA-like)	0	4.00	9.25	14.50	189
SOA from SVOCs	1	3.40	9.50	15.60	184
biomass burning	2	2.83	9.75	16.67	179
SOA set3*	-1	5.25	5.00	4.75	149
(BBOA-like)	0	4.70	5.25	5.80	144
SOA from	1	4.20	5.50	6.80	140
VOC/IVOCs biomass	2	3.65	5.75	7.85	135
burning and biogenics	3	3.15	6.00	8.85	131
POA set1**	-1	2.69	17.00	31.3	278
(HOA-like)	0	2.02	17.50	33.0	275
Rest of primary	1	1.34	18.00	34.7	272
anthropogenic sources	2	0.63	18.5	36.4	268
	3	0.0	19.00	38.0	266

SOA set1**	-1	4.90	7.00	9.10	172
(HOA-like)	0	4.38	7.25	10.1	167
SOA from rest of all anthropogenic in all volatility range	1	3.84	7.50	11.2	163
(SVOCs,IVOCs,VOCs)	2	3.30	7.75	12.2	158
	3	2.74	8.00	13.3	153

1

2 *Based on Ciarelli et al. (2016b).

3 **Molecular structure as in Koo et al. (2014) and Ciarelli et al. (2016a).

4

5 5.

6 The new version of the model underestimates the OA to a less extent than the previous version.
7 The only difference between the model runs is how the BBOA formation is treated. On L306-307
8 you write: “The modelled BBOA fraction on the other hand was generally higher than the
9 measurements, with an average MFB of 50% (Table S3, Figs. 6-7)”. I interpret this as that the
10 model improves the modeled total OA but at least partly for the wrong reason because it gives
11 too much BBOA.

12

13 The model improves mainly because more SOA is predicted for the investigated period, whereas
14 statistics for the POA fractions remained almost unchanged (Table 3 and Table 4 in the revised
15 manuscript). The BBPOA fraction remained almost unchanged respect to the VBS_BC scenario
16 (Table S4).

17 We reformulated the sentence at line 321 of the revised manuscript as below and added Table
18 S4:

19

20 *The modelled BBPOA fraction on the other hand was generally overpredicted as in our previous
21 application (Table S4), with an average MFB of 50% (Table S3, Figs. 6-7)*

22

23 *Table S4. Comparison of statistics for BBPOA in VBS_BC_NEW with VBS_BC (average of all sites in
24 February-March 2009)*

	Mean obs ($\mu\text{g m}^{-3}$)	Mean mod ($\mu\text{g m}^{-3}$)	MB ($\mu\text{g m}^{-3}$)	ME ($\mu\text{g m}^{-3}$)	MFB [-]	MFE [-]
VBS_BC	0.36	0.60	0.24	0.45	0.47	0.98
VBS_BC_NEW	0.36	0.59	0.23	0.43	0.50	0.97

25

26

27 Moreover, PMF analysis is also affected by uncertainties, especially regarding the separation
28 between the BBOA (primary) and SOA (secondary) fractions (Crippa et al., 2013).

29

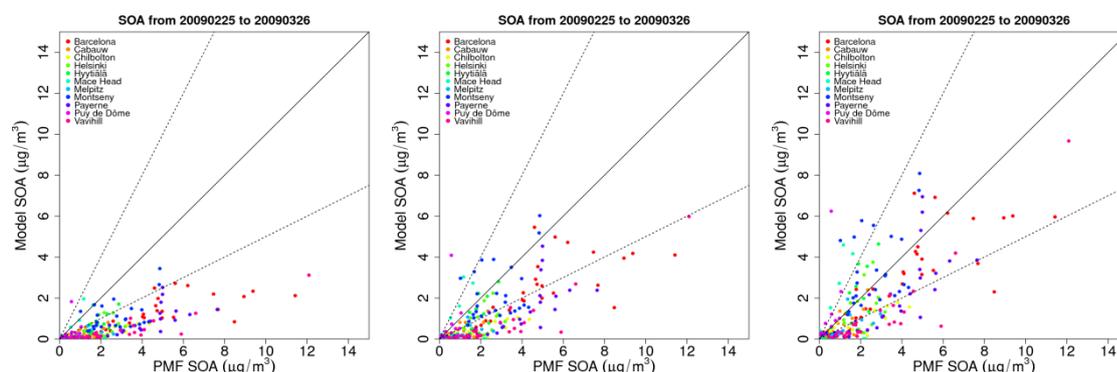
30 6.

31 In Ciarelli et al. (2016a) where you use the VBS_BC method you write: “Further aging of BSOA is
32 not considered in this study, based on previous modelling results showing overprediction of OA
33 when such process is taken into account (Lane et al., 2008; Murphy and Pandis, 2009). This implies

1 *that also further aging of POA vapors from BBOA-like emissions was not considered since it is*
 2 *performed in the same basis set.” This is a large assumption which I think might be one of the*
 3 *main reason why you get much less OA (especially SOA from biomass burning sources) when you*
 4 *run VBS_BC instead of VBS_BC_NEW. This needs to be discussed and explained in the*
 5 *manuscript. I also think that you should run a model simulation using VBS_BC but separating the*
 6 *POA vapors from BBOA and allow them to be further oxidized in the same way as the HOA*
 7 *vapors. Then you compare the model results from this method with the model simulations with*
 8 *your new VBS sets (VBS_BC_NEW). To me this is a more fair evaluation of your new biomass*
 9 *burning-like OA VBS parameterizations compare to the old parameterization from Koo et al.*
 10 *(2014) that to my understanding allowed oxidation of evaporated POA from biomass burning*
 11 *sources. If your new biomass burning VBS parameterization still gives substantially better*
 12 *agreement with the observations than the Koo et al. (2014) VBS parameterization, then your*
 13 *contribution to the field can be considered substantial and important.*

15 We thank the referee for this comment. We included Figure S4 in the manuscript where we
 16 compared the modelled OOA fraction as predicted by VBS_BC, VBS_BC with BBOA vapours
 17 allowed to be further oxidized as in Koo et al. (2014) and VBS_BC_NEW. The Koo et al. 2014 VBS
 18 approach with BBOA vapours allowed to get further oxidized (Figure S4 middle panel) also
 19 helped bringing model and observation in a better agreement, but to a lesser extent compared to
 20 VBS_BC_NEW (Figure S4 right panel). In order to emphasize the importance of aging processes
 21 we added the following statement at line 244 of the revised manuscript:
 22

23 *Improvements in the modelled SOA fraction were also observed using the original VBS approach*
 24 *(Koo et al. 2014) when aging of the biomass burning vapours were taken into account (Figure S4).*
 25
 26



27
 28 *Figure S4. Modelled versus PMF SOA; with VBS_BC (Ciarelli et al., 2016a) (left panel), with VBS_BC*
 29 *where BBOA vapours were allowed to be further oxidized (Koo et al. 2014) (middle panel), and with*
 30 *VBS_BC_NEW (right panel).*

31
 32 7.
 33 *On L49-54 you write: “Contributions to OA from residential combustion precursors in different*
 34 *volatility ranges were also assessed: our results indicate that residential combustion gas-phase*
 35 *precursors in the semi-volatile range contributed from 6 to 30%, with higher contributions*
 36 *predicted at stations located in the southern part of the domain. On the other hand, higher*
 37 *volatility residential combustion precursors contributed from 15 to 38% with no specific gradient*
 38 *among the stations.”*

39 I don't understand how you can separate the SVOC molecules in the gas-phase from the SVOC
 40 molecules in the particle phase. If we assume equilibrium partitioning between a condensed
 41 liquid phase and the air, then the same molecule species are cycled back and forth between the
 42 gas-and particle phase because of evaporation and condensation. Do you mean: additional OA
 43 formed because of SVOC oxidation in the gas-phase as compared to additional OA formed as a

1 consequence of IVOC oxidation in the gas-phase? Related to this I also wonder if all POA species
2 (which are SVOCs) are allowed to evaporate (assuming equilibrate with the gas-phase at all
3 times) and form more oxidized organic compounds that become SOA in the model when they re-
4 condense. Thus, is it correct that all POA species eventually end up as more oxidized SOA species
5 in the model? Or is only a fraction of the POA species allocated to the gas-phase and the rest is
6 fixed in the particles based on the initial fresh POA VBS distribution (Fig S1)?

7
8 Yes, in the sentence we refer to the amount of OA formed due to SVOC oxidation in the gas-phase,
9 and further condensation, and amount of OA formed as a consequence of IVOC oxidation in the
10 gas-phase followed by further condensation.

11 Not all the POA (SVOCs) species are allowed to evaporate in the model and end up to SOA. The
12 POA species (SVOCs) at $\log_{10}C^*=-1$ is used as a proxy for all non-volatile species and will only
13 reside in the particle phase. We added this information in the caption of Fig. S1 as:

14
15 *The lowest bin ($\log_{10}C^*=-1$) is used as a proxy for all non-volatile species which will only reside in*
16 *the particle phase.*

17
18 For the other bins, the amount of SVOCs allocated to the gas-phase depends on the absorptive
19 mass: e.g. a compound with a $C^*=10 \mu\text{g m}^{-3}$ will reside 10%, 50% and 90% in the gas phase at C_{OA}
20 = $100 \mu\text{g m}^{-3}$, $10 \mu\text{g m}^{-3}$ and $1 \mu\text{g m}^{-3}$, respectively. Likewise, the proportion of this compound in
21 the gas-phase increases with increasing temperature. As a consequence, at lower OA
22 concentrations or at higher temperature, the oxidation of this compound is expected to proceed
23 more rapidly.

24
25 We modified the sentence slightly (line 49) in the revised text as:

26
27 *Contributions to OA from residential combustion precursors in different volatility ranges were also*
28 *assessed: our results indicate that residential combustion gas-phase precursors in the semivolatile*
29 *range (SVOC) contributed from 6 to 30%, with higher contributions predicted at stations located in*
30 *the southern part of the domain. On the other hand, the oxidation products of higher volatility*
31 *precursors (the sum of IVOCs and VOCs) contribute from 15 to 38% with no specific gradient*
32 *among the stations.*

33
34 8.

35 On L156-159 you write: "Hourly emissions of biogenic VOCs, such as monoterpenes, isoprene,
36 sesquiterpenes, xylene and toluene, were calculated using the Model of Emissions of Gases and
37 Aerosols from Nature MEGANv2.1 (Guenther et al., 2012) for each grid cell in the model domain."

