Simulation of organics in the atmosphere: evaluation of EMACv2.54 with the Mainz Organic Mechanism (MOM) coupled to the ORACLE (v1.0) submodel

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Abstract. An updated and expanded representation of organics in the chemistry general circulation model EMAC (ECHAM5/MESSy for Atmospheric Chemistry) has been evaluated. First, the comprehensive Mainz Organic Mechanism (MOM) in the submodel MECCA (Module Efficiently Calculating the Chemistry of the Atmosphere) was activated with explicit degradation of organic species up to five carbon atoms and a simplified mechanism for larger molecules. Second, the ORACLE submodel (version

5 1.0) considers now condensation on aerosols for all organics in the mechanism. Parameterizations for aerosol yields are used only for the lumped species that are not included in the explicit mechanism. The simultaneous usage of MOM and ORACLE allows an efficient estimation, not only of the chemical degradation of the simulated volatile organic compounds, but also of the contribution of organics to the growth and fate of (organic) aerosol, with a complexity of the mechanism largely increased compared to EMAC simulations with more simplified chemistry. The model evaluation presented here reveals that the OH

10 concentration is well reproduced globally, while significant biases for observed oxygenated organics are present. We also investigate the general properties of the aerosols and their composition, showing that the more sophisticated and process-oriented secondary aerosol formation does not degrade the good agreement of previous model configurations with observations at the surface, allowing further research in the field of gas-aerosol interactions.

1 Introduction

15 Volatile Organic Compounds (VOCs) play a pivotal role in the atmosphere by constraining the total oxidant level and serve as precursors of ozone (O_3), carbon dioxide (CO_2) and aerosols (Heald and Kroll, 2020). Due to the complexity of the chemistry of VOCs, a comprehensive and explicit representation thereof is mostly still missing in global and regional model simulations (Heald et al., 2005). To capture this full complexity, model simulations would become rather computationally expensive and slow in performance. However, missing this complexity also substantially limits the current understanding of the budget of

20 secondary pollutants, e.g., O_3 and aerosols. The challenges are twofold: 1) to understand and include the chemical degradation pathways, and 2) to also represent all other influencing processes (e.g. deposition, multiphase chemistry) in already complex global/regional models.

A chemical mechanism that stands out for size and detailed oxidation of many important VOCs is the Mainz Organic Mechanism (MOM, Sander et al., 2019). MOM represents the chemistry of alkanes, alkenes, terpenes (isoprene and monoterpenes)

25 and monocyclic aromatics. The mechanism has been employed to study the impact of isoprene $OH-$recycling above pristine tropical forests (Taraborrelli et al., 2012), oxidation of monoterpenes as a source of HO_2 (Hens et al., 2014; Mallik et al., 2018) and the influence of aromatics on tropospheric ozone (Taraborrelli et al., 2021). Furthermore, MOM has been used with extensions in order to simulate product yields of β-caryophyllene oxidation (van Eijck et al., 2013), the oxidation of alkyl amines and formamide as source of HNCO (Rosanka et al., 2020), the atmospheric losses of stabilised Criegee intermediates

30 (Vereecken et al., 2017), and the most recent OH-recycling mechanisms in isoprene oxidation (Novelli et al., 2020). Yet, a full evaluation of the VOC distribution predicted by MOM in a global numerical model has not been published.

Furthermore, a more detailed chemical mechanism, which reduces the number of lumped species of larger VOCs, allows an explicit coupling of the VOC chemistry with an interactive aerosol phase partitioning and an organic compound ageing, without losing the chemical identity of the organic compounds. Previous studies (e.g. Farina et al. (2010); Tsimpidi et al.

35 (2016)), which treat the organic aerosol with the help of a volatility basis set (VBS) (Donahue et al., 2011), usually use lumped species to represent tracers with similar volatility and age structure (e.g. O:C ratio, e.g. Ng et al. (2010)) therefore without any chemical identity or detailed degradation scheme.

In this study we present a simulation and an evaluation of the ECHAM/MESSy Atmospheric Chemistry (EMAC) general circulation model (Jöckel et al., 2010, 2016) with a complex organic chemical mechanism (MOM, Sander et al., 2019), ac-

40 counting not only for the gas phase chemistry, but also for the losses via uptake/condensation into aerosols (via the ORACLE submodel) and cloud droplets (via the SCAV submodel). As the EMAC model has been largely evaluated in the past and for most of the components there were no significant changes, we focus on the evaluation of organic tracers and aerosols. Most importantly, general properties of the aerosols (such as aerosol optical depth (AOD) and particulate concentration below 2.5 $\mu g\,m^{-3}$) will be discussed, as these could be strongly affected. Furthermore, changes to the global hydroxyl radical distribution

45 influenced by the new chemistry adopted in this study are discussed.

A comparison for VOCs with the MIM chemical mechanism developed by Pöschl et al. (2000) that has been evaluated by Pozzer et al. (2007) and used previously (Jöckel et al., 2006, 2016) is not shown here as in such mechanism (i) most of organics

are either lumped, e.g. methyl vinyl ketone (MVK) and methancrolein (MACR), or missing, e.g. aromatics and monoterpenes; (ii) primary species common to MIM and MOM would be influenced only by the different sinks (mainly OH), and a detail

50   description of OH budget is presented here; (iii) the model bias with respect to secondary species, e.g. oxygenated VOCs, has been linked to a mis-representation or lack thereof processes like in-cloud chemistry (Rosanka et al., 2021b; Franco et al., 2021). Therefore any comparison of VOC simulations between MOM and MIM would not give any additional information on the model-observation discrepancy and aid any future model improvement.

The model set-up is presented in Sect. 2, followed by the description of the observational dataset used for the evaluation

55   (Sect. 3), which is then presented for different tracers and aerosol components. This model evaluation is the basis for future studies on complex organic chemistry with EMAC.

2   Model configuration

EMAC is a numerical chemistry and climate simulation system that includes submodels describing tropospheric and middle-atmosphere processes and their interaction with oceans, land, and human influences (Jöckel et al., 2016). It uses the second

60   version of the Modular Earth Submodel System (MESSy2) to link multi-institutional computer codes. The core atmospheric model is the 5th generation European Centre Hamburg general circulation model (ECHAM5 Roeckner et al., 2006). For the present study, we applied EMAC (ECHAM5 version 5.3.02, MESSy version 2.54.0) in the T63L31-resolution, i.e. with a spherical triangular truncation of T63 (corresponding to a quadratic Gaussian grid of approx. $1.8°$ by $1.8°$ in latitude and longitude) and 31 vertical hybrid pressure levels up to 10 hPa, with roughly 22 levels in the troposphere. The dynamics have

65   been weakly nudged (Jeuken et al., 1996; Jöckel et al., 2006) towards the ERA-interim data (Berrisford et al., 2011) of the European Centre for Medium-Range Weather Forecasts (ECMWF) to reproduce the actual day-to-day meteorology in the troposphere. In this study we simulated two years (2009-2010), with the first year used as spin-up time.

The anthropogenic emissions are based on the Emissions Database for Global Atmospheric Research (EDGARv4.3.2 Crippa et al., 2018), vertically distributed following Pozzer et al. (2009). These prescribed emissions are included in the model via

70   the OFFEMIS submodel (Kerkweg et al., 2006b). The biogenic emissions of Non-Methane Volatile Organic Compounds (NMVOC) are calculated on-line using the Model of Emissions of Gases and Aerosol from Nature (MEGANv2.04, Guenther et al., 2006, 2012). Lightning NO_x production is based on the parametrization of Grewe et al. (2001), while the algorithm of Yienger (1995) is used for soil NO_x emissions, as described in detail in Jöckel et al. (2016).

Biomass burning emissions are calculated daily online based on dry matter burned from observations and fire type (Kaiser

75   et al., 2012). The emission factors for different tracers and fire types are taken from Andreae (2019) and Akagi et al. (2011). The ONEMIS submodel (Kerkweg et al., 2006b) calculates natural emission fluxes of sea-salt (Guelle et al., 2001) and of dust (Klingmüller et al., 2018; Astitha et al., 2012). Oceanic emissions and deposition are calculated online with the AIRSEA submodel (Pozzer et al., 2006; Fischer et al., 2012; Lana et al., 2011) for DMS, CH_3COCH_3, CH_3OH, C_5H_8, HCN, and CH_3CN (a net sink for CH_3OH, HCN, and CH_3CN, a net source for the others). For C_2–C_3 alkanes and alkenes, the oceanic

80   offline emissions from Inness et al. (2012) have been adopted.

In Table 1 the total emissions are listed for all primary species emitted in the model.

Table 1: . Emissions of primary emitted species for the year 2010 used in this study. The units are in $\mathrm{Tg(species)\,yr^{-1}}$ with the exception of $\mathrm{NO_x}$, in $\mathrm{Tg(N)\,yr^{-1}}$

Tracer	extended name	Anthropogenic	Natural/Biogenic	Biomass Burning
BC	Black Carbon	4.34		1.84
OC	Organic Carbon	11.05		15.53
SO2	Sulfur Dioxide	99.35		1.95
NOx	nitrogen oxides	34.50	6.09	3.98
CO	carbon monoxide	537.16	106.84	289.51
NH3	ammonia	57.67		4.07
C2H6	ethane	9.00	1.32	2.91
C3H8	propane	10.50	1.46	0.52
HCN	hydrogen cyanide		2.13	
CH3CN	acetonitrile			1.03
NC4H10	n-butane	9.90		0.12
IC4H10	i-butane	4.20		0.04
MEK	methyl ethyl ketone	1.00	0.18	0.45
CH3CHO	acetaldehyde	2.00	15.35	2.80
CH3COCH3	acetone	1.10	35.84	1.29
CH3CO2H	acetic acid	6.52	3.45	13.20
CH3OH	methanol	9.71	105.54	6.32
HCOOH	formic acid	3.56	3.45	2.32
CH3COCO2H	pyruvic Acid		0.36	
HCHO	methanal,formaldehyde	4.50	5.17	4.15
C2H4	ethene	5.40	24.55	3.55
C3H6	propene	4.26	15.76	3.01
C2H2	acetylene	5.40		0.23
BUT1ENE	1-butene	1.46	6.23	0.07
TBUT2ENE	1,2-dimethylethylene	1.46		0.05
CBUT2ENE	2-butene	1.46		0.20
MEPROPENE	methylpropene	1.46		0.20
BENZENE	benzene	5.82		1.42
TOLUENE	toluene	7.80	0.35	0.83

LXYL	xylenes	7.24		0.28
LTMB	trimethylbenzenes	0.95		0.06
PHENOL	phenol	1.70		2.02
STYRENE	styrene	1.87		0.16
EBENZ	ethylbenzene	1.91		0.56
LHAROM	other aromatics	3.22		2.86
C5H8	isoprene		463.89	
APINENE	α-pinene		33.18	
BPINENE	β-pinene		18.71	
CARENE	3-carene		6.94	
SABINENE	sabinene		7.13	
CAMPHENE	camphene		3.20	
MBO	methyl butenol		1.36	
LTERP	lumped other terpenes		31.86	
LALK4	lumped pentanes	15.1		
LALK5	lumped higher alkanes	21.2		
OLE2	lumped higher alkenes	8.20		
DMS	Dimethyl sulfide		57.96	

Dry deposition and sedimentation are estimated by DDEP and SEDI submodel (Kerkweg et al., 2006a), while wet deposition is simulated by the SCAV submodel (Tost et al., 2006). The dissolution of species in the liquid phase mechanism was augmented by including liquid-gas equilibrium for all additional organics present in the mechanism with a Henry's law constant (solubility) above $10^3 \, \mathrm{mol \, L^{-1} \, atm^{-1}}$. For less soluble species, wet scavenging is not expected to be important (Crutzen and Lawrence, 2000). The Henry's law constants of most oxygenated VOCs of atmospheric relevance are unknown and estimation methods still quite uncertain (Wang et al., 2017). As the hydroxyl (and hydroperoxyl) group affects the solubility in water the most, the Henry's law constants of polyols from the compilation by Sander (2015) are taken as proxies.

In the chemistry submodel MECCA, we used the Mainz Organic Mechanism (MOM, Sander et al., 2019), with roughly 600 species and 1600 reactions. It originates from a reduced isoprene oxidation mechanism (Taraborrelli et al., 2009), which has been updated with recent kinetic data and expanded with efficient mechanisms of OH-recycling under low-NO conditions (Taraborrelli et al., 2012; Nölscher et al., 2014). The oxidation mechanism for α-pinene and β-pinene is based on the MCM (E. Jenkin et al., 2000) with modifications according to the theoretical work of L. Vereecken (Vereecken et al., 2007; Capouet et al., 2008; Nguyen et al., 2009; Vereecken and Peeters, 2012). The degradation of monocyclic aromatics follows the MCM (Jenkin et al., 2003; Bloss et al., 2005) but with some modifications for the chemistry of phenols (Cabrera-Perez et al., 2016). The complete mechanism used in this study is part of the electronic supplement.

Aerosol microphysics and gas/aerosol partitioning are calculated by the Global Modal-aerosol eXtension (GMXe) aerosol module (described by Pringle et al., 2010a, b). GMXe simulates the distribution of aerosol within interacting lognormal modes (in a similar approach to that of Vignati et al., 2004; Mann et al., 2010). The lognormal modes span four size categories

100 (nucleation ($<$ 5 nm radius), Aitken (5–50 nm), accumulation (50–500 nm), and coarse ($>$500 nm)), and are divided into a hydrophilic (4) and a hydrophobic (3) modes. The GMXe model has been extensively evaluated (Pozzer et al., 2012a, b; Tost and Pringle, 2012; Karydis et al., 2016).

Organic Aerosol (OA) formation is simulated by the submodel ORACLE (Tsimpidi et al., 2014, , v.1.0), where logarith-mically spaced saturation concentration bins are used to describe the organic aerosol components based on their volatility.

105 For the formation of primary (POA) and secondary (SOA) organic aerosol from the emissions and photochemical oxidation of semivolatile and intermediate volatility organic compounds the setup of Tsimpidi et al. (2016) is used. However, the SOA formation from the oxidation of the volatile organic compounds (VOC) in ORACLE has been modified to accommodate the photochemical production of components explicitly calculated by the MOM chemical mechanism. The effective saturation concentration of all the species present in the MECCA submodel is calculated based on their elemental composition (number

110 of carbon, oxygen, nitrogen, and sulfur atoms), following the molecular corridor approach (Li et al., 2016) and the study by Donahue et al. (2011). In Figure 1, the volatility versus the molar mass is shown for all tracers present in the model, ranging from high volatility – low molar mass to low volatility – high molar mass. These calculations result in 199 tracers which, under atmospheric conditions, can partition to the aerosol phase forming SOA (i.e., with a volatility lower than 3.2×10^3 μg m^{-3}), while the other 396 tracers are considered too volatile for any condensation on aerosol particles. Additionally, the enthalpy of

115 vaporization for the same condensing species has been estimated based on the study by Epstein et al. (2010). In addition to the 199 tracers, 11 additional "lumped species" for different oxidation levels of pentanes, higher alkanes, higher alkenes and terpenes have been added. Then, ORACLE calculates the partitioning of these organic species between the gas and particle phases by assuming a bulk equilibrium, and by further assuming that all organic compounds form a pseudo-ideal solution. The aerosol size distribution is determined by distributing the change in aerosol mass after the bulk equilibrium into each size mode

120 using a weighting factor (Tsimpidi et al., 2014).

The aerosol optical properties are calculated with the submodel AEROPT (Dietmüller et al., 2016), which is based on the scheme by Lauer et al. (2007) and makes use of predefined lognormal modes (i.e., the mode width σ and the mode mean radius have to be taken into account). Lookup tables with the extinction coefficient, the single scattering albedo, and the asymmetry factor for the shortwave, and extinction coefficient for the longwave part of the spectrum are pre-calculated with the help of Mie

125 theory-based explicit radiative transfer calculations (see Pozzer et al., 2012a; Dietmüller et al., 2016). The aerosol compounds explicitly considered for their refractve indices are organic carbon, black carbon, dust, sea salt, water-soluble compounds (WASO, i.e. all other water soluble inorganic ions, e.g.: NH_4^+, SO_4^{2-}, HSO_4^-, NO_3^-), and aerosol water (H_2O).
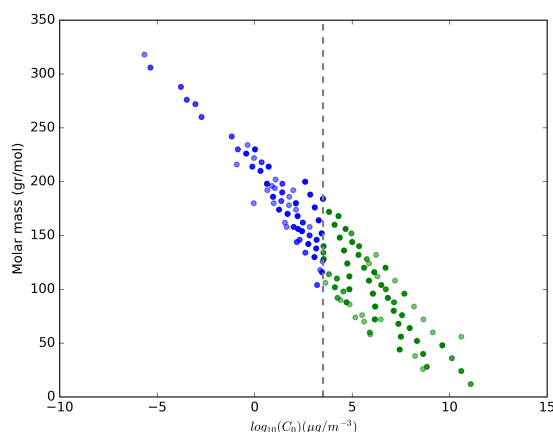
Figure 1. Saturation mass concentrations at 298 K (Li et al., 2016) versus molar mass of organic tracers in EMAC. The blue dots represent those included in ORACLE, i.e., organic tracers which, under atmospheric conditions, are allowed to condense explicitly on aerosols, the green dots represent those organic tracers always in the gas phase. The dashed line represents the maximum volatility considered in ORACLE (i.e. 3.2×10^3 µg m^{-3}) for the VOC oxidation products.

3 Observational data

3.1 Aircraft measurements

130   We used the database of aircraft measurements of trace gases produced by Emmons et al. (2000). It is based on observations from numerous aircraft campaigns that took place during the period 1990–2001 to create observational-based climatologies of chemical species relevant to tropospheric chemistry. Although these measurements cover only limited time periods and regions, they provide valuable information about the vertical distribution of the analysed trace gases. Note that the field campaigns used in this evaluation have been extended, also including observations after the year 2000, such as those from the TOPSE and

135   TRACE-P campaigns.

In addition to the Emmons et al. (2000) database, we also included the aircraft measurements for organic aerosols presented by Heald et al. (2011). This dataset includes organic aerosol measurements from 17 aircraft campaigns during the period 2001–2009. Here, similar to Emmons et al. (2000), we consider the aircraft campaigns representative for the period and the regions, i.e., as an observational-based climatology. Therefore, we compared these data with the model results for the year

140   2010, yielding an improved evaluation of the vertical distribution of the organic aerosols in the troposphere.

3.2 Station measurements

3.2.1 NOAA-INSTAAR

Data from the National Oceanic and Atmospheric Administration (NOAA) Institute of Arctic and Alpine Research (INSTAAR) Global Monitoring program were also used in this study. The network consists of 44 background stations from the NOAA

145 Global Greenhouse Gases Reference Network (GGGRN) (Pollmann et al., 2008), where pairs of whole air samples are collected weekly and shipped to a central laboratory for analyses. For this study, we considered measurements of ethane, propane, iso- and n-butane from this network.

3.2.2 EPA

The Clean Air Markets Division of the U.S. Environmental Protection Agency (EPA) operates the Clean Air Status and Trends

150 Network (CASTNET), with a total of 97 stations. Here, we include weekly filter pack data from 81 stations for SO_4^{2-}, NO_3^-, NH_4^+, Na^+, Mg^{2+}, Ca^{2+}, K^+ and Cl^- for the year 2010. The data can be downloaded at www.epa.gov/castnet, last access on December 10, 2020.

3.2.3 IMPROVE

In order to evaluate the simulated regional background OA concentrations, we use monthly averaged $PM_{2.5}$ OA measurements

155 during the year 2010 from the Interagency Monitoring of Protected Visual Environments (IMPROVE) program (http://views.cira.colostate.edu/fed, last access on September 21, 2021). IMPROVE is a cooperative measurement effort in the United States designed to characterize current visibility and aerosol conditions in scenic areas (primarily National Parks and Forests). This network includes 198 monitoring sites that are representative of the regional haze conditions over North America. IMPROVE collocated samplers collect 24 hour samples every three days.

160 #### 3.2.4 EMEP

The co-operative programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe (EMEP) is a scientifically-based and policy-driven programme under the Convention on Long-range Transboundary Air Pollution for international co-operation to solve transboundary air pollution problems. We use data from 42 stations, although the number of stations providing sufficient data for a certain species ranges from 22 to 42 (see Table 5). As Teflon filters are used pre-

165 dominantly, depending on the respective station, the concentrations of particulate nitrate can be systematically underestimated (Ames and Malm, 2001). The data were obtained from the EBAS database (http://ebas.nilu.no/, last access on September 21, 2021) and stations not providing full coverage of monthly mean values for the year 2010 were excluded from the analysis.

3.2.5 EANET

The Acid Deposition Monitoring Network in East Asia (EANET) regularly monitors acid deposition as from January 2001.

170 Thirteen countries participate currently in this effort, submitting data from a total of 54 sites. We use monthly averaged aerosol concentrations from 15 to 25 stations, with the data obtained from the Network Center for EANET, at https://monitoring. eanet.asia/document/public/index, last access on September 21, 2021. It is worth mentioning that EANET does not include OA observations. The simulated $PM_{2.5}$ OA over East Asia is evaluated against collected short-term measurement data as summarized by Jo et al. (2013).

175 ### 3.3 Remote sensing observations

3.3.1 MOPITT

The MOPITT (Measurement of Pollution in the Troposphere) is a sensor onboard the NASA's Terra satellite. We use the MOPO3JM version 8 product of MOPITT which provides monthly mean gridded column integrated CO, vertical profiles of CO mixing ratios at ten regularly spaced pressure levels from the surface up to $100\,\mathrm{hPa}$ as well as the corresponding averaging

180 kernels (Deeter et al., 2019). The MOPO3JM product is based on the joint near-infrared (NIR) and thermal-infrared (TIR) retrievals of CO. We apply the MOPITT averaging kernels on the EMAC CO profiles according to equation 1 to ensure the same level of smoothing as that in the MOPO3JM product.

$$x_{rtv} = Ax_{true} + (I - A)x_a \tag{1}$$

Here, x_{true} is the EMAC profile, x_a is the a priori profile, A is the averaging kernel matrix and I represents an identity matrix.

185 #### 3.3.2 MODIS

The MODerate resolution Imaging Spectroradiometer (MODIS) sensor is also located on the Terra satellite. Here, AOD550 data (i.e., Aerosol Optical Depth at $550\,\mathrm{nm}$) from the MODIS Level 3 (Col. 6.11) gridded product are used at a spatial resolution of $1° \times 1°$. The data are available through the Atmosphere Archive & Distribution System (LAADS) (https://ladsweb.modaps.eosdis.nasa.gov/ , last access on September 21, 2021). Here the Deep Blue algorithm (Hsu et al., 2004)

190 was used for the aerosol AOD.

3.3.3 IASI

Global observations of a suite of VOCs are retrieved from the thermal infrared measurements of the nadir-viewing IASI (Infrared Atmospheric Sounding Interferometer) instruments (Clerbaux et al., 2009). The VOC dataset exploited here consists of total columns of methanol, acetone, formic and acetic acids, and PAN, retrieved near-globally on a daily basis from the

195 IASI/Metop–A observations with the aid of the ANNI (Artificial Neural Network for IASI) v3 retrieval framework. This neural network-based retrieval approach does not rely on a priori information of the total column and, hence, the products can be

used directly for unbiased comparisons with model data (see Franco et al., 2018; Whitburn et al., 2016). The satellite products are filtered for measurements affected by clouds and poor retrieval performance. The uncertainties on the individual retrieved column can be large, but are considerably reduced by averaging numerous observations, as done in this study by comparing

200 annual averages. A full description of the ANNI framework, the characterization of the VOC products, and comparisons of the satellite data with independent measurements can be found in Franco et al. (2018, 2019, 2020) and references therein. For both, IASI and the model, daily gridded averages were constructed at the spatial resolution of the model grid. To have similar temporal coverage over the year between model and satellite observations, the EMAC daily averages were masked when the corresponding IASA data were missing for the same day and location.

205 ### 3.3.4 AERONET

The AOD observations have been obtained from the global AErosol RObotic NETwork (AERONET Holben et al., 1998; Dubovik et al., 2000). The cloud-screened quality-assured Level 2 AOD data used in this study were obtained from the website http://aeronet.gsfc.nasa.gov/cgi-bin/combined_data_access_new (last access on September 21, 2021) including AOD daily averages.

210 ### 3.4 Pseudo observations

Global annual averages of fine particulate matter with an aerodynamic diameter below 2.5 μm ($PM_{2.5}$) have been obtained from Hammer et al. (2020). In this dataset, a combination of satellite observed AOD, numerical model, and ground-based $PM_{2.5}$ measurements were used to estimate $PM_{2.5}$ on a global scale at high resolution.

4   Results

215 In Table 2, the comparison of the model results with the aircraft campaign data from Emmons et al. (2000) is presented for selected tracers. In general the model reproduces the main features observed, as more than 82 % of the simulated values are within a factor of 2 compared to the observations for all species. Nevertheless, for some species (such as the alkene C_4H_6), a clear underestimation is seen, cohering with former results (Pozzer et al., 2006).

4.1   CO

220 Figure 2 shows the seasonal (MAM: March, April, May; JJA: June, July, August; SON: September, October, November; DJF: December, January and February) mean modified EMAC and MOPITT CO vertical column densities (VCD). Here, we term it as "modified" EMAC VCDs because MOPITT averaging kernels are applied on the simulated CO profiles to account for the sensitivity of MOPITT. To highlight the difference in spatial patterns of EMAC and MOPITT, we also show the absolute bias in the bottom panel.