38 But into what VBS scheme are the BVOC oxidation products added? In Koo et al., (2014) and
39 Ciarelli et al. (2016a) you have a 4th VBS set for BVOC oxidation products which are not allowed
40 to age because then you get too much SOA. According to Section 3.3 all of the modeled SOA can
41 either be attributed to residential or non-residential combustion. What about the SOA from
42 BVOCs? Did you not consider BVOCs when you calculated the SOA formation in this new study? I
43 thought that the only difference between the base case model run in Ciarelli et al. (2016a) and in
44 this work was the VBS setup for the BBOA and it's transformation to SOA? This needs to be
45 clarified. At least for the southernmost stations I would expect that BSOA formation also is
46 substantial during the wintertime, and transport from south to north could bring this SOA to the

1 northern latitudes too.

2
3 Certainly the SOA formation from BVOCs is very important and it was always considered in all
4 the versions. There is, however, no separate set to allocate oxidation products from biogenic
5 precursors, therefore they follow the same oxidation pathways of biomass burning like aerosol,
6 including aging. We are currently working on an updated version of CAMx in which biogenic
7 sources will be separated. In order to address the question of the referee, we performed a
8 sensitivity test with no biogenic formation (where the reactions of isoprene, monoterpene and
9 sesquiterpene against the OH, O₃ and NO₃ oxidants were turned off) and compared the results
10 with the base case (VBS_BC_NEW). The contribution of biogenic SOA is then retrieved by
11 calculating the difference between SOA in the reference simulation (including biogenic SOA
12 formation) and the one with no biogenic SOA formation. Based on this test, BVOC contribution to
13 SOA was predicted to be around 20% for the stations at the lowest latitude (Spain) and a
14 decreasing trend with increasing latitude (less than 5% in Helsinki and Hyytiälä) was found
15 (Figure S5). This is consistent with higher temperatures and consequently more biogenic
16 emissions at locations in the south than those in the north. However, the most predominant
17 source was still predicted to be anthropogenic. We also included the snow cover for March 2009
18 as retrieved from the TERRA/MODIS instrument in Figure S6. Larger parts of the Scandinavian
19 countries were almost completely covered with snow, partially suppressing the emission of
20 biogenic precursors and in line with less contribution predicted from biogenic sources in
21 Helsinki and Hyytiälä by the model (for the investigated periods).

22 Comparisons between VBS_BC, VBS_BC_NEW and the sensitivity test with no biogenic SOA
23 formation, showed similar improvement, with differences occurring mainly in the southern
24 stations of Barcelona and Montseny (Figure S7). We revised the legends of Figures 11 and 12 to
25 make it more clear that the biomass burning set also includes biogenic SOA and we added results
26 from the sensitivity test at line 372 of the revised manuscript and at the last bullet point of the
27 conclusions as below:

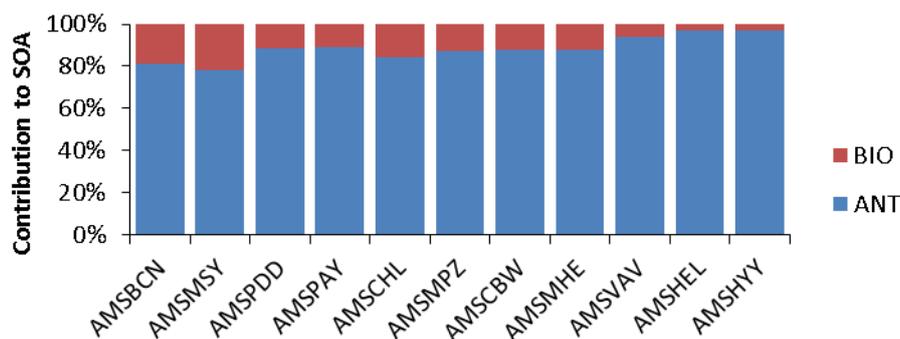
28
29 Line 372:

30
31 *Since biogenic SOA is included in the same set as the biomass burning (set3) for this model*
32 *application, we performed a sensitivity test with no SOA formation from biogenic precursors (where*
33 *the reactions of isoprene, monoterpene and sesquiterpene with OH, O₃ and NO₃ were turned off).*
34 *Our results indicated that for this period, biogenic precursors contribute to SOA to a lesser extent*
35 *(5-20%) than the anthropogenic ones, with higher contributions at southern stations consistent*
36 *with higher temperatures, and consequently more biogenic emissions compared to the northern*
37 *stations (Figure S5). The most predominant source was still predicted to be anthropogenic. Snow*
38 *cover for March 2009 as retrieved from the TERRA/MODIS revealed that larger parts of the*
39 *Scandinavian countries were almost completely covered with snow (Fig. S6), partially suppressing*
40 *the emission of biogenic precursors and in line with very low contribution predicted from biogenic*
41 *sources in Helsinki and Hyytiälä. Comparison of SOA from VBS_BC_NEW and the sensitivity test*
42 *with no biogenic SOA formation showed similar improvement with respect to VBS_BC, with*
43 *differences occurring mainly in the southern stations of Barcelona and Montseny (Fig. S7).*
44

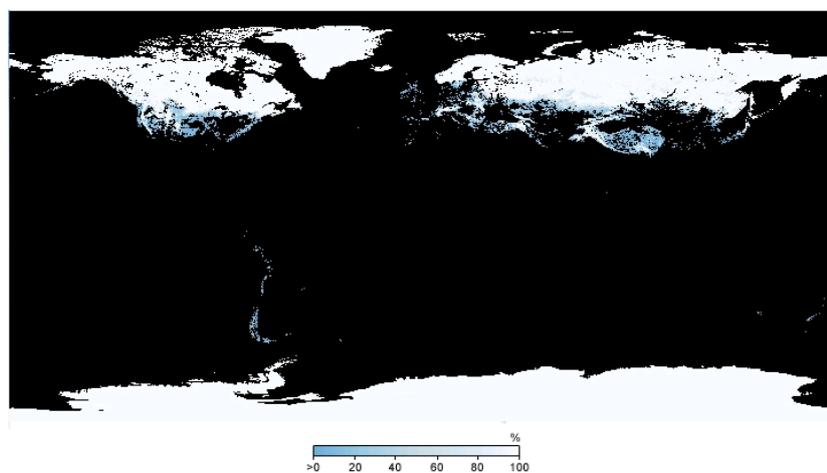
45 In the conclusions as last bullet point:

- 46
47 - *Model simulation performed with and without biogenic SOA formation revealed that, for*
48 *this period, biogenic SOA contributed only to a small extent to the total SOA (5-20%), with*
49 *an increasing gradient from north to south.*
50

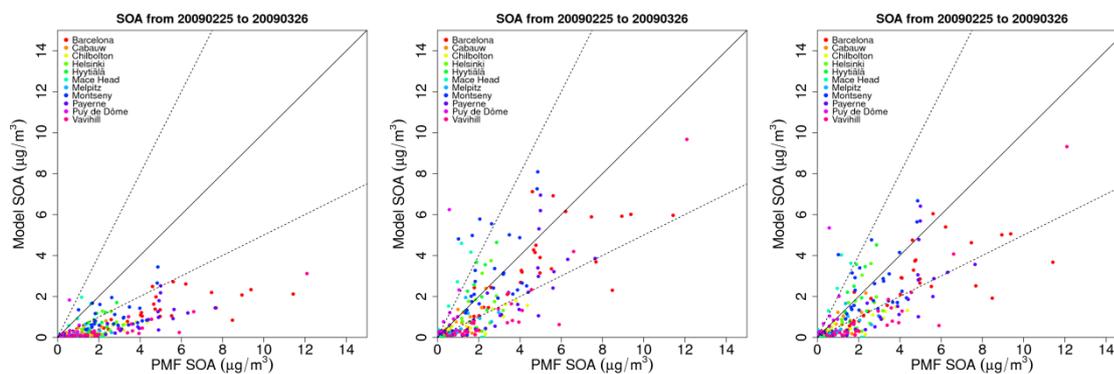
51



1
2 Figure S5. Biogenic and anthropogenic contribution to SOA at stations from south to north
3 retrieved as a difference between the predicted SOA in the reference simulation (including biogenic)
4 and a sensitivity test with no biogenic SOA formation.
5



6
7 Figure S6. Snow cover for March 2009 as retrieved by the TERRA/MODIS instrument.
8
9



10
11
12 Figure S7. Modelled versus PMF SOA; with VBS_BC (Ciarelli et al., 2016a) (left panel), with
13 VBS_BC_NEW (middle panel), and with VBS_BC_NEW but without biogenic SOA (right panel).
14

15 9.
16 On L170-173 you write: "The third set allocates oxidation products from traditional VOCs (xylene,
17 toluene, isoprene, monoterpenes and sesquiterpenes) and from non-traditional SOA precursors
18 retrieved from chamber data (~4.75 times the amount of organic material in the semi-volatile
19 range, Ciarelli et al., 2016b)." So do I understand it correctly that this 3rd VBS set for VOCs

1 originating from biomass burning only considers the traditional VOCs emitted from biomass
2 burning but not the traditional VOCs from other sources? I.e. the same traditional VOC species
3 but from other sources (vegetation and fossil fuel) is added to other separate VBS sets. This,
4 would be desirable since it allows you to distinguish SOA formed from biomass burning, biogenic
5 VOCs and VOCs from fossil fuel sources?
6

7 For this application we don't have a separate set to allocate oxidation products from biogenic
8 precursors, and they follow the same oxidation pathways of biomass burning like aerosol,
9 including aging. Fossil and non-fossil emissions are separated but biomass combustion from
10 residential heating and biogenic precursors are treated in the same set (as in Koo et al., 2014).
11 We strongly agree with the referee that a separate set, exclusively for biogenic precursors, would
12 be highly desirable and we are currently working on an updated version of CAMx which includes
13 such separation. The sensitivity test mentioned above suggests that BVOC emissions might
14 contribute to the total SOA mass by ~5-20%.

15
16 10.