225   We note that the spatial patterns are in good agreement between simulation and observations. In particular, the elevated CO background in the outflow regions (over oceans) in the northern hemisphere is well represented during boreal winter (DJF)

Species	N.points	MM	MSTD	OM	OSTD	$\overline{MM/OM}$	PF2	RMSE
CO	457	90.41	32.63	94.86	72.11	1.03	100.0	63.991
C_2H_4	454	25.16	139.23	45.93	175.49	1.06	89.2	110.05
C_2H_6	473	539.19	320.22	826.09	544.14	0.70	100.0	409.24
C_3H_6	332	6.25	63.13	13.70	53.09	0.40	93.6	32.64
C_3H_8	472	94.96	123.26	164.99	225.57	0.89	93.2	149.02
CH_3COCH_3	246	520.61	274.71	608.50	310.84	0.92	97.9	291.65
CH_3OH	37	595.76	369.59	913.86	373.06	0.66	100.0	426.52
CH_3OOH	366	210.71	190.79	376.80	321.19	0.66	96.7	251.34
HCHO	213	198.08	377.76	192.24	299.65	1.44	84.5	235.36
HCOOH	53	32.67	7.05	58.92	43.55	0.87	96.2	49.41
CH_3COOH	53	13.50	7.08	51.08	28.31	0.34	100.0	46.51
HNO_3	416	151.33	188.49	162.15	285.72	1.25	82.4	237.42
H_2O_2	411	634.08	611.96	745.48	875.21	1.09	91.7	516.44
PAN	395	62.46	71.30	162.60	186.81	0.61	96.7	185.79
O_3	506	68.23	76.00	51.06	26.10	1.31	92.8	62.54

Table 2. Summary of simulated and observed mixing ratios of different tracers in the Emmons et al. (2000) database. N.points is the number of points used for the statistical estimation. The arithmetic mean of the model simulated mixing ratios (MM), the observed mixing ratios (OM), and the corresponding standard deviations (MSTD, OSTD) in $\mathrm{pmol/mol}$ are listed in the subsequent columns. For CO and O_3 the units are in $\mathrm{nmol/mol}$. PF2 denotes the percentage of simulated points within a factor of 2 with respect to the observations, and RMSE represents the root mean square error between simulated and observed points.

and spring (MAM). The outflow region around south America in SON is also simulated well. Over land, a good agreement is found for Europe, central and Eastern United States, northern Africa, Australia, Russia, and the Indian subcontinent with a mean bias within $\pm 1 \times 10^{18}$ molecules cm^{-2}. During the biomass burning seasons (JJA in central Africa, north and north-east China and SON in south America), we observe an overestimation of $\sim 30\%$ by EMAC. By comparing EMAC's total CO columns to IASI CO satellite retrievals, Rosanka et al. (2021c) found that EMAC tends to underestimate CO in Indonesia in SON 2015. In 2015, a particularly strong El Niño led to severe peatland fires, which resulted in large CO emissions. Rosanka et al. (2021c) attribute the underestimation to a too low biomass burning emission factor for peatland used by EMAC. Here, we do not find any underestimation of CO in Indonesia in SON (see Fig. 2), since the year 2010 was a year with little biomass burning emissions in Indonesia (van der Werf et al., 2017). Following their analysis, the recent biomass burning emission factor estimate by Andreae (2019) suggests that EMAC underestimates the CO emission factor by about 10 % in Central South America and Africa. It must however be stressed that the uncertainties on biomass burning emissions are substantial, depending on regions and species (Carter et al., 2020). In contrast, in South America the overprediction of EMAC's CO columns can be
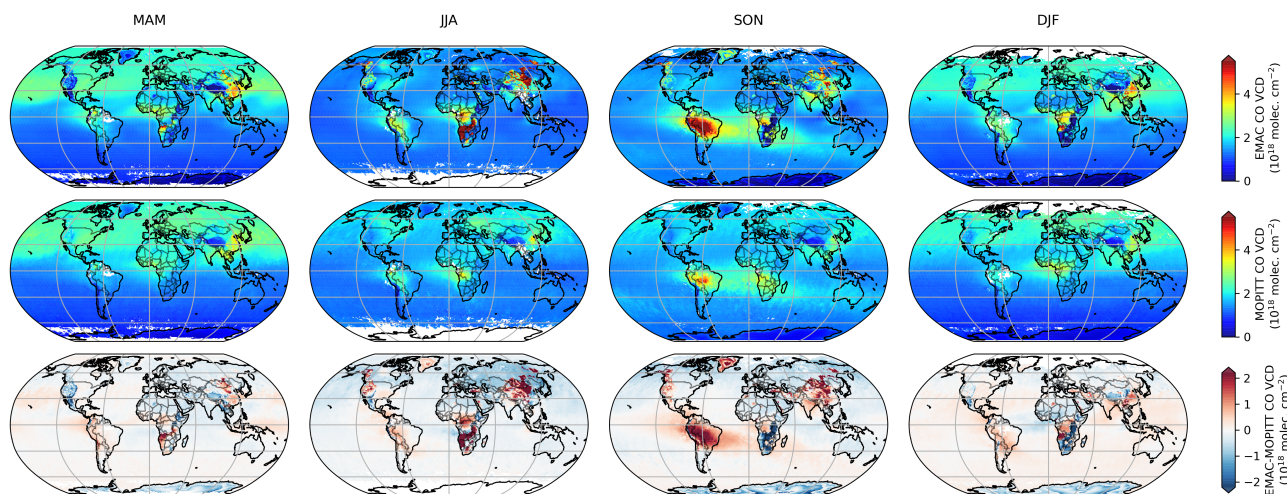
Figure 2. Global seasonal mean maps of CO vertical column densities (VCD) for the year 2010 for EMAC (top), MOPITT (middle), and bias (EMAC - MOPITT), (bottom).

partially attributed to EMAC's tendency to overestimate biogenic emissions of CO precursors in this region (Rosanka et al., 2021b, c).

Figure 3 shows the 2010 annual mean measured and simulated surface CO mixing ratio at the WDCGG stations sorted according to their latitude coordinates. The relative bias at all stations is also shown on a global map in the inset of Figure 3. Similar latitudinal gradients are seen for the measurements and simulations with high values around the mid-latitudes of the northern hemisphere. The measured and simulated CO agree within 1σ annual variability for 106 out of 113 stations for which data were available for the year 2010. The bias between model and simulation was found to be less than 20 % of the observations for 96 stations.

4.2 Volatile Organic Compounds

4.2.1 C_2-C_4 Alkanes

Alkanes are VOC ubiquitously present in the atmosphere, mainly emitted from anthropogenic activities. In Figure 4 the scatter plots of model results and in-situ observations from the NOAA/INSTAR database are presented. The statistic for each plot is summarized in Table 3. The model seems to reproduce satisfactorily the mixing ratios of the C_2-C_4 alkanes with more than 98, 91, 84 and 79 % of the simulated values lying within a factor of two to the observations for C_2H_6, C_3H_8, $i-C_4H_{10}$ and $n-C_4H_{10}$, respectively. Furthermore, the average ratios show that a slight overestimation is present for i-butane and n-butane, whereas the model tends to underestimate the mixing ratios of ethane and propane. This is confirmed by the comparison with
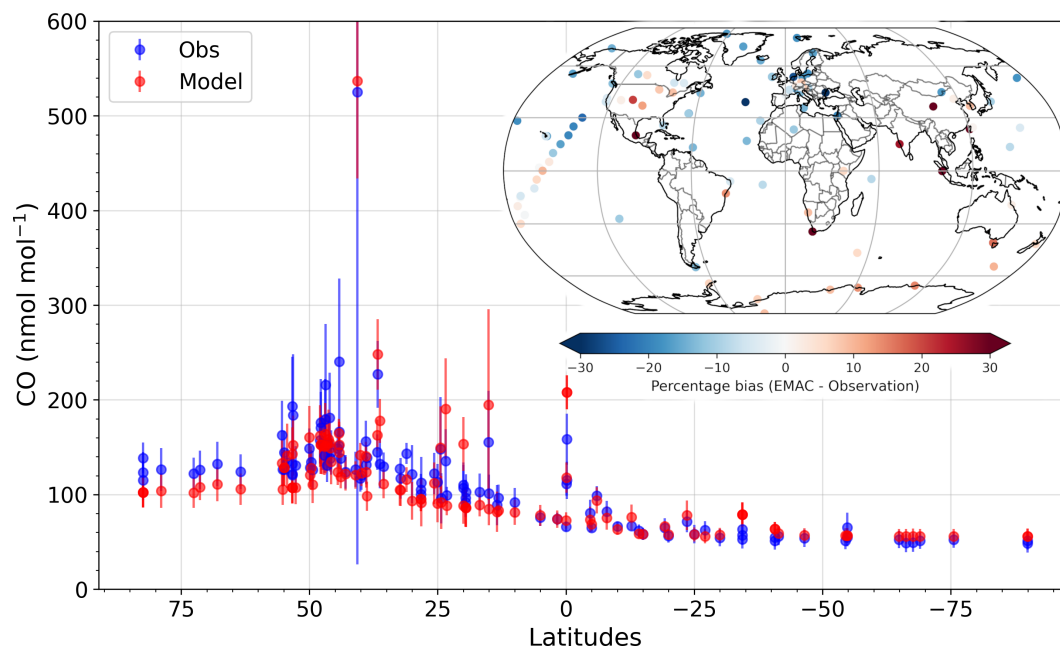
Figure 3. Latitudinal gradient of the annual mean (2010) of the measured and simulated surface CO mixing ratio at the WDCGG measurement stations. The error bars show the 1σ standard deviation of the annual mean (based on daily mean output). The map in the inset shows the annual bias between the simulation and measurements at the locations of the WDCGG stations.

255   the Emmons et al. (2000) database (Table 2), which shows that both, ethane and propane, are underestimated by the model, also with respect to the vertical profile (column $\overline{MM/OM}$).

     Figure 4 shows also a noticeable underestimation of the mixing ratios in the region between $30°$ N and $0°$ N, for propane and the butanes. This is clearly due to the underestimation of the oceanic emissions, as these stations (i.e., at Mahe Island, Seychelles (SEY), The American Samoa Observatory (SMO), Ascension Island, UK (ASC), and Easter Iland, Chile (EIC)) are all

260   strongly influenced by oceanic emissions. It must be pointed out that for $i-C_4H_{10}$ and $n-C_4H_{10}$, no oceanic emissions where included in the simulation, but that these are necessary for a correct representation of butanes, as already shown previously (Pozzer et al., 2010).

4.2.2 C_2-C_3 Alkenes

Differently from alkanes, the alkenes are mostly emitted by the biosphere. As shown in Table 2, the numerical simulation

265   of alkenes diverges more from the observations than the simulated alkanes do. Both, C_2H_4 and C_3H_6, are underestimated compared to the observations (see model mean, MM, against observed mean, OM in Tab. 2). Nevertheless, while C_2H_4 is overall reasonably reproduced (average of the ratios equal to 1.06, see Table 2), for C_3H_6 a strong underestimation is present (average of the ratios equal to 0.4, see Table 2). This is shown in Fig. 5, where examples of the vertical distribution of C_2H_4
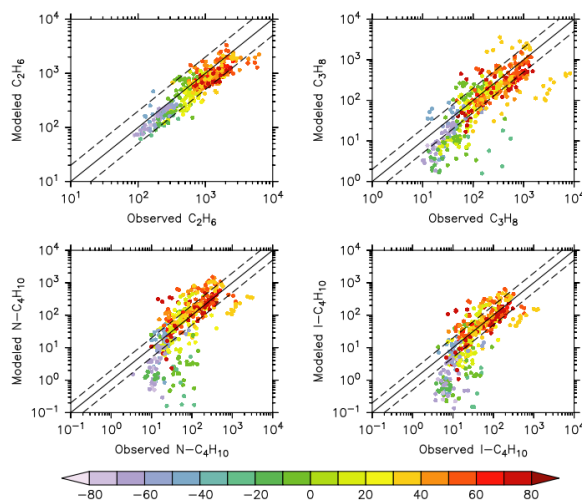
Figure 4. Scatter plot of measured and simulated surface alkanes mixing ratios at the NOAA/INSTAAR measurement stations for the year 2010. The units are in $\mathrm{pmol\,mol^{-1}}$. The color code denotes the latitude of the stations.

Species	N.points	MM	MSTD	OM	OSTD	$\overline{\mathrm{MM/OM}}$	PF2	RMSE
C_2H_6	450	742.54	551.02	1038.32	845.09	0.77	98.4	621.54
C_3H_8	447	262.87	417.25	393.13	745.48	0.91	91.5	755.93
$i-C_4H_{10}$	436	70.60	97.44	73.73	126.46	1.23	84.8	124.23
$n-C_4H_{10}$	423	160.49	231.75	146.89	293.97	1.46	79.6	307.80

Table 3. Summary of simulated and observed mixing ratios of different tracers in the NOAA/INSTAAR database (station observations). The columns are as in Table 2

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are shown. The issues in simulating C_3H_6 have been already pointed out by Pozzer et al. (2006), where similar results were
270 obtained with large underestimation of this tracer.

4.2.3 CH_3OH

CH_3OH is the most abundant oxygenated VOC is the Earth's atmosphere (Singh et al., 2001), primarily emitted by the terrestrial vegetation (Jacob et al., 2005). Other sources include biomass burning, the oceans and secondary formation in the troposphere (e.g., Millet et al., 2008; Stavrakou et al., 2011). The annual global distribution of CH_3OH total columns obtained from
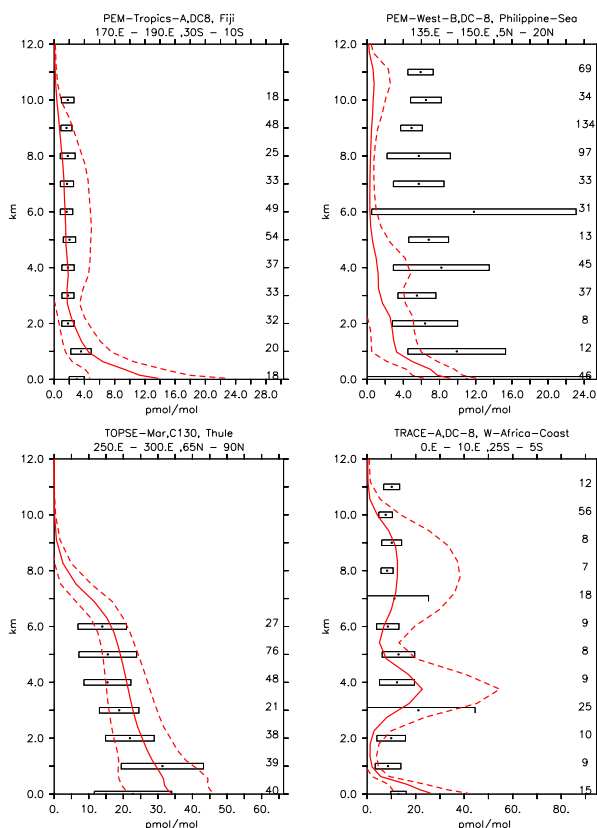
Figure 5. Vertical profiles of C_2H_4 in $pmol\,mol^{-1}$ for some selected campaigns from Emmons et al. (2000). Asterisks and boxes represent the average and the standard deviation (w.r.t. space and time) of the measurements in the region, respectively. The simulated average is indicated by the red line and the corresponding simulated standard deviation w.r.t. time and space by the dashed lines. On the right hand side, the number of measurements is listed.

the IASI measurements and EMAC of the year 2010 as well as their differences are presented in Fig. 6. Over land, the satellite and model spatial distributions of CH_3OH are relatively consistent, with the main source regions observed within the tropics (mainly over the Amazon Basin and central Africa), in Southeast Asia, and at Northern Hemisphere mid- and high latitudes. However, important differences in terms of column magnitude exist. Over the tropical forests, EMAC indeed simulates annual CH_3OH columns up to two times larger than those retrieved from the IASI observations (3.0–3.5×10^{16} molecules cm^{-2}). This can be partly ascribed to the high temperature bias that exists in the model over these areas (Hagemann and Stacke, 2015), which induces an excess of biogenic VOC emissions from the MEGAN submodel. Furthermore, dry deposition of methanol in tropical rainforests is likely under-represented by the Wesely (1989) approach used here (Karl et al., 2004). The potential contribution of an additional non-stomatal pathway favourable under humid conditions (Müller et al., 2018) has been shown by Emmerichs et al. (2021) for a less soluble species. On the other hand, EMAC underestimates the CH_3OH columns at mid- and
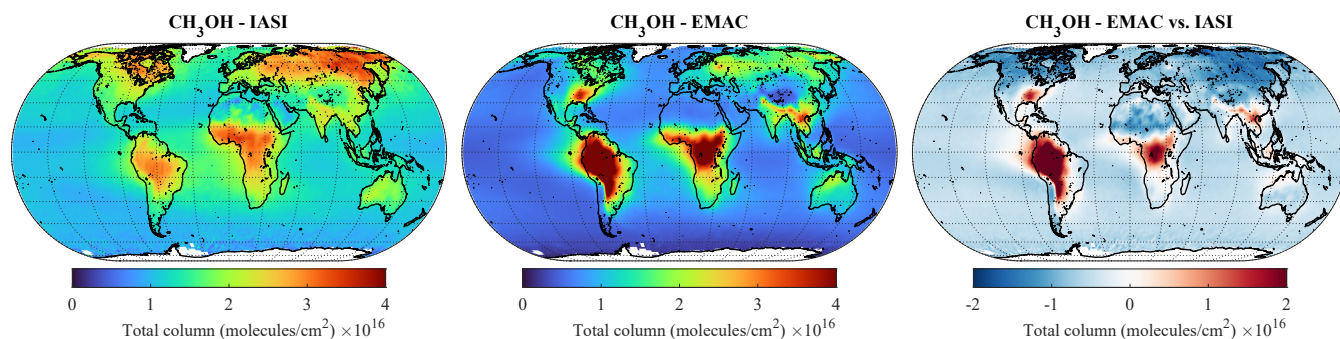
Figure 6. Annually averaged CH_3OH total columns (in $molecules\,cm^{-2}$) from IASI satellite observations (left), simulated by EMAC (middle), and the EMAC–to–IASI column differences (right), for the year 2010.

high latitudes of the Northern Hemisphere, indicating that biogenic and/or biomass burning VOC emissions are too low during summertime in these regions. Southeast US is the region in North America where most of the simulated CH_3OH enhancement exists, driven by substantial biogenic emissions in summertime, while larger columns are measured by IASI during the same season further northwards in the boreal regions. Over the oceans, EMAC underestimates the observed CH_3OH columns by $\sim 5 \times 10^{15}$ $molecules\,cm^{-2}$, which might result from an insufficient transport from the continental source regions and/or from missing secondary source(s) (see e.g., Bates et al., 2021; Müller et al., 2016). This is confirmed by the comparison of model results with the Emmons et al. (2000) database, where the methanol model mean is considerably lower than the observed one.

4.2.4 CH_3COCH_3

Acetone is the one of the most abundant oxygenated VOCs in the Earth's atmosphere after CH_3OH (Singh et al., 2001). Its sources include the terrestrial vegetation, the oxidation of hydrocarbon precursors of biogenic and anthropogenic origin, the oceans and biomass burning (e.g., Jacob et al., 2002; Pozzer et al., 2010; Fischer et al., 2012). The acetone total columns obtained from the EMAC simulation and the IASI observations exhibit major discrepancies in terms of global distribution (Figure 7). The satellite instrument detects the largest acetone columns (up to 2×10^{16} $molecules\,cm^{-2}$) at mid- and high latitudes of the boreal hemisphere, ascribed to important emissions of biogenic precursors during summertime (Franco et al., 2019), but a moderate burden at low latitudes and over the tropical forests. It is worth noting that this pattern is in agreement with the global acetone measurements obtained with the ACE–FTS satellite limb sounder (Dufour et al., 2016). Conversely, EMAC simulates strong hotspots of acetone within the tropics, especially over South America and Africa, with annually averaged columns larger than 2×10^{16} $molecules\,cm^{-2}$, but underestimates the acetone abundance by up to a factor of 2 in the Northern Hemisphere. Such a mismatch between satellite and model distributions points to major deficiencies in the current emission inventories of acetone and its precursors. For example, the extremely large acetone columns simulated by EMAC over the Persian Gulf and the Indo Gangetic Plain can be attributed to the highly elevated emissions of propane – an important precursor of acetone – in these regions. In vegetated regions, an underestimation of acetone dry deposition, accounting globally
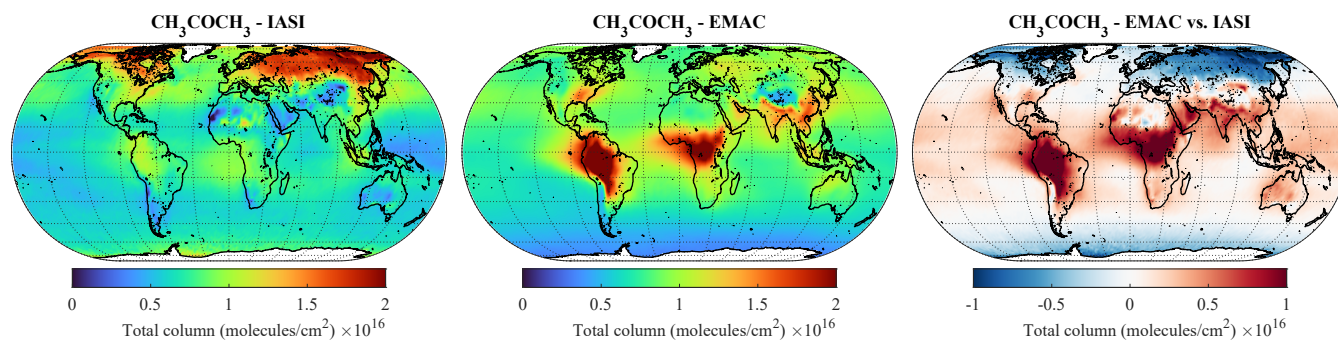
Figure 7. Same as Fig. 6, but for CH_3COCH_3.

for 20 % of the total loss (Khan et al., 2015), likely contributes to the mismatch. According to measurements, significant amounts of acetone are removed during night through non-stomatal uptake (Karl et al., 2004; Müller et al., 2018). However, over remote areas and the oceans, the simulated acetone abundance is consistent with the IASI measurements, with vertical
310 column integrals in the range of 0.5–1.0×10^{16} molecules cm^{-2}. The model, nevertheless, simulates a slight overestimation over the oceans at low latitudes compared to IASI, especially in the outflows of the tropical hotspots. Compared to the aircraft observations, the model results present a much better agreement than when compared against remote sensed data, with only a somewhat small bias (see Tab. 2). This apparent agreement with the observations is due to the uneven distribution of the field campaign present in the observational dataset (see Emmons et al. (2000), Fig.1 and Huijnen et al. (2019), Fig.1). In fact, most of
315 the campaigns in which acetone was measured took place over the ocean, where the model is correct or slightly overestimating the total column observed by IASI. In contrast, only few campaigns in the Northern Hemisphere are present in the dataset (such as ABLE-3B, and POLINAT-2) for which the model strongly underestimates the observed values. As a result of the sparsity of the aircraft observations used, Table 2 presents a quite fair agreement between model and aircraft observations, an agreement which is, however, not corroborated by the more spatially complete comparison with the IASI total column.

320 ### 4.2.5 HCOOH

Formic acid is the dominant organic acid in the troposphere and a product of the degradation of a large suite of VOC precursors, but its observed abundance is generally severely underestimated by state-of-the-art global models (e.g., Millet et al., 2015; Paulot et al., 2011; Stavrakou et al., 2012). Similarly, in our simulation the EMAC model largely underestimates the HCOOH total columns derived from the IASI observations by up to a factor of 4, in particular in remote environments (see Fig. 8).
325 Although the two main tropical source regions identified by IASI – the Amazon Basin and central Africa – are reproduced by EMAC, the magnitude of the simulated HCOOH columns are too low in comparison to the satellite measurements. It also has to be mentioned that the apparent agreement over Amazonia is possibly due to the high temperature bias in the region and the subsequent excess of simulated isoprene emissions during the dry season. Over the other source regions (e.g., Southeast Asia and Southeast US), the model underestimation is more pronounced, in particular in the Northern Hemisphere.
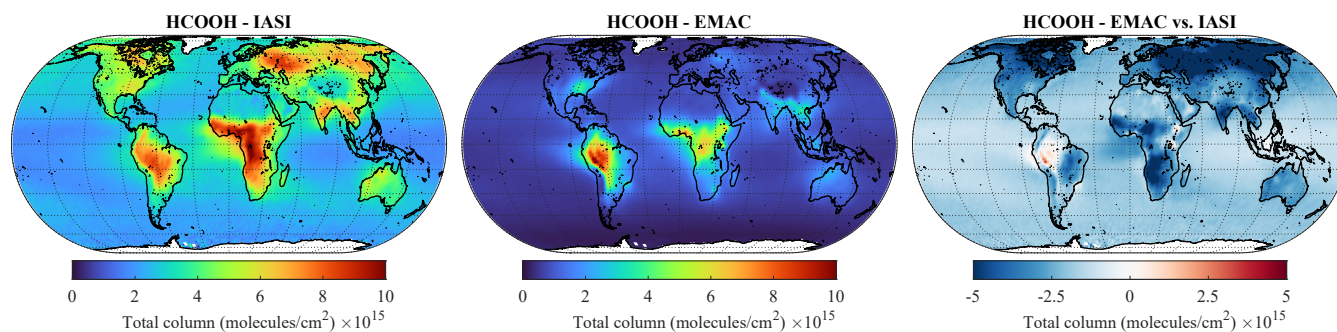
Figure 8. Same as Fig. 6, but for HCOOH.

330 The large enhancement of HCOOH columns observed with IASI over western Russia ($\sim 8 \times 10^{15}$ molecules cm^{-2}), attributed to the August 2010 wildfires, is not reproduced by EMAC ($< 2 \times 10^{15}$ molecules cm^{-2}) and suggests that the biomass burning emissions of VOCs are underestimated.

The general underestimation of simulated versus observational data is also confirmed by the comparison with the aircraft database (Emmons et al., 2000), as shown in Table 2. Although this underestimation of the model results is less apparent compared to that of the total column observations, it must be noted that only a limited number of merged data (53, see Table 2) is available for the comparison with aircraft observations and therefore such a comparison provides only an indication rather than a quantitative estimate. It must be stressed that Franco et al. (2021) showed the importance of in-cloud chemistry for this tracer, which is missing in this study. The lack of adequate in-cloud chemistry would therefore explain the almost ubiquitous underestimation of this tracer.