17 On L232-235 you write: "*In spite of the improvements with respect to earlier studies, modelled OA*
18 *is still lower than measured (mean bias MB from -0.1 $\mu\text{g m}^{-3}$ up to -3.1 $\mu\text{g m}^{-3}$) at most of the sites,*
19 *with only a slight overestimation at a few locations (MB from 0.3 $\mu\text{g m}^{-3}$ up to 0.9 $\mu\text{g m}^{-3}$)." Here I
20 think you also should mention that the model might underestimate the OA formation because no
21 gradual BVOC oxidation is considered. Or maybe even more if you did not consider any biogenic
22 SOA formation?
23*

24 As we stated earlier, we do consider SOA formation from biogenic precursors and they follow the
25 same oxidation pathways of biomass burning like aerosol, including aging and as we wrote
26 above, we strongly agree with the referee that a separate set, exclusively for biogenic precursors,
27 would be highly desirable. However there could also be other reasons for the under-prediction of
28 the modelled SOA fraction presented here (as also addressed in the reply to referee #2). Marine
29 OA emissions are not included in our simulation. Gantt et al., (2015) showed that primary
30 marine organic aerosol has a weaker coastal-to-inland concentrations gradient than sea-salt
31 aerosol with some inland European cities having more than 10% of the submicron organic
32 aerosol mass as a marine source. Fire emissions, which were not included for this study, are
33 likely to be less important for this comparison since there were few fires activity data during the
34 considered periods (as also addressed in the reply to referee 2).

35 Moreover, aqueous phase SOA formation is not considered in this model application, which
36 might be important for explaining the remaining discrepancies between model and retrieved
37 OOA from measurements.
38

39 11.

40 Was the influence of NO considered when you divided the SOA precursors into the different VBS
41 bins as was done by Koo et al. (2014)?
42

43 Yes, the influence of NO was considered as in Koo et al. (2014) and it was based on smog
44 chamber data (Murphy and Pandis, 2009 and Hildebrandt et al., 2009).
45
46

47 To summarize: The model results looks reasonable and the agreement between the model and
48 observations are as good as you could expect both when using the new VBS set and the old VBS
49 set from Ciarelli et al. (2016a). But to me it still remain to be shown that the new VBS
50 parameterization for biomass burning-like OA substantially improves the model performance as
51 to compared to the VBS parameterization developed by Koo et al. (2014). I.e. you need to
52 compare the model results from the simulations with your new VBS parameterization with a
53 simulation using the Koo et al., (2014) VBS parameterization where you also allow the

1 evaporated BBOA material to be further oxidized in the gas-phase. I also think you need to
2 evaluate if not at least part of the reason why the model underestimates the OA is because it
3 underestimates or maybe not even considers biogenic SOA formation.
4
5

6 We thank the reviewer for appreciating our model results. In the revised manuscript we
7 improved the description of methods and added sensitivity tests to give a more comprehensive
8 picture of this model application. The comparison of the results with those from Koo et al.
9 (2014) clearly shows the improvement in the model performance (Fig. S4).
10

11 Minor specific comments:

12
13 L47, Page 1: Here you use the term “transportation precursors”. I think you mean precursors
14 from the road transportation sector. I think you should change the formulation a bit to make this
15 clearer.
16

17 Done.

18
19 L78-79 You write: “Moreover, numerous ambient studies of open burning plumes from aircraft do
20 not show a net increase in OA, despite observing oxidation (Cubison et al., 2011; Jolleys et al.,
21 2012).”

22 I suggest that you reformulate this sentence and instead write something like: *Moreover,*
23 *numerous ambient studies with aircraft of open biomass burning plumes do not show a net increase*
24 *in OA, despite observed oxidation (Cubison et al., 2011; Jolleys et al., 2012).*

25 When I first read this sentence I thought the open burning plumes came from the aircraft but
26 then I realized that the aircrafts were only used for the measurements of the open biomass
27 burning plumes.
28

29 Done.

30
31 L98-103: The sentence: “Ciarelli et al. (2016a) showed that allowing for evaporation of primary
32 organic particles as available in European emission inventories degraded OA performance (further
33 under-predicted OA but with the POA to SOA ratio in a better agreement) whereas model
34 performance improved when volatility distributions that implicitly account for missing semi-
35 volatile material (increasing POA emissions by a factor of 3) were deployed.” is hard to understand.
36 I suggest that you split it into two or three sentences. What do you mean with “degraded OA
37 performance”? Do you mean: degraded the model performance concerning the modeled total OA
38 mass?
39

40 Yes. We modified the sentence to make it clearer:

41 *Ciarelli et al. (2016a) showed that allowing for evaporation of primary organic particles as*
42 *available in the European emission inventories degraded the model performance for the total OA*
43 *mass (further under-predicted OA but the POA to SOA ratio in a better agreement with*
44 *measurements). In the same study, on the other hand, model performance improved when volatility*
45 *distribution that implicitly accounts for missing semivolatile material (increasing POA emissions by*
46 *a factor of 3) was deployed.*
47

48 On L112-115 you write: “This indirect accounting of missing organic material could be used in the
49 absence of more detailed gridded emission inventories, keeping in mind that the amount of higher
50 volatility compounds was specifically derived from studies conducted with diesel engines (Robinson
51 et al., 2007).”

52 In fact I think the Robinson et al., (2007) study was only performed on one single diesel engine
53 (a single-cylinder Yanmar diesel generator), which I expect do not represent modern diesel car

1 engines very well.
2 I suggest that you instead of “diesel engines” at least write: a *single diesel engine*.
3
4 The sentence was modified as:
5 *This implies that, in these applications, the new emitted organic mass (POA + SVOCs + IVOCs) is 7.5*
6 *times higher than in original emissions (i.e., $OM = (3*POA) + (1.5*(3*POA))$) which could be used as*
7 *an indirect method to account for missing organic material in the absence of more detailed gridded*
8 *emission inventories.*
9 .
10 On L284-287 you write: “*On the other hand, the remote station of Mace Head showed a positive*
11 *bias for SOA (MFB = 30%), even though model and measurement concentrations were very similar*
12 *(0.54 and 0.35 $\mu\text{g m}^{-3}$, respectively), which could be*
13 *attributed to an overestimated contribution from the boundaries.”*
14 What do you mean by “*overestimated contribution from the boundaries*”? Is it the influence from
15 the model boundary conditions?
16
17 Yes, in this case from the western boundary of the model domain.
18 On L337-340 you write: “*The model results indicate that non-residential combustion and*
19 *transportation precursors contribute about 30-40% to SOA formation (with increasing*
20 *contribution at urban and near-industrialized sites) whereas residential combustion (mainly*
21 *related to wood burning) contribute to a larger extent, i.e., around 60-70%.”*
22 I suggest that you change to:
23 *The model results indicate that non-residential combustion and transportation precursors*
24 *contribute to about 30-40 % of the SOA formation (with increasing contribution at urban and near-*
25 *industrialized sites) whereas residential combustion (mainly related to wood burning) contribute*
26 *to a larger extent, i.e., around 60-70%.*
27
28 We agree and changed the sentence as suggested.
29
30 On line L349-351 you write: “*In the southern part of the domain, the higher temperature will*
31 *favour more organic material in the semi-volatile range to reside in the gas-phase, rendering it*
32 *available for oxidation.”*
33 I would also expect that the higher UV-light intensity in the south caused more SOA formation
34 because of higher OH concentrations.
35
36 We agree with the referee. In the southern part of the domain more OH should be available to
37 react with secondary organic aerosol precursors. We revised the sentence at line L366-368 as
38 below:
39
40 *In the southern part of the domain, where more OH is available, the higher temperature will favour*
41 *more organic material in the semi-volatile range to reside in the gas-phase, rendering it available*
42 *for oxidation.*
43
44 On line L351-351 you write: “*On the other hand, no south-to-north gradient was predicted for the*
45 *higher volatility class of precursors.”*
46 Do you mean?
47 *On the other hand, no south-to-north gradient was predicted for the SOA formed from the higher*
48 *volatility class of precursors.*
49
50 Yes. We thank the referee for this comment and we corrected the sentence as suggested.
51
52 On L 291-294 you write: “*Mostly traffic-related HOA was underestimated at the urban site*
53 *Barcelona (Table S2, Fig. 6), with the model not able to reproduce the diurnal variation of HOA at*

1 *this urban site likely due to poorly reproduced meteorological conditions or too much dilution*
2 *during day time in the model (Fig. S2)."*

3 Can it not also be because of too weak diurnal variations in the HOA emissions from traffic in the
4 model?

5 Reflection: But in the case of Helsinki it seem as if the model instead gives substantially more
6 HOA during the morning (6 UTC, 8 am local time, and 15 UTC, 5 pm local time), which is what
7 you would expect if the HOA mainly came from the local traffic. But surprisingly to me the
8 observations do not indicate any increased local HOA contribution during the morning and
9 afternoon rush hours in Helsinki. Could it be related to the vehicle fleet in Helsinki (i.e. is the
10 road traffic very much dominated by gasoline cars which do not emit much primary HOA but
11 precursors for SOA formation) ?

12
13 HOA in Barcelona as determined by PMF analysis displays an atypical diurnal variation with a
14 late peak in the morning and no clear increase in the night. The reason for this behavior is still
15 unknown and is not captured by the model. The site of Barcelona is located in a complex area, i.e.
16 on the coast and close to mountains, which is difficult to model with such a coarse model
17 resolution (0.25x0.25 deg).

18 On the other hand, it is possible that emissions for Helsinki are not realistic in the model
19 (Karvosenoja et al., 2008). Fountoukis et al. (2014) also reported similar over-prediction at the
20 site of Helsinki for the primary organic fraction during the February- March 2009 period.

23 24 **REFERENCES**

25
26 Ciarelli, G., Aksoyoglu, S., Crippa, M., Jimenez, J.-L., Nemitz, E., Sellegri, K., Äijälä, M.,
27 Carbone, S., Mohr, C., O'Dowd, C., Poulain, L., Baltensperger, U. and Prévôt, A. S. H.:
28 Evaluation of European air quality modelled by CAMx including the volatility basis set
29 scheme, *Atmos. Chem. Phys.*, 16 (16), 10313–10332, doi:10.5194/acp-16-10313-2016, 2016a.

30 Ciarelli, G., El Haddad, I., Bruns, E., Aksoyoglu, S., Möhler, O., Baltensperger, U. and
31 Prévôt, A. S. H.: Constraining a hybrid volatility basis set model for aging of wood burning
32 emissions using smog chamber experiments, *Geosci. Model Dev.*, accepted, 2016b.