340 4.2.6 CH$_3$COOH

Acetic acid is the second most abundant carboxylic acid in the troposphere and, based on the IASI retrievals, presents a spatial pattern, regional seasonality, and vertical abundance, which resemble those of HCOOH (Franco et al., 2020). Like the latter, CH$_3$COOH is produced from the oxidation of various tropospheric precursors, but has emission factors from biomass burning that are 3 to 10 times larger than those of HCOOH (Akagi et al., 2011; Andreae, 2019). CH$_3$COOH is more difficult to detect in the infrared IASI spectra and its retrievals are subject to larger uncertainties, in particular over the oceans (see Franco et al., 2020). Therefore, we limit here the comparison with EMAC to the continents, excluding measurements over desert areas that are altered by surface emissivity artefacts (Fig. 9). From the comparison, conclusions similar as for HCOOH can be drawn for CH$_3$COOH: the two main tropical source regions are relatively well reproduced by EMAC (with a better agreement over Africa in this case), whereas the observed CH$_3$COOH levels are underpredicted in the Northern Hemisphere by up to a factor of 4. The comparison with aircraft observations (see Table 2) confirms again this strong underestimation also over the ocean, as the only campaign in the dataset including CH$_3$COOH measurements is the PEM-Tropics-A, which was performed over the Pacific ocean.
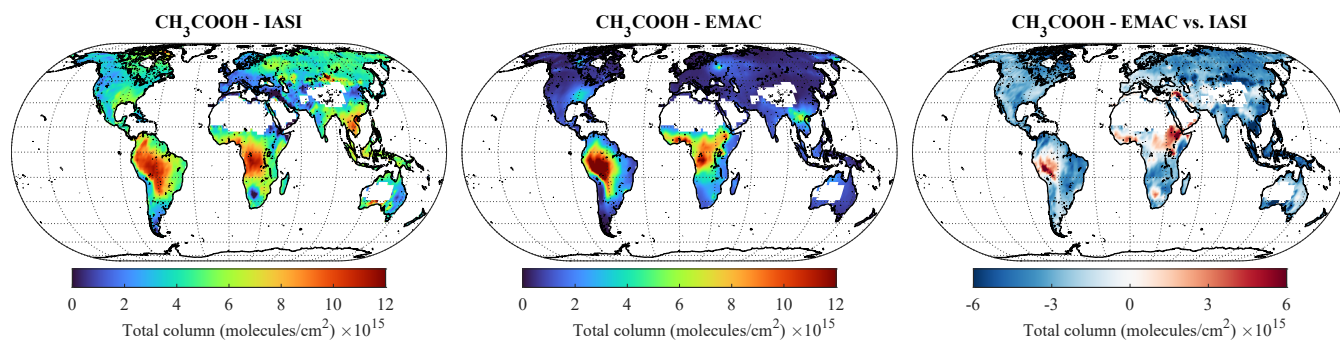
Figure 9. Same as Fig. 6, but for CH_3COOH. In this figure area above the ocean were excluded.

These results confirm that the VOC emissions and oxidation pathways leading to the formation of CH_3COOH in the tropo-sphere are still poorly understood and constrained (e.g., Khan et al., 2018; Paulot et al., 2011). For example, acetaldehyde – a major CH_3COOH precursor via its reaction with OH (Lei et al., 2018) – is well known to be largely underestimated by global models (Millet et al., 2010; Wang et al., 2019). On the other hand, the large model versus observations differences in Southeast Asia also point to missing emissions from biomass burning. Finally, in-cloud chemistry could be important in the CH_3COOH formation, analogously to formic acid (Franco et al., 2021), and this process could bring model results and observations to a closer agreement.

4.2.7 PAN

Owing to its complex photochemical sources and its thermal instability, PAN (Peroxyacetylnitrate), the main tropospheric reservoir species of NO_x, is a very challenging tracer to simulate. The comparison with the IASI data reveals that the model reproduces correctly the main spatial patterns of PAN, with the source regions and main outflows over the oceans being correct. However, the model constantly underestimates the observed PAN columns over the globe. The satellite column values are indeed between two and four times the simulated PAN columns, with the most pronounced negative bias observed at Northern Hemisphere mid- and high latitudes. The same conclusion can be drawn from the comparison with the aircraft emissions (Table 2), for which the model clearly underestimates the osberved mixing ratios. A closer inspection reveals that PAN is especially underestimated in the middle and upper-troposphere. The model–to–observations discrepancies can mostly be attributed to the unsatisfactory representation of different VOCs. For example, we have seen that the model results do not agree with observations for acetone, which is an important precursor of the peroxyacetyl radical in the free troposphere (Fischer et al., 2014). Furthermore, the strongest model's underestimation appears to be exactly where CH_3COCH_3 is at most underestimated, confirming that deficiencies of simulated precursor patterns are the main cause of the PAN biases. Additionally, sensitivity simulations suggested that the PAN formation in global models is more sensitive to the representation of VOCs (Fischer et al., 2014). Finally, an insufficient vertical transport of VOCs from the planetary boundary layer to the free troposphere in the model might also reduce the amount of PAN, because PAN is more stable at the lower temperatures of the free troposphere.
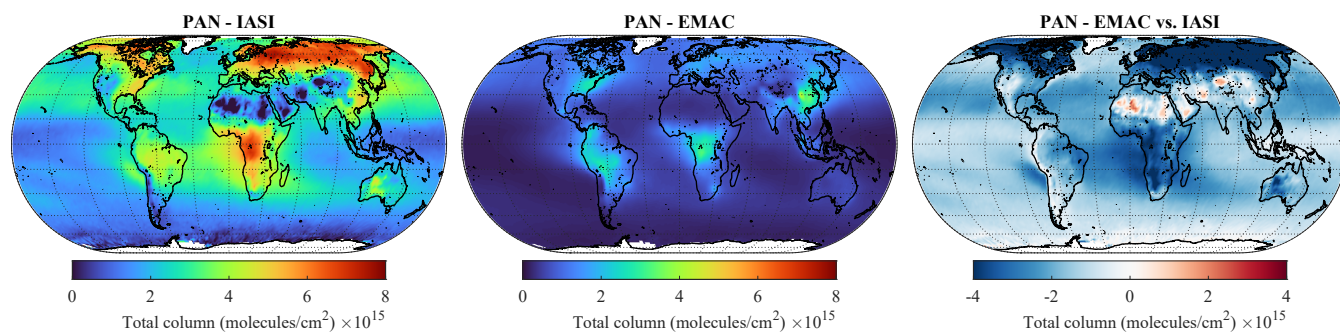
Figure 10. Same as Fig. 6, but for PAN.

4.3 OH

The simulated distribution of the hydroxyl radical (OH) is in line with the findings by Lelieveld et al. (2016) (further denoted as L16), who earlier thoroughly analysed the MOM performance in EMAC with a setup featuring a simplified treatment of aerosol microphysics and gas/aerosol partitioning. The total OH turnover (composition of annual production and loss terms,

380   shown in Fig. 11) of 234 $\mathrm{Tmol\,yr^{-1}}$ in 2010 is 7 % less than that found by L16 and is consistent with the addition of the explicit treatment of secondary organic formation processes of aerosols and changes in trace gas emission fluxes. The OH production in the VOC- and ROOH-initiated reactions is 3 % lower in both, the free troposphere (FT), and the boundary layer (BL). This is compensated by the increased share of primary production (P, via the $O(^1D)+H_2O$ pathway), especially in the BL (4 % increase vs. 2 % in the FT). Regarding the partitioning of the OH sinks, however, no substantial changes can be noted

385   (see Fig. 11, right panel). Together with the reduction of the secondary sources (S), the resulting OH recycling probability r_{OH} (defined as $1 - P/(S + P)$, see details in L16) establishes at 59 % and 62 % in the BL and FT, respectively. Being about 5 % lower than the estimate reckoned by L16, such high r_{OH} values signify still highly stable (buffered) OH concentrations and therefore a likewise stable tropospheric oxidative capacity obtained with this model set-up.

The simulated annual air mass-weighted average hydroxyl concentrations are 12.1 (troposphere), 12.0 (FT) and 13.6 (BL)

390    $10^{15}\,\mathrm{molecules\,cm^{-3}}$ in the year 2010, which correspond to OH chemical removal lifetimes of 1.59, 1.78 and 0.53 s, respectively. The diagnosed tropospheric OH inter-hemispheric gradient (NH/SH ratio) is 1.17, lower than that estimated by L16 (1.20) due to the increased OH reactivity via VOC and SOA in the NH and at the lower end of the model estimates reviewed there. By not being in agreement with the measurement-based estimates suggesting hemispheric symmetry in tropospheric OH (Patra et al., 2014; Wolfe et al., 2019), the pronounced asymmetry in atmospheric models results from asymmetric OH

395   production due to skewed distributions of O_3 and NO_x prevailing in the NH, and calls for further studies in this direction.

Overall, the simulated tropospheric hydroxyl radical distribution is comparable to that thoroughly analysed by L16 with a minor increase in reactivity of up to 5 % when calculated from the changes to the CH_4 and MCF (CH_3CCl_3) lifetimes against removal by OH (τ_{OH}). The here estimated $\tau_{OH}(CH_4)$ values are 8.4 and 4.4 years in the FT and BL, respectively; the tropospheric $\tau_{OH}(MCF)$ value is obtained to be 4.9 years.
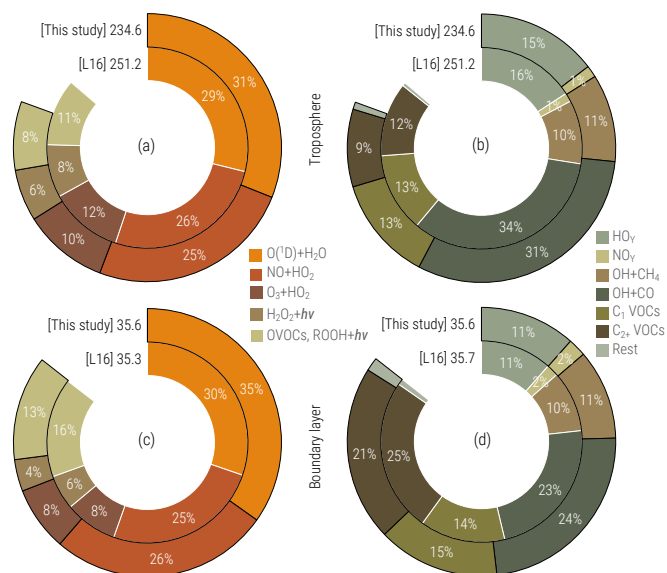
Figure 11. Simulated OH production (left) and sink (right) by category in the troposphere (top) and boundary layer (bottom) in this study and by Lelieveld et al. (2016) (denoted L16). Values are annual totals in $\mathrm{Tmol/yr}$ for 2010. Percentages denote fractions attributed to particular categories (see L16 for for details).

4.4 Aerosol Optical Depth

In order to evaluate the overall performance of the model in reproducing aerosol distribution, the AOD at 550 nm simulated by the model is compared to satellite based and station observations. Figure 12 shows the annual average AOD of the simulation and of the observations (satellite). The distribution is remarkably similar, with the high AOD regions (Northern Africa and Soth Eastern Asia) being well simulated by the model. Open ocean AOD of $\simeq 0.2$ AOD units are reproduced by the model, with slightly underestimated AOD over the central Atlantic (possibly due to slightly underestimated dust outflow from the northern Africa region). To quantify the model capability to reproduce the AOD, in Figure 13, the model daily AODs are compared to the collocated (in space and time) observations from MODIS and the AERONET instruments (middle and bottom row, respectively). For comparison, the same scatter plot has been produced comparing MODIS and AERONET directly (top row). The model has difficulties in reproducing the daily variability of AERONET AOD, with only 58 % of the simulated AOD within a factor of 2 to the observational data. Even the correlation is considerably low, with an R^2 equal to 0.33. Very similar results are obtained by comparing the model results to the satellite AOD observations, with again only 57 % of the simulated data within a factor of 2 to the observations. Once monthly averages are used for the inter-comparison, the statistics remain almost unchanged with just a small improvement in the slope of the fitting curve (see Fig. 13, central column). Finally, using the annual averages for the intercomparison, the coefficients of determination R^2 almost double (0.633 and 0.567 for the comparison of the model with MODIS and AERONET data, respectively), while more than 80 % of the model results are
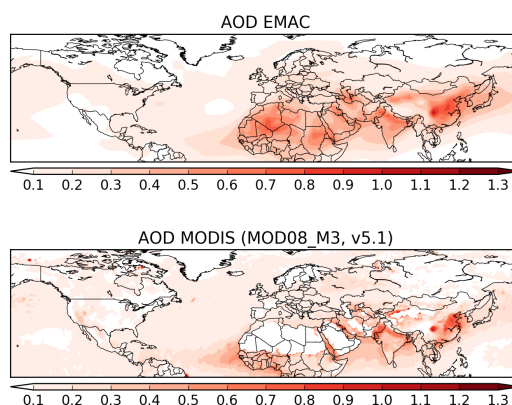
Figure 12. Global map of AOD from model results and the MODIS observations for the year 2010 (annual average).

within a factor of 2 to the observations (either satellite or in-situ). To put these results into context, the same analysis has been performed comparing the MODIS data and AERONET stations. Although the satellite observations outperform (slightly) the model results compared to the AERONET measured AOD in the case of the daily and monthly averages, for the annual averages the model seems to perform equally well, with a similar coefficient of determination and a fraction of values within a factor of 2 to the observations. Due to the intrinsic characteristics of the model (such as its relative coarse resolution) it is not expected to have a good representation of the short term variability.