33 Crippa, M., DeCarlo, P. F., Slowik, J. G., Mohr, C., Heringa, M. F., Chirico, R., Poulain, L.,
34 Freutel, F., Sciare, J., Cozic, J., Di Marco, C. F., Elsasser, M., Nicolas, J. B., Marchand, N.,
35 Abidi, E., Wiedensohler, A., Drewnick, F., Schneider, J., Borrmann, S., Nemitz, E.,
36 Zimmermann, R., Jaffrezo, J.-L., Prévôt, A. S. H., and Baltensperger, U.: Wintertime aerosol
37 chemical composition and source apportionment of the organic fraction in the metropolitan
38 area of Paris, *Atmos. Chem. Phys.*, 13, 961-981, doi:10.5194/acp-13-961-2013, 2013.

39 Donahue, N. M., Chuang, W., Epstein, S. A., Kroll, J. H., Worsnop, D. R., Robinson, A. L.,
40 Adams, P. J. and Pandis, S. N.: Why do organic aerosols exist? Understanding aerosol
41 lifetimes using the two-dimensional volatility basis set, *Environ. Chem.*, 10(3), 151,
42 doi:10.1071/EN13022, 2013.

1 Fountoukis, C., Megaritis, A. G., Skyllakou, K., Charalampidis, P. E., Pilinis, C., Denier van
2 der Gon, H. A. C., Crippa, M., Canonaco, F., Mohr, C., Prévôt, A. S. H., Allan, J. D., Poulain,
3 L., Petäjä, T., Tiitta, P., Carbone, S., Kiendler-Scharr, A., Nemitz, E., O'Dowd, C., Swietlicki,
4 E. and Pandis, S. N.: Organic aerosol concentration and composition over Europe: insights
5 from comparison of regional model predictions with aerosol mass spectrometer factor
6 analysis, *Atmos. Chem. Phys.*, 14(17), 9061–9076, doi:10.5194/acp-14-9061-2014, 2014.

7

8 Gantt, B., Johnson, M. S., Crippa, M., Prévôt, A. S. H., and Meskhidze, N.: Implementing
9 marine organic aerosols into the GEOS-Chem model, *Geosci. Model Dev.*, 8, 619–629,
10 doi:10.5194/gmd-8-619-2015, 2015.

11 Hodzic, A., Kasibhatla, P. S., Jo, D. S., Cappa, C. D., Jimenez, J. L., Madronich, S., and Park,
12 R. J.: Rethinking the global secondary organic aerosol (SOA) budget: stronger production,
13 faster removal, shorter lifetime, *Atmos. Chem. Phys.*, 16, 7917–7941, doi:10.5194/acp-16-
14 7917-2016, 2016.

15 Jo, D. S., Park, R. J., Kim, M. J., Spraklen, D. V., Effects of chemical aging on global
16 secondary organic aerosol using the volatility basis set approach, *Atmos., Environ.*, 81, 230-
17 244, 2008

18 Karvosenoja, N., Tainio, M., Kupiainen, K., Tuomisto, J. T., Kukkonen, J. & Johansson, M.
19 Evaluation of the emissions and uncertainties of PM_{2.5} originated from vehicular traffic and
20 domestic wood combustion in Finland. *Boreal Env. Res.* 13: 465–474, 2008.

21 Koo, B., Knipping, E. and Yarwood, G.: 1.5-Dimensional volatility basis set approach for
22 modeling organic aerosol in CAMx and CMAQ, *Atmos. Environ.*, 95, 158–164,
23 doi:10.1016/j.atmosenv.2014.06.031, 2014.

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27 **Responses to the comments of anonymous referee #2**

28

29 Thank you for your comments that helped to improve our manuscript. Please find below your
30 comments in blue, our responses in black and modifications in the revised manuscript in *italic*.

31

32 [Ciarelli et al. follow up two other recent publications by augmenting the CAMx VBS](#)

1 implementation with their new parameterization for emission and aging of BBOA emissions. The
2 study itself is a useful application and soundly conceived. The authors find better model-
3 measurement agreement than their previous implementation, but I am troubled by some aspects
4 of their methods and analysis, as described below. Their inclusion of the factor of 3 multiplier to
5 account for missing SVOCs was an approach originally recommended for Mexico City but has not
6 been used for Europe by previous EUCAARI model studies (e.g. Fountoukis et al., 2014). I am
7 open to the authors' interpretation/justification for this choice (especially if I've misinterpreted
8 the situation), but on its face this is a rather critical assumption that could put major aspects of
9 the paper's conclusions in jeopardy. Moreover, the application of modeled PM_{2.5} mass to PM_{1.0}
10 measurements raises questions about how much of the model agreement is spurious.
11 Considering both of these potential biases together, it is concerning that the model predictions
12 for SOA and POA are still lower in many cases than the VBS predictions published by Fountoukis
13 et al. (2014) for the same model scenario. I could recommend this paper for publication after
14 these issues are resolved.

15
16
17 Specific comments:

18
19 1. Page 4, line 108-113: The ratio of semivolatile to nonvolatile material is, as the authors know, a
20 function of the emission source, fuel, and operating conditions – I think it is overly simplistic and
21 actually unhelpful to state that the ratio is predicted to be “roughly 3.” The Shrivastava et al.
22 (2011) and Tsimpidi et al. (2010) studies argued that those SVOCs at Mexico City were missing
23 from the inventories because the emissions were parameterized using ambient observations of
24 OA, which would have already equilibrated to atmospheric conditions. On the other hand, the
25 emission factors used to inform the gridded inventories of Europe and the US are, to my
26 knowledge, derived from laboratory scale tests, where much of those SVOCs are notoriously
27 condensed in the particle phase in undiluted exhaust. My reading of Fountoukis et al. (2014)
28 does not lead me to believe that they enhanced their SVOC emissions by a factor of 3 over POA.
29 Rather, I believe they simply repartitioned the existing POA, and they added an additional
30 1.5*POA for the IVOCs as the authors state. Ciarelli et al. (2016a) shows that the extra SVOCs are
31 needed to improve the model performance (i.e. VBS_BC did much better than VBS_ROB), but I
32 disagree that there is evidence that SVOCs are underestimated in European inventories by so
33 much. Instead, I would argue the real source of this mass is still unknown and is probably a
34 combination of underestimated SOA yields, aqueous processing, aging of anthropogenic and
35 biogenic SOA and some missing SVOCs as well.

36
37 At minimum, a considerable amount of rewriting in the methods, conclusions and abstract is
38 necessary so that the authors communicate explicitly that an unknown fraction of these SVOCs
39 are very likely double-counted and that this parameter needs to be refined and probably lowered
40 in the future as more explicit pathways are added to the model.

41
42
43 It is true that our previous studies indicated a deterioration of the model performance for OA
44 when evaporation of primary organic particles was allowed while using the approach proposed
45 for the Mexico city study (Shrivastava et al. (2011); Tsimpidi et al. (2010)) led to a better
46 performance (VBS_BC in Ciarelli et al., 2016a). We agree with the referee that other factors such
47 as underestimation of SOA yields, aqueous processing and aging of anthropogenic and biogenic
48 SOA might also play a crucial role in addition to missing SVOCs and we also agree that the factor
49 of 3 used in this study for the inclusion of semi-volatile organic compounds might have high
50 uncertainties.

51 This choice however, was based on the recent European study by Denier van der Gon et al.
52 (2015) rather than the Mexico City studies. The OA emissions in Europe have often been claimed

1 to be under-predicted in current inventories (Bergstrom et al., 2012; Fountoukis et al., 2014) but
2 only recent studies are starting to better elucidate the range of uncertainties related to them, in
3 particular because of the semi-volatile nature of such material. In the work of Denier van der
4 Gon et al. (2015) a revised residential wood combustion (named TNO-newRWC) emission
5 inventory was compiled for Europe using a bottom-up approach. The authors underlined the
6 importance of various sampling methods and measurement protocols or techniques influencing
7 particle emission factors using data from the survey of Nussbaumer et al. (2008a,b). The most
8 important sampling methods used by the countries participating in the survey, were filter
9 measurements of only solid particles (SP) and dilution tunnel (DT) measurements of solid
10 particles and condensable organics (or semivolatile organics). For conventional woodstoves, the
11 authors found a difference in PM emission factors by a factor of up to 5 between the two
12 techniques. The revised emission inventory (TNO-newRWC) was later compiled using the
13 average DT emission factor from different type of appliance (Table 2 in Denier van der Gon et al.,
14 2015) and compared with previously used emission inventory EUCAARI. The authors concluded
15 that the revised emissions were higher than those in the EUCAARI inventory by a factor of 2-3
16 which is similar to the correction factor used in our study and in Shrivastava et al. (2011) and
17 Tsimpidi et al. (2010). However, it should be noted that a substantial inter-country variation was
18 reported within the gridded emission inventories which might lead to over or underestimation
19 of emissions depending on the country (for example the ratio between the TNO-newRWC and
20 EUCAARI emission inventory was around 1-3 in France and up to a factor of 5-10 in Sweden and
21 Finland).

22 Denier van der Gon et al. (2015) also used the revised emission inventory in two commonly used
23 chemical transport models carrying the VBS scheme to perform the organic chemistry: PMCAMx
24 and EMEP model. They found that the revised emission inventory substantially improved the
25 agreement between measured and predicted organic aerosol for the same period presented in
26 this study (Feb-Mar 2009) with results in line with the VBS_BC scenario performed in Ciarelli et
27 al. (2016a) and VBS_BC_NEW presented here. Therefore, we think that the correction factor
28 proposed in this study (factor of 3) can be used until detailed emission inventories including
29 semivolatile compounds are available for the modeling community. Moreover, other explicit SOA
30 formation pathways must be included as more experimental data will be available.

31 We inserted the following statements in the abstract, conclusions and method part as suggested
32 by the referee.

33 In the abstract as below:

34
35 *Although the new parameterization leads to a better agreement between model results and*
36 *observations, it still under-predicts the SOA fraction suggesting that uncertainties in the new*
37 *scheme and other sources and/or formation mechanisms remain to be elucidated. Moreover, a more*
38 *detailed characterization of the semivolatile components of the emissions is needed.*
39

40 In the method at line 171 of the revised manuscript:

41
42 *In order to include gas-phase organics in the semivolatile range in the absence of more detailed*
43 *inventory data, we used the approach of increasing the standard emissions by a factor of 3*
44 *proposed by previous studies (Shrivastava et al., 2011; Tsimpidi et al., 2010) which is also in line*
45 *with the recent European study on the revision of the residential wood combustion emissions*
46 *(Denier van der Gon et al., 2015). This approach of including the semivolatile compounds can be*
47 *used until detailed emission inventories with more realistic inter-country distribution of the*
48 *emissions become available (e.g. Denier van der Gon et al., 2015).*
49

50 In the conclusions, line 417 of the revised manuscript:

51

1 On the other hand, the modelled BBPOA was higher than the measurements at several stations
2 indicating the need for further studies on residential heating emissions, their volatility distribution
3 and oxidation pathway of the semivolatile organic gases. In addition, more detailed emission
4 inventories are needed to characterize the semivolatile components better, as proposed by Denier
5 van der Gon et al. (2015).

6
7 2. I agree with the first reviewer that there needs to be significant more description of the VBS
8 framework used here. The diagrams in Ciarelli et al. (2016b) are helpful and there should be a
9 table or diagram in this manuscript that summarize that information for the entire VBS picture
10 including emissions and aging.

11
12 We agree and revised the part about the VBS scheme as suggested also by Referee #1 in Section
13 2.2 as below. We added Table 1 to summarize the description of the VBS spaces.

14 2.2 Organic aerosol scheme

15
16 *The biomass burning organic aerosol scheme was constrained using recently available wood burning*
17 *smog chamber data (Bruns et al., 2016) as described in Ciarelli et al. (2016b). The model deploys*
18 *three different basis sets (Donahue et al., 2011) to simulate the emissions of organics from biomass*
19 *burning and their evolution in the atmosphere. The first set allocates fresh emissions into five volatility*
20 *bins with saturation concentrations ranging between 10^{-1} and $10^3 \mu\text{g m}^{-3}$ following the volatility*
21 *distribution and enthalpy of vaporization proposed by May et al. (2013). In order to include gas-phase*
22 *organics in the semivolatile range in the absence of more detailed inventory data, we used the*
23 *approach of increasing the standard emissions by a factor of 3 proposed by previous studies*
24 *(Shrivastava et al., 2011; Tsimpidi et al., 2010) which is also in line with the recent European study on*
25 *the revision of the residential wood combustion emissions (Denier van der Gon et al., 2015). This*
26 *approach of including the semivolatile compounds can be used until detailed emission inventories with*
27 *more realistic inter-country distribution of the emissions become available (e.g. Denier van der Gon et*
28 *al., 2015). The second set allocates oxidation products from SVOCs after shifting the volatility by one*
29 *order of magnitude. The third set allocates oxidation products from the traditional VOCs and biogenic*
30 *precursors (xylene, toluene, isoprene, monoterpenes and sesquiterpenes) and from non-traditional*
31 *SOA precursors retrieved from chamber data (~4.75 times the amount of organic material in the*
32 *semivolatile range, Ciarelli et al., 2016b). Primary and secondary semivolatile compounds react with*
33 *OH in the gas-phase with a rate constant of $4 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ (Donahue et al., 2013), which*
34 *decreases their saturation concentration by one order of magnitude. This implies that also aging of*
35 *biogenic products is implicitly taken into account. A reaction rate of $4 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ was also*
36 *applied to the rest of the anthropogenic sources (referred to as HOA) in order to be consistent among*
37 *all the other anthropogenic sources as already proposed by more recent studies for the range of*
38 *saturation concentrations used here (Donahue et al., 2013). No heterogeneous oxidation of organic*
39 *particles or oligomerization processes is included in the model. The new model parameterization*
40 *described in this study is referred to as VBS_BC_NEW throughout the paper to distinguish it from the*

1 *previous base case called VBS_BC as given in Ciarelli et al. (2016a). All the VBS sets are listed in*
2 *Table 1. More details on the VBS scheme can be found in Ciarelli et al. (2016b) and Koo et al. (2014).*

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22 *Table 1. Properties of the VBS space. Oxygen numbers for each volatility bin were calculated using*
23 *the group-contribution of Donahue et al. (2011). Hydrogen numbers were calculated from the van*
24 *Krevelen relation (Heald et al., 2010).*

	log (C*)	Oxygen number	Carbon number	Hydrogen number	Molecular weight
POA set1*	-1	4.11	11.00	17.89	216

(BBOA-like)	0	3.43	11.75	20.07	216
Primary biomass burning (BBPOA)	1	2.73	12.50	22.27	216
	2	2.01	13.25	24.49	216
	3	1.27	14.00	26.73	215
SOA set2*	-1	4.53	9.00	13.47	194
(BBOA-like)	0	4.00	9.25	14.50	189
SOA from SVOCs biomass burning	1	3.40	9.50	15.60	184
	2	2.83	9.75	16.67	179
SOA set3*	-1	5.25	5.00	4.75	149
(BBOA-like)	0	4.70	5.25	5.80	144
SOA from VOC/IVOCs biomass burning and biogenics	1	4.20	5.50	6.80	140
	2	3.65	5.75	7.85	135
	3	3.15	6.00	8.85	131
POA set1**	-1	2.69	17.00	31.3	278
(HOA-like)	0	2.02	17.50	33.0	275
Rest of primary anthropogenic sources	1	1.34	18.00	34.7	272
	2	0.63	18.50	36.4	268
	3	0.0	19.00	38.0	266
SOA set1**	-1	4.90	7.00	9.10	172
(HOA-like)	0	4.38	7.25	10.1	167
SOA from rest of all anthropogenic in all volatility range (SVOCs,IVOCs,VOCs)	1	3.84	7.50	11.2	163
	2	3.30	7.75	12.2	158
	3	2.74	8.00	13.3	153

1

2 **Based on Ciarelli et al. (2016b).*

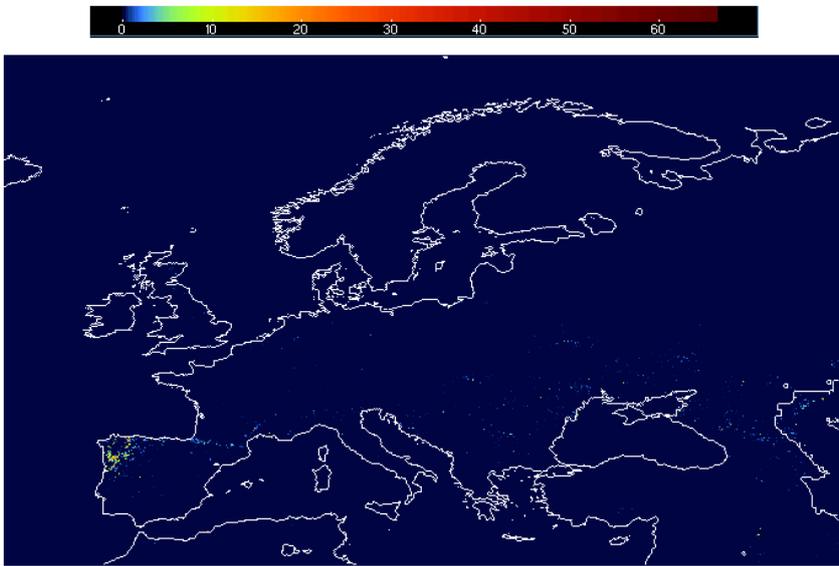
3 ***Molecular structure as in Koo et al. (2014) and Ciarelli et al. (2016a).*

4

5 3. What is being done about wildfires in the model? Were there any during the EUCAARI
6 scenario? Are they represented well in the emissions inputs? If so, how do they effect the source
7 apportionment analysis that is presented?

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Emissions from wildfires were not considered for this application since they were not delivered in the EURODELTA3 exercise for the year 2009 (Bessagnet et al., 2016). We analyzed the fire emission data (non-domestic fires) as available in IS4FIRES data (Sofiev et al., 2009) obtained by re-analysis of fire radiative power data from the MODIS instrument. Figure 1 below shows the cumulative emissions from wildfires in kg/s in March 2009. Significant fires occurred mainly in the north of Portugal. We think that the effect on the simulated OA concentrations might be quite limited since all the investigated stations are located quite far from that area.



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Figure 1. Cumulative emissions from wildfires in kg/s during the month of March 2009 as in IS4FIRES (Sofiev et al., 2009).

4. On page 5, lines 150-151, the authors point out that CAMx is predicting PM_{2.5}. But the evaluation is against AMS observations which I presume are primarily PM_{1.0}. Doesn't this fact make the frequent underprediction in SOA even more troubling? Is anything more specific known about the diameter of PM_{2.5} particles to allow the authors to estimate the fraction that would be PM_{1.0} and thus more applicable to the measurements?

This issue was discussed in Aksoyoglu et al. (2011) where PM₁ and PM_{2.5} measurements in Payerne during both winter (January 2007) and summer (June 2006) periods were compared. The authors concluded that the differences between the two fractions were usually rather small (Figure 14 in Aksoyoglu et al., 2011). These results are also supported by a recent study where comparisons between the organic matter concentrations in PM₁ and PM_{2.5} fractions in winter were found to be in the same range (Bozzetti et al., 2016).

5. Given that points 1 and 4 would lead one to expect substantial overprediction by the model, please also explain why the current predictions are lower than those in Fountoukis et al. (2014) at many sites.

We don't expect substantial overprediction due to particle size as we explained above at point 4. Even though both model simulations (this study and Fountoukis et al., 2014) mostly cover the same domain and time period, some differences are expected due to model resolution, different input data used in simulations as well as the differences in chemical mechanisms. Fountoukis et al. (2014) account for marine OA emissions which are not included in our simulations. In Fountoukis et al. (2014), the emissions were calculated based on the scheme of O'Dowd et al. (2008) and the organic aerosol fractions allocated in both fine and coarse mode. Gantt et al.,

1 (2015) showed that primary marine organic aerosol have a weaker coastal-to-inland
2 concentrations gradient than sea-salt aerosol with some inland European cities having more
3 than 10% of the submicron organic aerosol mass as a marine source. Differences in fire
4 emissions, even if present, are likely to be less important for this comparison since there were
5 few fires activity data during the considered periods (as addressed in comment 3).