4.5   Fine particulate mater ($PM_{2.5}$)

The comparison of model results for $PM_{2.5}$ (i.e. fine particles with an aerodynamic diameter smaller than 2.5 µm) was performed against the dataset of Hammer et al. (2020). Although this dataset is not a pure observational dataset, it has a global coverage and has been constrained from in-situ measurements. The comparison is done for $PM_{2.5}$ at 35 % relative humidity, i.e. dry fine particulate mass (in µg m^{-3}). In Figure 14, the maps of the annual average of the model results and the pseudo-observation dataset are shown. Although the distribution patterns appear to be similar, the model tends to underestimate the fine particle concentration over northern India and eastern China, on the one hand, while the opposite happens over east Africa and the Middle East. On the other hand side, the model seems to reproduce $PM_{2.5}$ quite accurately over both Europe and North America, and even the locally enhanced levels of $PM_{2.5}$ (~ 30 µg m^{-3}) in Canada from Boreal forest biomass burning are nicely reproduced by the model.

In Figure 15, the scatter plot of the two datasets is shown, while in Table 4 the statistics for the different regions presented in the figures are listed. Due to the large grid resolution difference, the pseudo-observations have been aggregated to the grid resolution of the model. As already noted from the global map, the model tends to underestimate $PM_{2.5}$ over South Asia and East Asia by $\sim 40\,\%$ and $\sim 20\,\%$, respectively. Nevertheless, in both regions, more than 70 % of the model results are within
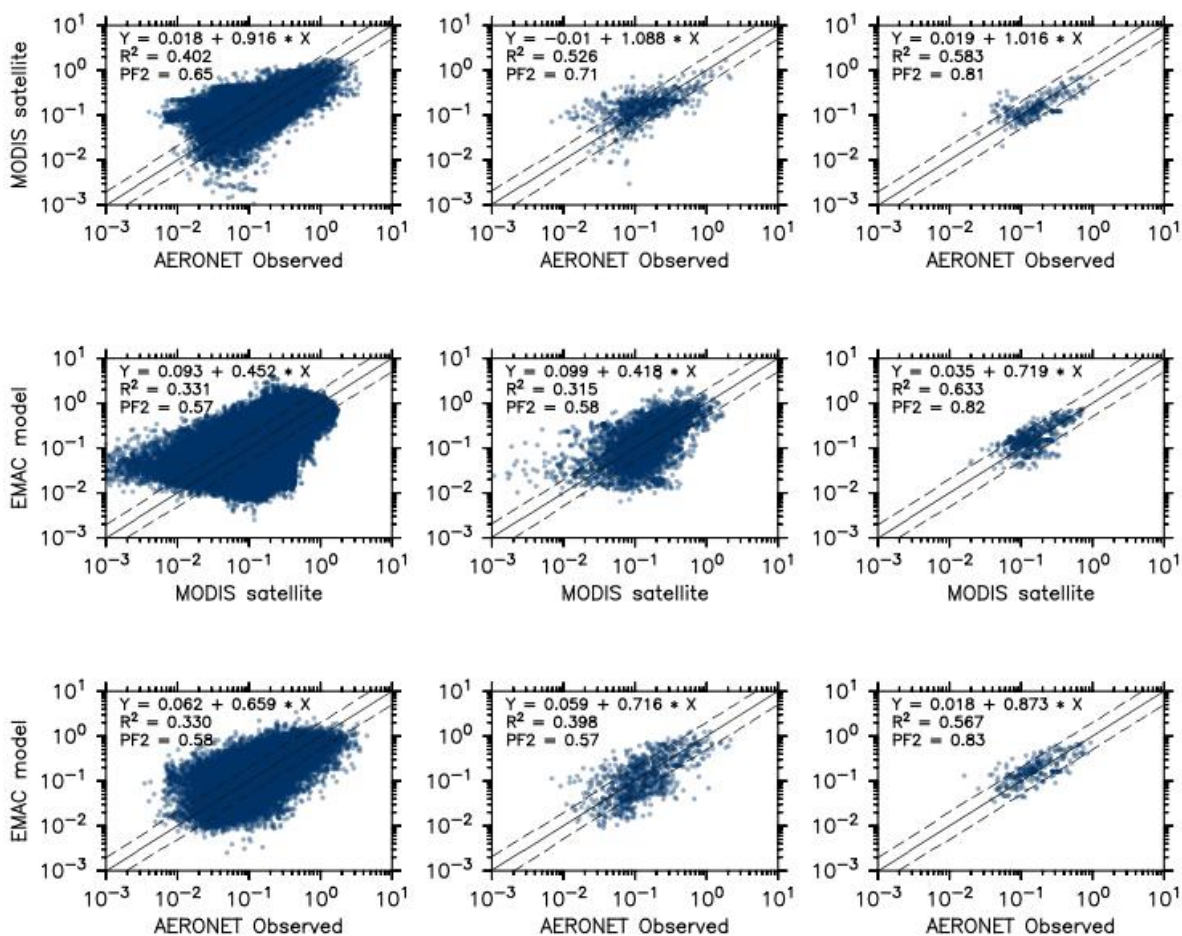
Figure 13. Scatter plots of AOD estimated by the EMAC model in this study versus the MODIS and the AERONET observations. Left, Middle and Right: scatter plots using daily, monthly and annual averages, respectively. Both, model and satellite based observations, were sampled at the AERONET locations. In each plot the coefficients of the linear fit, the coefficient of determination and the fraction of data within a factor of 2 are listed.

a factor of 2 of the pseudo-observations. The model agrees well, however, with data from Europe and North America, with more than 95 % of the model results within a factor of two. The overall comparison indicates that the model agrees well with the pseudo-observations, as the spatial-temporal averages of the two datasets are very close (17.1 $\mu g\,m^{-3}$ for the model and
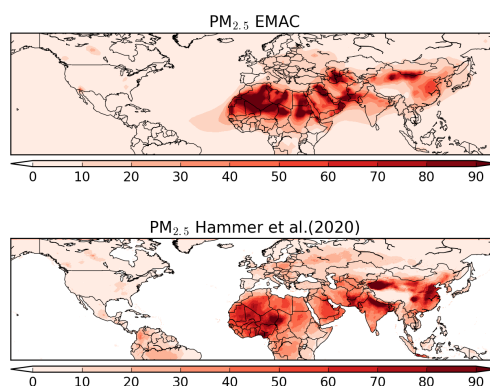
Figure 14. Global map of $PM_{2.5}$ from model results and the Hammer et al. (2020) dataset for the year 2010 (annual average) in μgr/m^3. The data from Hammer et al. (2020) does not contain values over the ocean.

19.4 $\mu g\,m^{-3}$ for the pseudo-observations), with more than 70 % of the model simulated $PM_{2.5}$ within a factor of two of the

440   pseudo-observed $PM_{2.5}$.
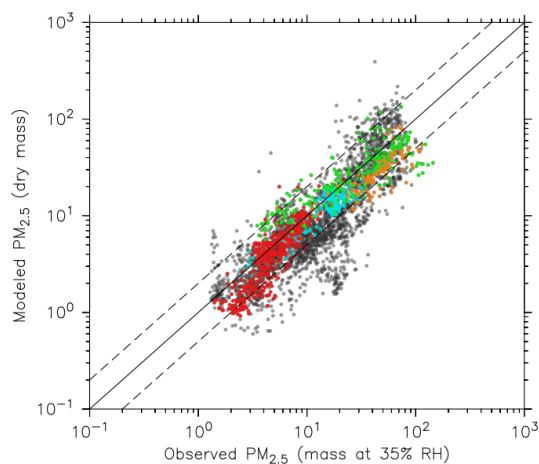
Figure 15. Scatter plots of $PM_{2.5}$ of model results versus data from Hammer et al. (2020) for the year 2010 (annual average) in $\mu g\,m^{-3}$. Light blue, red, green, and orange colors depict points located in Europe, North America, East Asia, and South Asia, respectively. Grey points indicate the remaining parts of the world.

Region	MM	OM	MM/OM	PF2
Europe	11.4	14.3	0.80	98.8
North America	4.8	5.2	0.92	95.2
South Asia	31.2	50.3	0.62	72.6
East Asia	31.2	37.1	0.84	82.1
World	18.4	19.4	0.94	71.4

Table 4. Summary for simulated and pseudo-observed, annually averaged $PM_{2.5}$. MM and OM denote the arithmetic mean of the simulated and observed concentrations, respectively, in $\mu g m^{-3}$. PF2 is the percentage of simulated points within a factor of 2 with respect to the observations.

4.6 Aerosol Composition

For the evaluation of the simulated mass concentrations of sulfate, nitrate, ammonium, sodium and five species related to sea spray and organic aerosols, we use in-situ measurements from different monitoring networks, as described in Sect. 3.2. Co-located time series of simulated and observed quantities were obtained by bilinear interpolation of the gridded model data
445 at ground level to the respective site location. The analysis is based on monthly mean concentrations, which are derived from daily (model data, EMEP observations) and weekly (EPA) data, with the exception of EANET, which directly provides monthly averages. Note that some monitoring stations are located relatively close to each other, such that the reported concentrations may not be independent from each other, which can lead to an overestimation of the degrees of freedom in the calculation of quantities such as the root mean square error.

450 ### 4.6.1 Sulfate (SO_4^{2-})

Observed particulate sulfate concentrations are reproduced well by the model. The monthly mean concentration is matched closely for North America (EPA) and slightly underestimated for Europe (EMEP) and East Asia (EANET) (see Table 5). For EPA and EMEP data, more than 80% of the simulated monthly mean concentrations lie within a factor of two of the observations, and more than 70% for EANET. The standard deviation of observed monthly mean values is lower than the root
455 mean square error (RMSE) for all monitoring networks, which is an indication for a good quality of the model results (Barna and Lamb, 2000). Also, RMSE is lower in the present study compared to a similar analysis by Pozzer et al. (2012a) in which, however, a longer time period of four years (2005-2008) was investigated. Pozzer et al. (2012a) also report a relatively large spread (observation standard deviation equal to $5.3\,\mu g m^{-3}$) of the measured sulfate concentrations in EANET, which is likely to be caused by a comparably low number of stations which cover a large region with strong spatial gradients.
460 The close overall agreement of average concentrations simulated by the model (MM) with the observations (OM) for EPA can partly be attributed to underestimated high concentrations in summer (composite of June, July and August, "JJA"), which are compensated by overestimated lower concentrations from autumn to spring (see Figure 16). Relative deviations are largest

Species	Network	$N_{station}$	MM	MSTD	OM	OSTD	$\overline{MM/OM}$	PF2	RMSE
SO_4^{2-}	EPA	81	1.92	0.99	1.88	1.20	1.35	84.3	0.93
SO_4^{2-}	EMEP	42	1.68	1.05	1.79	1.21	1.37	83.7	0.95
SO_4^{2-}	EANET	25	2.83	1.65	3.58	4.06	1.58	71.0	3.49
NO_3^-	EPA	81	1.89	1.97	0.77	1.07	4.29	36.9	1.88
NO_3^-	EMEP	22	3.34	2.89	1.93	2.15	3.75	55.3	2.97
NO_3^-	EANET	23	3.34	3.34	1.45	2.43	8.36	32.6	3.47
NH_4^+	EPA	81	1.09	0.89	0.73	0.53	1.84	64.8	0.77
NH_4^+	EMEP	27	1.31	1.17	0.92	0.86	1.69	62.0	0.92
NH_4^+	EANET	23	1.40	1.35	1.00	1.14	2.38	54.7	1.07
Na^+	EPA	81	0.16	0.22	0.16	0.36	2.19	61.1	0.23
Na^+	EMEP	24	0.57	0.43	0.60	0.73	2.03	53.1	0.57
Na^+	EANET	21	0.92	0.81	1.22	1.67	2.89	46.8	1.53
Mg^{2+}	EPA	81	0.05	0.06	0.05	0.05	2.06	42.7	0.06
Mg^{2+}	EMEP	22	0.17	0.13	0.07	0.09	4.65	32.6	0.16
Mg^{2+}	EANET	15	0.29	0.21	0.24	0.26	2.38	57.8	0.27
Ca^{2+}	EPA	81	0.06	0.12	0.26	0.27	0.60	16.2	0.37
Ca^{2+}	EMEP	28	0.14	0.25	0.15	0.25	1.60	51.5	0.24
Ca^{2+}	EANET	19	0.23	0.22	0.75	1.97	1.44	45.2	2.07
K^+	EPA	81	0.03	0.05	0.07	0.04	0.83	19.8	0.08
K^+	EMEP	25	0.09	0.13	0.08	0.07	1.42	60.0	0.14
K^+	EANET	20	0.12	0.09	0.26	0.34	0.98	47.1	0.37
Cl^-	EPA	81	0.35	0.65	0.14	0.51	5.92	24.7	0.53
Cl^-	EMEP	24	2.16	1.59	0.86	1.05	37.24	29.5	1.82
Cl^-	EANET	17	2.63	2.55	1.90	2.88	4.38	39.2	2.62
OA	IMPROVE	155	1.32	1.11	0.92	0.73	1.73	0.65	1.01
OA	EMEP	12	1.43	0.77	2.55	2.27	0.83	0.60	2.35
OA	EASIA	9	9.20	9.91	16.07	11.41	0.51	0.42	9.25

Table 5. Summary of simulated and observed monthly averaged aerosol concentrations for SO_4^{2-}, NO_3^-, NH_4^+, Na^+, Mg^{2+}, Ca^{2+}, K^+, Cl^- and organic aerosols (OA) and different observational networks (second column). $N_{station}$ is the number of stations providing data for the respective species and network; note that this is *not* the sample size for the shown statistics. The next columns provide the arithmetic mean of the simulated (MM) and observed concentrations (OM), and the respective standard deviations (MSTD, OSTD) in μgm^{-3}. PF2 denotes the percentage of simulated points within a factor of 2 with respect to the observations, and RMSE represents the root mean square error between simulated and observed points.

in winter and autumn, when observed concentrations are much lower than simulated concentrations. In Europe (EMEP), the highest concentrations are observed during the winter months, which is captured by the model.