6 Another difference is the way the boundary conditions for OA are taken into account. Fountoukis
7 et al. (2014) used fixed boundary conditions based on measured average background
8 concentrations in sites close to the boundaries of the domain whereas we derived OA boundary
9 fields from MACC reanalysis data (Inness et al., 2013; Benedetti et al., 2009). In our study, OA
10 fields at the domain boundaries are distributed as half –half between POA and SOA, as
11 prescribed by the EURODELTA3 exercise, whereas in Fountoukis et al. (2014) OA at the
12 boundaries are assumed to be all oxidized (SOA).

13 In addition to the input data, different gas-phase mechanisms used in both studies (CB05 in this
14 study, SAPRC99 in Fountakis et al., 2014) might lead to different results. One has also to keep in
15 mind the different grid resolution ($0.25^{\circ} \times 0.25^{\circ}$ in this study, $36\text{km} \times 36\text{km}$ in Fountoukis et al.,
16 2014) while comparing the two studies.

17 6. Page 9, lines 269-272: This discussion of Fig. 5 is very light. If there is not more to discuss, I
18 recommend removing the figure and just stating the improvement in MB and r
19

20 We prefer to keep Fig. 5 since the figure allows the readers to see the differences for POA and
21 SOA. We combined the two paragraphs where the discussion involves Fig. 5 as follows in line
22 284-294 of the revised manuscript:
23

24 *Comparison of results from this study (VBS_BC_NEW) with the earlier one (VBS_BC, Ciarelli et al.,*
25 *2016a) suggests that the new VBS scheme predicts higher SOA concentrations by about a factor of 3*
26 *(Fig. 5) and improves the model performance when comparing assessed OOA from measurements*
27 *with modelled SOA (Table 4). POA concentrations, on the other hand, are clustered below $1 \mu\text{g m}^{-3}$*
28 *except in Barcelona (Fig. 5), showing an $R^2=0.36$ (Table 3). Although predicted POA concentrations*
29 *at Barcelona were lower than the measurements, $\text{MFB}=-47\%$ and $\text{MFE}=69\%$ were still in the range*
30 *for acceptable performance criteria ($\text{MFE} \leq +75\%$ and $-60 < \text{MFB} < +60\%$, Boylan and Russell,*
31 *2006). On the other hand, the model over-predicted the POA concentrations at Hyytiälä ($\text{MFB}=131\%$*
32 *and $\text{MFE}=131\%$), Helsinki ($\text{MFB}=95\%$ and $\text{MFE}=100\%$) and Cabauw ($\text{MFB}=76\%$ and $\text{MFE}=86\%$)*
33 *mainly due to the overestimated BBPOA fraction as seen in Fig. 6.*

34
35 7. How does the BBOA doubling sensitivity case fit in the context of the VBS_BC_NEW case which
36 is multiplied by 3 and then by 1.5 again? What fraction of that total added vapor mass makes it
37 into the particle phase? This is related to point 8
38

39 The BBOA doubling sensitivity case performed in Ciarelli et al. (2016a) with the original VBS
40 scheme (Koo et al., 2014) was reported in order to show that although the model performance
41 for total OA concentration improved significantly, that was not the case for the OA components,
42 with POA being over-predicted at almost all the sites and no significant effect was observed on
43 the modelled SOA concentrations (Figure 10). The rest of the comment is addressed in comment
44 Nr. 8 (below).
45

46 8. The description and discussion of BBOA aging should be expanded. Please summarize the

1 aging process as described in Ciarelli et al. (2016b). How is this similar/different to the aging of
2 the traditional biogenic SOA? I assume the authors are not using the Koo et al. (2014) approach
3 where the BBOA ages once and then stops ? What is the fractional contribution of the various
4 volatility bins to the total in time and space? Do they actually need 4 VBS bins to represent the
5 aging, or would just using one bin and an IVOC precursor also work reasonably well? Why did
6 they not use the O:C obtained from these AMS data to constrain the aging of the BBOA or the
7 SOA?
8

9 A total number of 3 sets were used to describe the evolution of organic material. The first set was
10 used to distribute the primary emissions (set1). Two other sets were used to model the
11 formation and evolution of SOA. Oxidation products of SVOC material arising from primary
12 emissions were allocated to set2, whereas oxidation products from NTVOCs (non-traditional
13 VOCs) were allocated to set3. The specific molecular structures for each of the sets and bins were
14 retrieved using the group contribution approach and the Van Krevelen relation (Donahue et al.,
15 2011; Heald et al., 2010). The oxidation of semi-volatile material would tend to increase the
16 compounds' oxygen number and decrease their volatility and carbon number, due to
17 functionalization and fragmentation. We assume that the oxidation of the primary semi-volatile
18 compounds with C11-C14 decreases their volatility by one order of magnitude and yields C9-C10
19 surrogates, placed in set2, based on the work of Donahue et al. (2011, 2012). Based on these
20 assumptions and using the group contribution approach, the oxygen numbers for set2 is
21 predicted to vary between 2.26 and 4.56. Thus, the model implicitly accounts for the addition of
22 1.1 to 1.5 oxygen atoms and the loss of 2.75 to 4.25 carbon atoms, with one oxidation step. Set3
23 was constrained based on the PTR-MS data. The measurements suggested an average NTVOC
24 carbon and oxygen number of about 7 and 1, respectively. Based on reported molecular
25 speciation data (e.g. Kleindienst et al., 2007), we expect the products of C7 compounds to have a
26 C5-C6 carbon backbone. These products were placed in set3 following a kernel function based
27 on the distribution of naphthalene oxidation products. At least two oxygen atoms were added to
28 the NTVOC mixture upon their oxidation. The overall O:C ratio in the whole space roughly spans
29 the range from 0.1 to 1.0. Multigeneration chemistry (aging) is also accounted for by the model.
30 Unlike the 2D-VBS, the 1.5D-VBS does not use different kernel functions, to discretize the
31 distribution of the oxidation products according to their $\log(C^*)$ and O:C ratios, when
32 functionalization and fragmentation occur. Instead, to reduce the computational burden of the
33 simulations, the model assumes that the oxidation of a given surrogate yields one other
34 surrogate with lower volatility, higher oxygen number and lower carbon number. These
35 properties should be considered as a weighted average of those relative to the complex mixture
36 of compounds arising from functionalization and fragmentation processes. Accordingly, the 1.5D-
37 VBS approach represents the functionalization and fragmentation processes effectively while
38 reducing the parameter space and the computational burden. Gas-phase products in the semi-
39 volatile range in set2 and set3, once formed, can further react with a rate constant of 4×10^{-11}
40 $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ as proposed by previous studies (Donahue et al., 2013; Grieshop et al., 2009;
41 Robinson et al., 2007), further lowering the volatility of the products by one order of magnitude.
42 This implies that for every additional oxidation step, the organic material receives around 0.5
43 oxygen atoms.

44 However, we don't have a separate set to allocate oxidation products from biogenic precursors,
45 and they follow the same oxidation pathways of biomass burning like aerosol as in the previous
46 case (Ciarelli et al., 2016a), including aging. We are currently working on an updated version of
47 CAMx that includes the separation of biogenic sources.
48

49 Minor Issues/Typos

50
51 1. Page 2, line 53: What do the authors mean by "higher volatility?" Are these IVOCs or VOCs?
52 And do they mean that the products of these and the semivolatile precursors contributed 15 to

1 38%?

2

3 Higher volatility refers to IVOCs and VOCs. Only the products of IVOCs and VOCs contributed to
4 15 to 38%. We rephrase for clarification as below:

5

6 *On the other hand, the oxidation products of higher volatility precursors (the sum of IVOCs and*
7 *VOCs) contribute from 15 to 38% with no specific gradient among the stations.*

8

9 2. Page 3, line 62: Consider replacing “qualitatively” with “nominally.” They are very similar for
10 sure but while qualitatively to me suggests one knows a lot about the relative importance of each
11 source (just not the actual numbers), nominal suggests you just know that the sources are there
12 and you can name them. The latter to me is more representative of our knowledge of sources for
13 SOA.

14

15 Done.

16

17 3. Page 3, lines 65-71: Please also mention aqueous-phase formation and the importance of
18 solubility in water somewhere here to make the picture more complete.

19

20 We added the following sentence at line 70-75 of the revisited manuscript to mention the
21 importance of aqueous-phase formation as below:

22

23 *The physical and chemical processes leading to the formation of SOA are numerous, e.g. oxidation*
24 *and condensation, oligomerization or aqueous-phase formation, and they are very uncertain and*
25 *currently under debate (Hallquist et al., 2009; Tsigaridis et al., 2014; Fuzzi et al., 2015; Woody et*
26 *al., 2016). Moreover, the solubility of organic compounds in water is also a crucial parameter*
27 *affecting the life time of organic particles and gases in the atmosphere (Hodzic et al., 2016).*

28

29 4. Page 3, line 82: Consider removing the word “common.” And refer to SOA explicitly here. For
30 example: “Most CTMs today account for SOA formation from biogenic and anthropogenic...A few
31 models also include SOA formation from intermediate volatility,,,”.

32

33 Done.

34

35 5. I don't think you need a hyphen in “semi-volatile” anywhere in the text, but this is your
36 preference.

37

38 Done.

39

40 6. Page 4, line 114-115: The higher volatility emission parameters were also constrained using
41 monitoring network measurements in the previous modeling studies. Several studies have
42 played with 1.5 factor for instance and it has remained as the parameter of choice despite
43 uncertainties.

44 We thank the referee for this comment. We reformulated and shortened the sentence from line
45 116-119 of the revised manuscript as below:

46

47 *This implies that, in these applications, the new emitted organic mass (POA + SVOCs + IVOCs) is 7.5*
48 *times higher than in original emissions (i.e., $OM = (3*POA) + (1.5*(3*POA))$) which could be used as*
49 *an indirect method to account for missing organic material in the absence of more detailed gridded*
50 *emission inventories.*

51

7. Page 7, lines 193-199: I was confused by this group of sentences. Consider rewriting for clarity. Maybe something like, “We assumed OA emissions from SNAP2 (emissions from non-industrial combustion plants in the Selected Nomenclature for Air Pollution) and SNAP10 (emissions from agriculture, about 6% of POA in SNAP2), to be representative of biomass burning emissions and thus comparable to the BBOA PMF factor. OA from all other SNAP categories were compared against HOA-like PMF factors. Unfortunately, gridded emissions for SNAP2 include other emission sources (i.e., coal burning which might be important in eastern European countries like Poland). We could not resolve our emission inventory with sufficient detail to separate the contribution of coal for these European cities (Crippa et al., 2014).”

We agree and modified the sentence as suggested by the referee (line 205 in the revised manuscript).

8. Page 8, line 219: Please do not call it deposition “capacity” as this suggests something about the ability of the sea to hold pollution. Please reword. “Efficiency” might make more sense. Or just say “reduced deposition”. Also change on page 9, line 267

Done.

9. Page 8, line 236: Please provide some statistic for this statement.

We added the statistics: ($R^2=0.72$).

10. Fig. 3: Consider adding error bars to this plot showing variability to make this figure more useful.

Done.

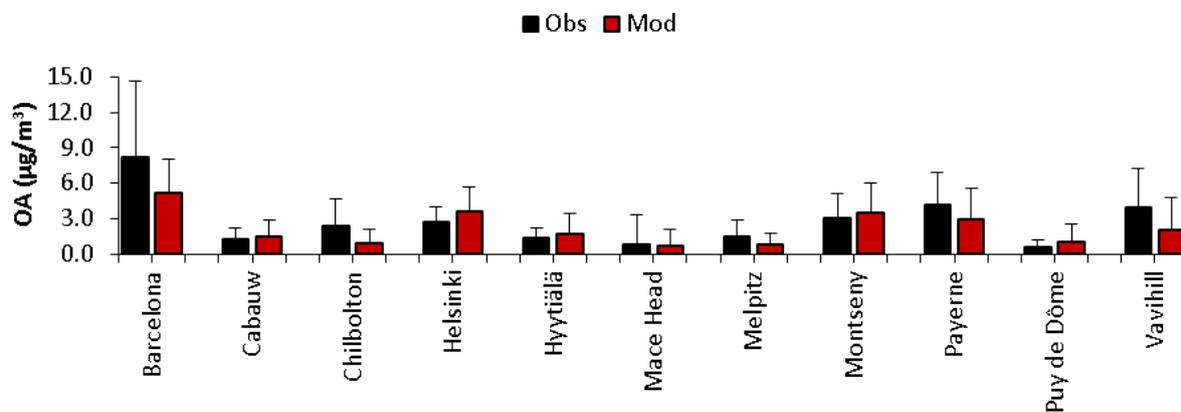


Figure 3. Observed (black) and modelled (VBS_BC_NEW) (red) average OA mass at AMS sites for the period between 25 February and 26 March 2009.

11. Page 9, lines 258-262: This sentence needs to be split into two sentences and reworded for clarity.

We reworded the sentences at line 274-278 of the revised manuscript as below:

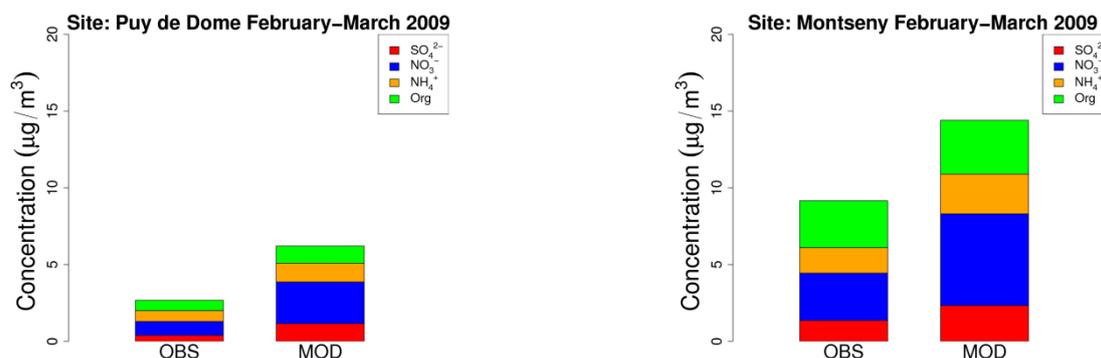
Bergström et al. (2012) reported that emissions of organic carbon (OC) from the residential heating sector in Sweden were lower than those in Norway by a factor of 14 in spite of its higher wood usage by 60%. This indicates an underestimation of emissions from residential heating in the

1 *emission inventory.*

2
3 12. Page 10, line 288-290: Do you have evidence from other PM species or pollutants to back up
4 this claim?

5
6 We added a comparison for the modelled PM₂₅ components for Puy de Dome and Montseny. At
7 both sites all the components were over-predicted (Fig. S3). We added the following sentence at
8 line 304 of the revised manuscript.

9
10 *as confirmed by the over-prediction of other PM species at these sites (Fig. S3).*



12
13 *Figure S3. Comparison of modelled non-refractory PM₂₅ components at Puy de Dome and Montseny*
14 *with the AMS measurements in February-March 2009.*

15
16 13. Page 10, line 291-305: This sentence should be revised for clarity. The authors have blamed
17 the meteorology and the host model configuration itself but why not the emissions? The activity
18 data for the emissions could be wrong, or the emission factors could be wrong, no? Ok, CAMx has
19 issues like any other CTM, but what makes the authors so sure that most of the problem is not in
20 the emissions data?

21
22 We agree with the referee. Emissions might also represent a large source of uncertainties,
23 recently, even more than previously thought. We added more emphasis on this point at line 311-
24 315 of the revised manuscript as below:

25
26 *In addition, the gridded emission inventories still represent a large source of uncertainties for CTM*
27 *applications. The majority of the NO_x (NO+NO₂) emissions in Europe arises from the transportation*
28 *sector (SNAP7), which might have much larger uncertainties than previously thought (Vaughan et*
29 *al., 2016).*

30
31 14. Page 10, line 296: course should be spelled coarse

32
33 We corrected the typo.

34
35 15. Page 10, line 308-315: The authors can also add here the potential double counting of SVOC
36 emissions and the application of PM_{2.5} prediction to a (nominal) PM_{1.0} measurement

37
38 We modified the sentence from line 330 of the revised manuscript in order to include other
39 reasons for the over prediction of the BBOA fraction as below:

40
41 4) *The simplistic way of accounting for the semi-volatile part of primary emissions might lead, in*
42 *some areas, to the double counting of such compounds.*

43 5) *Uncertainties in the retrieved BBOA fraction from PMF analysis.*

16. Page 11, line 316-318: How many of the peaks were captured well? What statistic determines how well they were captured? Unless this statement can be quantified, please remove it.

We removed the sentence.

17. Page 11, line 322: Please consider changing “likely” to “possibly.”

Done.

18. Figure 10. Please consider using median values in these plots rather than averages. 1) It will more effectively reduce the influence of extreme pollution days. 2) It will be more consistent with your use of percentiles. Consider also adding percentiles for the model run data.

Done.

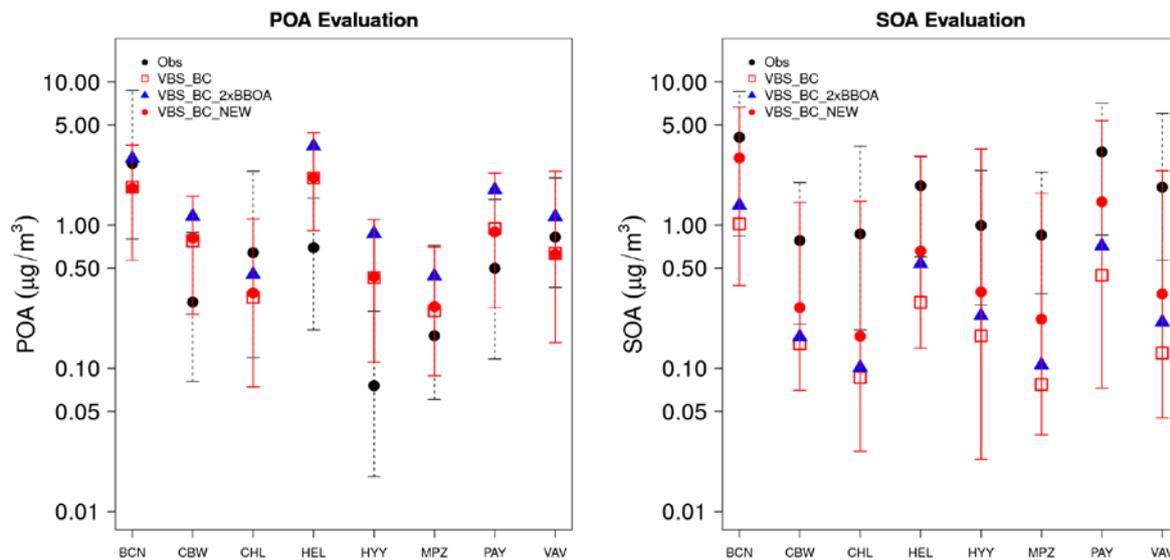


Figure 10. POA (left) and SOA (right) median concentrations at 8 AMS sites for February-March 2009 in the VBS_BC, VBS_BC_2xBBOA and VBS_BC_NEW cases. Dotted lines indicate the 10th and 90th quartile range (also reported in red for the VBS_BC_NEW case). Data for the Puy de Dôme and Montseny sites at higher layers are not available for the VBS_BC_2xBBOA scenario.

19. Figure 11: This data would be better represented as a bar plot since the x-axis is not really a continuum, even though you are trying to approximate one by ordering them south-north.

We agreed and replaced the Figure 11 with a bar plot.

20. Tables: please add one more significant figure to all data. I can't figure out why the mean biases are different than the differences in the mean model and mean obs. Is it a rounding issue?

The observed differences are indeed due to the rounding. However, we prefer to keep one significant digit in the tables.

21. Page 13, line 380-388: Please quantify “reasonably good.” Compared to what?

We modify the sentence at line 413 as below:

1 *Predicted HOA concentrations were in the range of those retrieved from the PMF analysis..*

2
3 22. Figure 11: Is BBOA actually just primary BBOA? Please make this clear in this figure and
4 throughout the text as it gets confusing.

5
6 We thank the reviewer for this comment that was also addressed by referee #1. Yes, BBOA refers
7 only to primary BBOA. We changed the legend in Figure 11 as presented in comment 19. We
8 changed BBOA to BBPOA in the whole manuscript.