465   The East-West gradient of observed annual mean concentrations in North America is represented well in the model, although the amplitude is underestimated: lower values in the West are overestimated while higher concentrations in the East are underestimated (Figure 17). This feature also lead to a good agreement between observed and simulated mean concentrations in Table 5. The North-South gradient over Europe is also captured by the model. Despite the less dense spatial distribution of monitoring stations providing data for particulate sulfate, one can observe a correspondence between simulated and observed

470 annual mean concentrations, especially over Japan. One outlier in Japan with a very low observed annual mean concentration is located at a relatively high altitude ("Happo", 1850 m), so that the comparison to model data on ground level may not be appropriate for this station. The same holds for two EMEP stations, namely Jungfraujoch (Switzerland) at 3578 m, and Chopok (Slovakia) at 2008 m, where annual mean concentrations are largely overestimated.
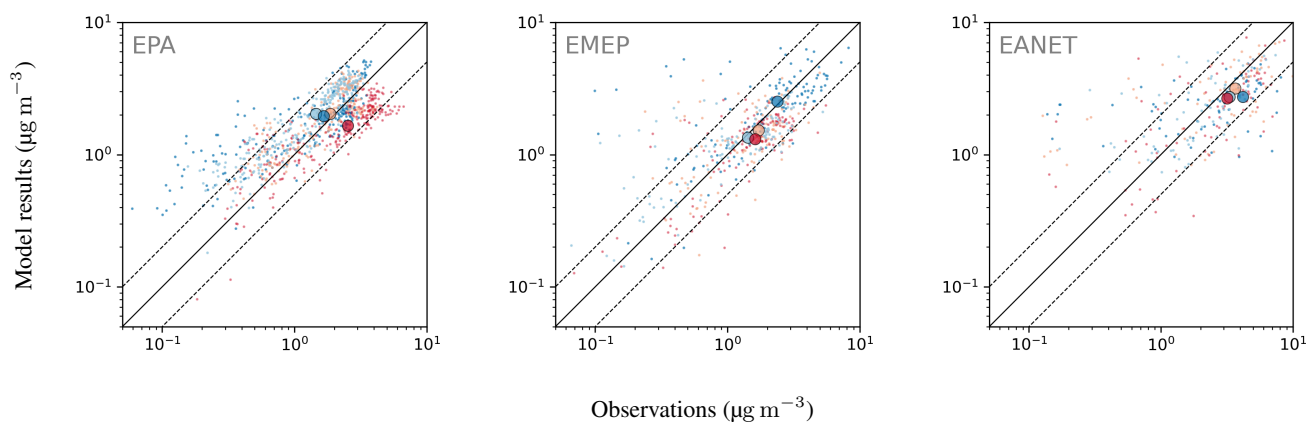
Figure 16. Scatter plots of observed and simulated monthly average SO_4^{2-} concentrations for the year 2010 and three observational networks: EPA, EMEP, and EANET (left to right). The coloring of the points represents a categorization into seasons (dark blue: DJF, orange: MAM, red: JJA, light blue: SON), the respective seasonal averages of monthly concentrations are depicted as large circles. Dashed lines denote the interval of a factor of 2 of the observations. The simulated concentrations were obtained by sampling the modeled data at the respective station locations using bilinear interpolation over neighbouring grid points.

4.6.2   Nitrate (NO_3^-)

475 Nitrate is less well represented than sulfate, showing a general overestimation of observed concentrations with an average ratio of simulated to observed concentrations by at least 3.75. This comparably large ratio is dominated by a few stations with small concentrations, where the median ratios lie between 1.70 and 2.84. About half (EMEP) to two thirds (EPA, EANET) of the simulated monthly mean concentrations exceed a factor of 2 with respect to the observations. For EANET and EMEP, the number of monitoring stations is substantially lower than for EPA, which may partly explain the larger spread in both, the
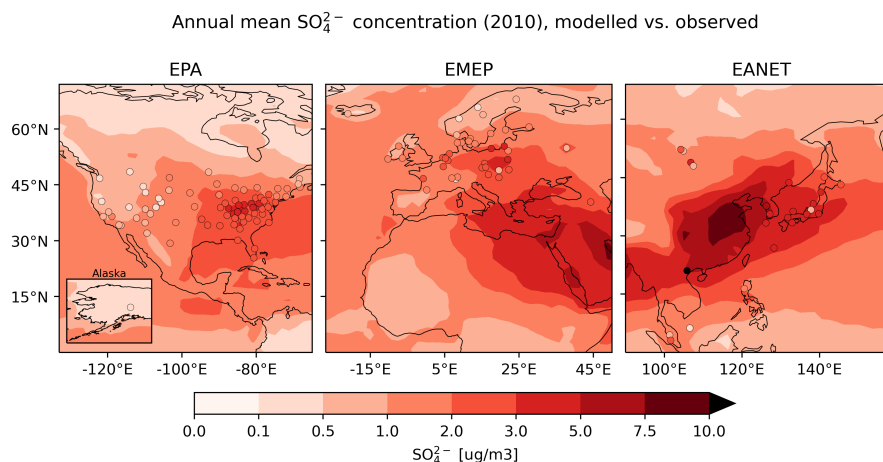
Figure 17. Annual mean SO_4^{2-} concentrations for the year 2010 for the model and three observational networks: EPA, EMEP, and EANET (left to right). Simulated data are shown as shaded contours, while the observational data are depicted as circles.

480 model results and observations (OSTD, MSTD). The RMSE is larger than the observed standard deviations for all considered networks, suggesting a less faithful representation of this species. This overestimation may be attributed to the usage of Teflon filters, as nitrate can evaporate from the filters under warm and dry conditions (Ames and Malm, 2001). Schaap (2003), Schaap et al. (2004) and de Meij et al. (2006) showed that particulate ammonium and nitrate partially evaporate from the filters at temperatures between 15 to 20°C and can evaporate completely at temperatures above 20°C. Therefore, this effect

485 predominantly affects measurements during the warmer seasons, when nitrate concentrations are close to the annual minimum. An indication for overestimation due to evaporation would then be a closer agreement between model and observation in the colder winter months. However, both in relative and absolute terms, the overestimation of monthly mean nitrate concentrations is more pronounced in winter than in summer for the three considered networks (Figure 18). All regions show the same seasonal cycle with respect to averaged monthly mean concentrations; a maximum in winter and a minimum in summer, both

490 for model results and observations. The spatial gradient of annual mean concentrations is captured well for North America (EPA), although the concentrations towards the East coast are generally overestimated. The low number of monitoring stations for EANET and EMEP does not allow us to draw solid conclusions; yet we can report that the North-South gradient of nitrate over Europe is reproduced by the model, except for an outlier at high altitude in Central Europe (Figure 19). The region with highest simulated annual mean concentrations and strong spatial gradients is East Asia, however it is scarcely covered by

495 monitoring stations reporting full coverage for the considered year 2010.

4.6.3 Ammonium (NH_4^+)

Considering the ratio of averaged monthly mean ammonium concentrations, the model overestimates the observed concentrations, yet to a lower degree than for nitrate (Table 5). This feature is also apparent in the fraction of simulated monthly
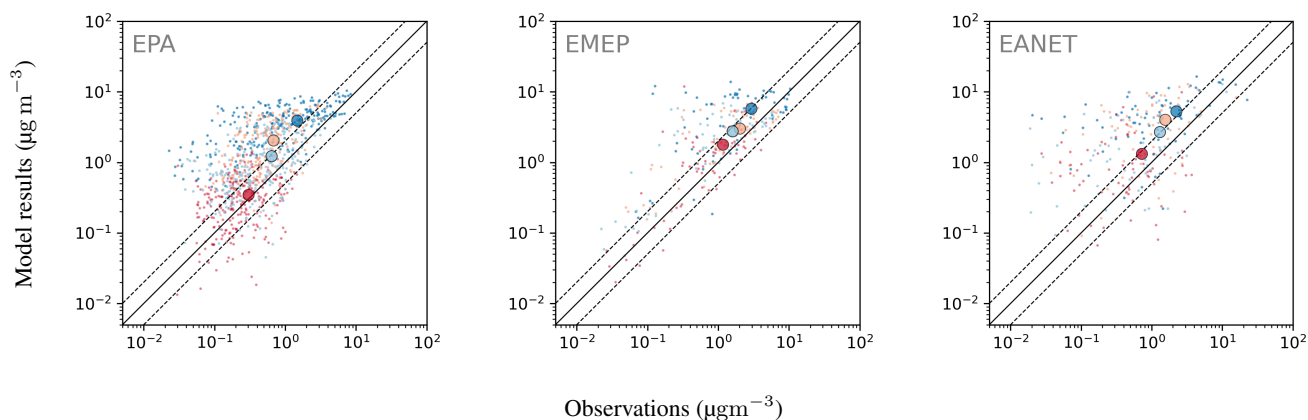
Figure 18. As in Figure 16, but for NO_3^-.
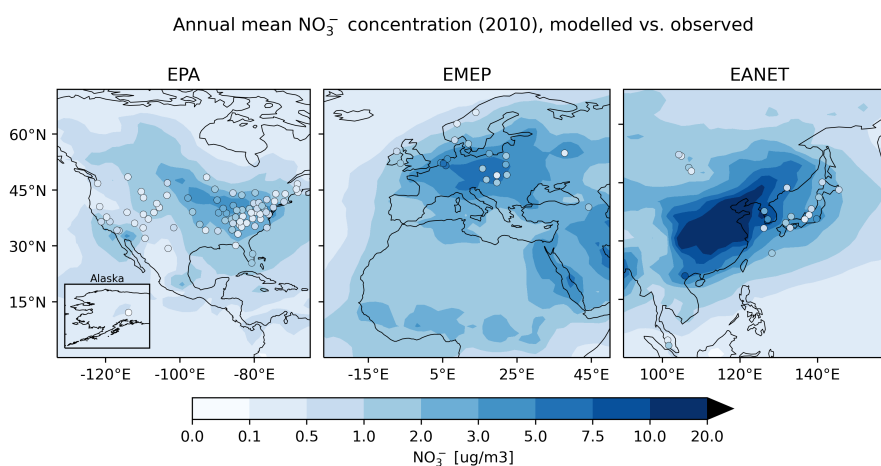
Figure 19. As in Figure 17, but for NO_3^-.

mean values within a factor of two of the observations: 54.7% for the network in East Asia and more than 60% for Europe

500 and North America. The magnitude of overestimation is similar for the three networks, ranging from 40% to 50%. RMSE values are close to the standard deviation of observations in all networks, again indicating a good representation by the model. The largest concentrations occur during the winter months (Figure 20). While the degree of overestimation is similar for the different seasons in EMEP and EANET, this does not hold for EPA: summer concentrations are systematically underestimated, whereas autumn to spring concentrations are generally overestimated. The monthly mean concentrations for winter and spring

505 constitute most of the values outside the factor of 2 regarding the observations for all considered regions. Both the observed North-South and East-West gradients of annual mean concentrations are represented well for the EPA network ((Figure 21), though the simulated gradient is less pronounced.