9
10
11 **REFERENCES**

12
13 Aksoyoglu, S., Keller, J., Barmpadimos, I., Oderbolz, D., Lanz, V. A., Prévôt, A. S. H., and
14 Baltensperger, U.: Aerosol modelling in Europe with a focus on Switzerland during summer
15 and winter episodes, *Atmos. Chem. Phys.*, 11, 7355-7373, doi:10.5194/acp-11-7355-2011,
16 2011.

17 Benedetti, A., Morcrette, J.-J., Boucher, O., Dethof, A., Engelen, R. J., Fisher, M., Flentje, H.,
18 Huneeus, N., Jones, L., Kaiser, J. W., Kinne, S., Mangold, A., Razinger, M., Simmons, A. J.,
19 and Suttie, M.: Aerosol analysis and forecast in the European Centre for Medium-Range
20 Weather Forecasts Integrated Forecast System: 2. data assimilation. *J. Geophys. Res.*, 114,
21 D13205, 2009.

22 Bessagnet, B., Pirovano, G., Mircea, M., Cuvelier, C., Aulinger, A., Calori, G., Ciarelli, G.,
23 Manders, A., Stern, R., Tsyro, S., García Vivanco, M., Thunis, P., Pay, M. T., Colette, A.,
24 Couvidat, F., Meleux, F., Rouïl, L., Ung, A., Aksoyoglu, S., Baldasano, J. M., Bieser, J.,
25 Briganti, G., Cappelletti, A., D'Isidoro, M., Finardi, S., Kranenburg, R., Silibello, C.,
26 Carnevale, C., Aas, W., Dupont, J. C., Fagerli, H., Gonzalez, L., Menut, L., Prévôt, A. S. H.,
27 Roberts, P., and White, L.: Presentation of the EURODELTA III intercomparison exercise –
28 evaluation of the chemistry transport models' performance on criteria pollutants and joint
29 analysis with meteorology, *Atmos. Chem. Phys.*, 16, 12667-12701, 10.5194/acp-16-12667-
30 2016, 2016.

31 Bozzetti, C., Daellenbach, K. R., Hueglin, C., Fermo, P., Sciare, J., Kasper-Giebl, A., Mazar,
32 Y., Abbaszade, G., El Kazzi, M., Gonzalez, R., Shuster-Meiseles, T., Flasch, M., Wolf, R.,
33 Křepelová, A., Canonaco, F., Schnelle-Kreis, J., Slowik, J. G., Zimmermann, R., Rudich, Y.,
34 Baltensperger, U., El Haddad, I. and Prévôt, A. S. H.: Size-Resolved Identification,
35 Characterization, and Quantification of Primary Biological Organic Aerosol at a European
36 Rural Site, *Environ. Sci. Technol.*, 50(7), 3425–3434, doi:10.1021/acs.est.5b05960, 2016.

37 Ciarelli, G., Aksoyoglu, S., Crippa, M., Jimenez, J.-L., Nemitz, E., Sellegri, K., Äijälä, M.,

1 Carbone, S., Mohr, C., O'Dowd, C., Poulain, L., Baltensperger, U. and Prévôt, A. S. H.:
2 Evaluation of European air quality modelled by CAMx including the volatility basis set
3 scheme, *Atmos. Chem. Phys.*, 16(16), 10313–10332, doi:10.5194/acp-16-10313-2016, 2016a.
4 Ciarelli, G., El Haddad, I., Bruns, E., Aksoyoglu, S., Möhler, O., Baltensperger, U. and
5 Prévôt, A. S. H.: Constraining a hybrid volatility basis set model for aging of wood burning
6 emissions using smog chamber experiments, *Geosci. Model Dev.*, accepted, 2016b.
7 Denier van der Gon, H. A. C., Bergström, R., Fountoukis, C., Johansson, C., Pandis, S. N.,
8 Simpson, D. and Visschedijk, A. J. H.: Particulate emissions from residential wood
9 combustion in Europe – revised estimates and an evaluation, *Atmos. Chem. Phys.*, 15(11),
10 6503–6519, doi:10.5194/acp-15-6503-2015, 2015.
11 Donahue, N. M., Epstein, S. A., Pandis, S. N. and Robinson, A. L.: A two-dimensional
12 volatility basis set: 1. organic-aerosol mixing thermodynamics, *Atmos. Chem. Phys.*, 11(7),
13 3303–3318, doi:10.5194/acp-11-3303-2011, 2011.
14 Donahue, N. M., Kroll, J. H., Pandis, S. N. and Robinson, A. L.: A two-dimensional volatility
15 basis set – Part 2: Diagnostics of organic-aerosol evolution, *Atmos. Chem. Phys.*, 12(2), 615–
16 634, doi:10.5194/acp-12-615-2012, 2012.
17 Donahue, N. M., Chuang, W., Epstein, S. A., Kroll, J. H., Worsnop, D. R., Robinson, A. L.,
18 Adams, P. J. and Pandis, S. N.: Why do organic aerosols exist? Understanding aerosol
19 lifetimes using the two-dimensional volatility basis set, *Environ. Chem.*, 10(3), 151,
20 doi:10.1071/EN13022, 2013.
21 Fountoukis, C., Megaritis, A. G., Skyllakou, K., Charalampidis, P. E., Pilinis, C., Denier van
22 der Gon, H. A. C., Crippa, M., Canonaco, F., Mohr, C., Prévôt, A. S. H., Allan, J. D., Poulain,
23 L., Petäjä, T., Tiitta, P., Carbone, S., Kiendler-Scharr, A., Nemitz, E., O'Dowd, C., Swietlicki,
24 E. and Pandis, S. N.: Organic aerosol concentration and composition over Europe: insights
25 from comparison of regional model predictions with aerosol mass spectrometer factor
26 analysis, *Atmos. Chem. Phys.*, 14(17), 9061–9076, doi:10.5194/acp-14-9061-2014, 2014.
27 Gantt, B., Johnson, M. S., Crippa, M., Prévôt, A. S. H., and Meskhidze, N.: Implementing
28 marine organic aerosols into the GEOS-Chem model, *Geosci. Model Dev.*, 8, 619-629,
29 doi:10.5194/gmd-8-619-2015, 2015.
30 Grieshop, A. P., Logue, J. M., Donahue, N. M. and Robinson, A. L.: Laboratory investigation
31 of photochemical oxidation of organic aerosol from wood fires 1: measurement and

1 simulation of organic aerosol evolution, *Atmos. Chem. Phys.*, 9(4), 1263–1277,
2 doi:10.5194/acp-9-1263-2009, 2009.

3 Heald, C. L., Kroll, J. H., Jimenez, J. L., Docherty, K. S., DeCarlo, P. F., Aiken, A. C., Chen,
4 Q., Martin, S. T., Farmer, D. K. and Artaxo, P.: A simplified description of the evolution of
5 organic aerosol composition in the atmosphere, *Geophys. Res. Lett.*, 37(8),
6 doi:10.1029/2010GL042737, 2010.

7 Inness, A., Baier, F., Benedetti, A., Bouarar, I., Chabrillat, S., Clark, H., Clerbaux, C.,
8 Coheur, P., Engelen, R. J., Errera, Q., Flemming, J., George, M., Granier, C., Hadji-Lazaro,
9 J., Huijnen, V., Hurtmans, D., Jones, L., Kaiser, J. W., Kapsomenakis, J., Lefever, K., Leitão,
10 J., Razinger, M., Richter, A., Schultz, M. G., Simmons, A. J., Suttie, M., Stein, O., Thépaut,
11 J.-N., Thouret, V., Vrekoussis, M., Zerefos, C., and the MACC team: The MACC reanalysis:
12 an 8 yr data set of atmospheric composition, *Atmos. Chem. Phys.*, 13, 4073–4109,
13 doi:10.5194/acp-13-4073-2013, 2013.

14 Kleindienst, T. E., Lewandowski, M., Offenberg, J. H., Jaoui, M. and Edney, E. O.: Ozone-
15 isoprene reaction: Re-examination of the formation of secondary organic aerosol, *Geophys.*
16 *Res. Lett.*, 34(1), L01805, doi:10.1029/2006GL027485, 2007.

17 Nussbaumer, T., Czasch, C., Klippel, N., Johansson, L., and Tullin, C.: Particulate Emissions
18 from Biomass Combustion in IEA Countries, Survey on Measurements and Emission Factors,
19 International Energy Agency (IEA) Bioenergy Task 32, Zurich, 2008a.

20 Nussbaumer, T., Klippel, N., and Johansson, L.: Survey on Measurements and Emission
21 Factors on Particulate Matter from Biomass Combustion in IEA Countries, 16th European
22 Biomass Conference and Exhibition, Valencia, Spain, 2–6 June 2008, Oral Presentation OA
23 9.2, 2008b.

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

27 Robinson, A. L., Donahue, N. M., Shrivastava, M. K., Weitkamp, E. A., Sage, A. M.,
28 Grieshop, A. P., Lane, T. E., Pierce, J. R. and Pandis, S. N.: Rethinking Organic Aerosols:
29 Semivolatile Emissions and Photochemical Aging, *Science*, 315(5816), 1259–1262,
30 doi:10.1126/science.1133061, 2007.

1 Shrivastava, M., Fast, J., Easter, R., Gustafson Jr., W. I., Zaveri, R. A., Jimenez, J. L., Saide,
2 P. and Hodzic, A.: Modeling organic aerosols in a megacity: comparison of simple and
3 complex representations of the volatility basis set approach, *Atmos. Chem. Phys.*, 11, 6639–
4 6662, 2011.

5 Sofiev, M., Vankevich, R., Lotjonen, M., Prank, M., Petukhov, V., Ermakova, T., Koskinen,
6 J., and Kukkonen, J.: An operational system for the assimilation of the satellite information on
7 wild-land fires for the needs of air quality modelling and forecasting, *Atmos. Chem. Phys.*, 9,
8 6833-6847, doi:10.5194/acp-9-6833-2009, 2009.

9 Tsimpidi, A. P., Karydis, V. A., Zavala, M., Lei, W., Molina, L., Ulbrich, I. M., Jimenez, J. L.
10 and Pandis, S. N.: Evaluation of the volatility basis-set approach for the simulation of organic
11 aerosol formation in the Mexico City metropolitan area, *Atmos. Chem. Phys.*, 10, 525–546,
12 2010.

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