The North-South gradient of observations over Europe is also captured by the model, although the number of stations is again comparably low. The simulated spatial patterns in East Asia also match the observations arguably well.
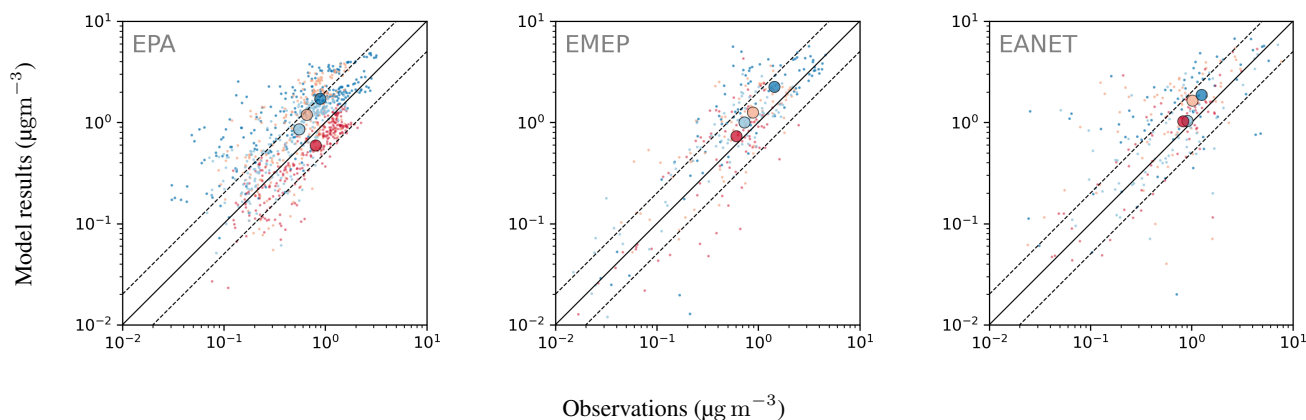
Figure 20. As in Figure 16, but for NH_4^+.
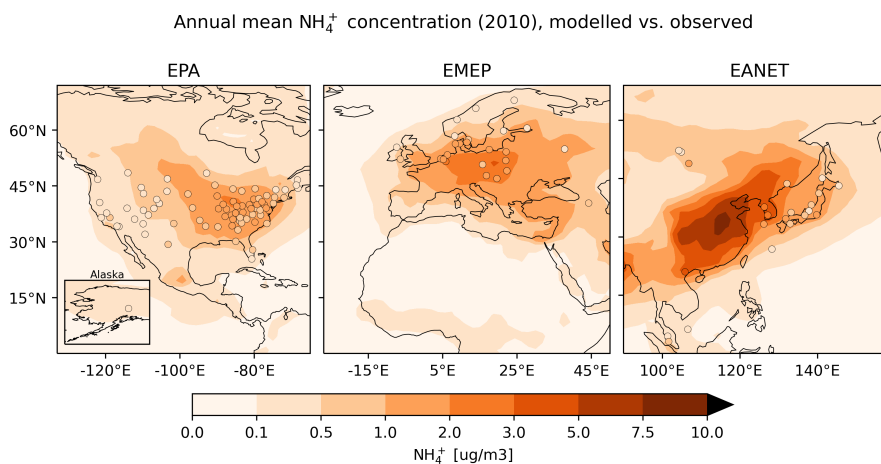
Figure 21. As in Figure 17, but for NH_4^+.

4.6.4 Dust and sea spray

510

This section provides an overview for species frequently found in dust and sea spray aerosol: sodium, calcium, magnesium, potassium and chloride. As the ocean is a large source of these water-soluble species, concentrations over the sea and coastal areas are large, as opposed to lower concentrations over the continents. Sodium, potassium, magnesium and calcium can also be found in desert dust, for instance in the Sahara, as reported by Reid et al. (2003) and Moreno et al. (2006). However, most

515 of the monitoring locations except for those in coastal areas are sampling quite remote sites far from the source regions, and thus can not be expected to display the full range of concentrations. In the following, we present the results for sodium in more detail, followed by a brief overview of the remaining species.

Sodium is represented well by the model, as averaged monthly mean concentrations from model and observations agree in general, particularly for EPA (Table 5). The mean ratio MM/OM, however, shows an average overestimation by a factor

520 of at least 2. The observational standard deviation OSTD for all regions is smaller than the RMSE, the latter being reduced compared to the results from a previous study by Pozzer et al. (2012a). For EMEP, more than 3 out of 5 simulated monthly mean values lie within a factor of 2 of the observations and more than 53% and 46% for EMEP and EANET, respectively, which is a substantial improvement compared to Pozzer et al. (2012a). The latter two networks offer again only a small number of stations. Considering the average of monthly mean concentrations separated by season, one can observe an underestimation

525 of summer concentrations for all networks (Figure 22).

As mentioned before, the regional distribution of stations does not cover those regions with high concentrations. However, including the information of all networks at once, one can observe that continental stations exhibit low annual mean concentrations, while high concentrations can be observed for instance at stations close to the coast (i.e. Japan, Florida, Denmark, Sweden), indicating that spatial features of the global sodium distribution are qualitatively captured (Figure 23).

530 Potassium, magnesium and calcium ions share spatial features with sodium in the model, exhibiting elevated values over the ocean, as well as over the Sahara and Gobi desert, and reduced concentrations over other continental areas.

The number of stations in EANET is quite low for all sea spray species which, on the one hand, allows for a few outliers to dominate mean values and errors. On the other hand, EPA offers a large number of stations, yet the correspondence of model and observations is also quite low for sea spray and dust species. Average monthly mean concentrations for magnesium are

535 represented well in the model, which is caused by a large overestimation of concentrations in winter months balancing an underestimation of summer concentrations (not shown).

Chloride concentrations are widely overestimated with respect to all three networks. The exceptionally high ratio $\overline{MM/OM}$ for EMEP is caused by two outliers with MM/OM> 1000 due to very low observed concentrations. Without these, $\overline{MM/OM}$ is better, with a value of 13.08.

540 ### 4.6.5 Organic Aerosols (OA)

Figure 25 shows the comparison of model calculated OA concentrations with measurements from the EMEP observational network over Europe, the IMPROVE network over rural North American locations, as well as short-term measurement data collected over East Asia as summarized by Jo et al. (2013). The comparison statistic is presented in Fig. 5. The model captures relatively well the monthly average concentrations of OA over these highly populated regions of the Northern Hemisphere.

545 This is rather encouraging, given the expected uncertainties of the emission inventory and the complex chemistry involved to simulate the secondary organic aerosol formation. It is worth emphasizing that the model considers the formation of SOA solely from the homogeneous gas-phase photochemical oxidation of its precursors. Therefore, the omission of other SOA formation pathways (e.g., from aqueous-phase and heterogeneous reactions) can add to the model bias. This is mostly evident during
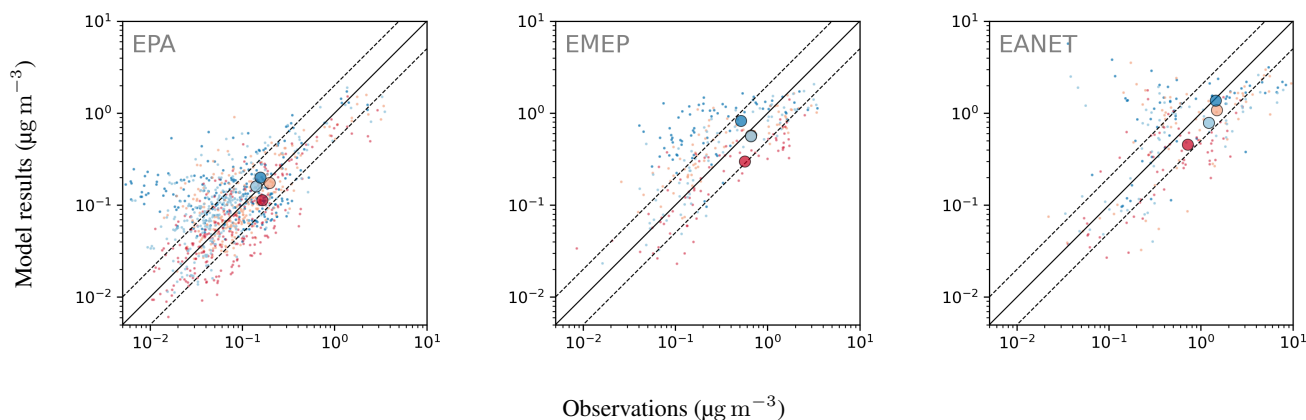
Figure 22. As in Figure 16, but for Na^+.
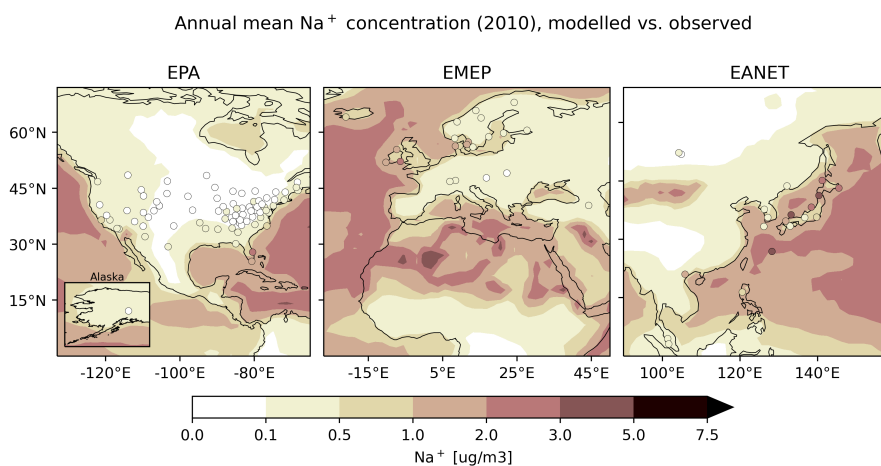
Figure 23. As in Figure 17, but for Na^+.

winter (e.g., over Europe), when the relative importance of these processes on SOA formation is increasing due to the lower

550 photochemical activity and the limited conversion of gas phase organic precursors to SOA. In addition, recent studies have provided strong evidence that the uptake of water-soluble gas-phase oxidation products (even small carbonyls like formaldehyde and acetic acid) can be the main driver of SOA pollution during haze events over Eastern Asia (Gkatzelis et al., 2020). Given the coarse resolution of the model and its inability to simulate these SOA formation pathways, the observed total OA concentrations are expected to be systematically underestimated by the model over Eastern Asia. Nevertheless, model results

555 are in general in reasonable agreement with observations with the exception of the strong underestimation over Beijing and Shijiazhuang, which brings the $\overline{MM/OM}$ to very low value (i.e. 0.51). Over Europe, the model also tends to underestimates OA, with $\overline{MM/OM}$ of 0.83 (see Tab. 5). The model performs worst during winter. Tsimpidi et al. (2016) has identified the lack
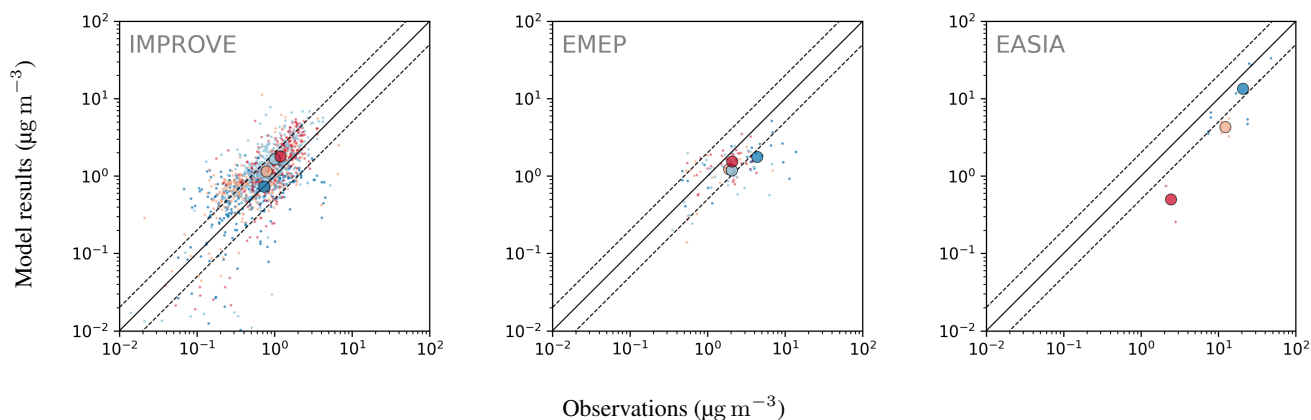
Figure 24. As in Figure 16, but for OA.

Annual mean OA concentration (2010), modelled vs. observed
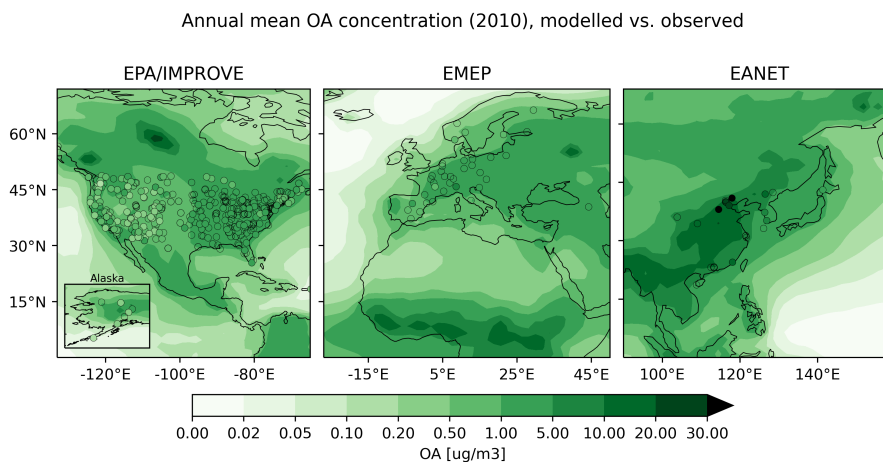
Figure 25. As in Figure 17, but for OA.

of biomass burning emissions as the main source of this discrepancy. Later, Kodros et al. (2020) and Paglione et al. (2020) have shown evidence that biomass burning also contributes significantly to SOA formation during wintertime following its

560 oxidation by the NO_3 radical in the dark. Over North America, the model tends to overestimate OA over rural areas with a $\overline{MM/OM}$ equal to 1.73. However, as shown in Fig. 24, part of this discrepancy is explained by the low values of OA over the US national parks.

Despite the agreement of the surface OA concentrations between model results and observations, the OA are strongly underestimated in the free troposphere. In Fig. 26, the model is compared with 12 field campaign measurements (Heald et al., 2011).

565 Our results show similar agreement to the one obtained by Heald et al. (2011), with the simulated values below the observed one.
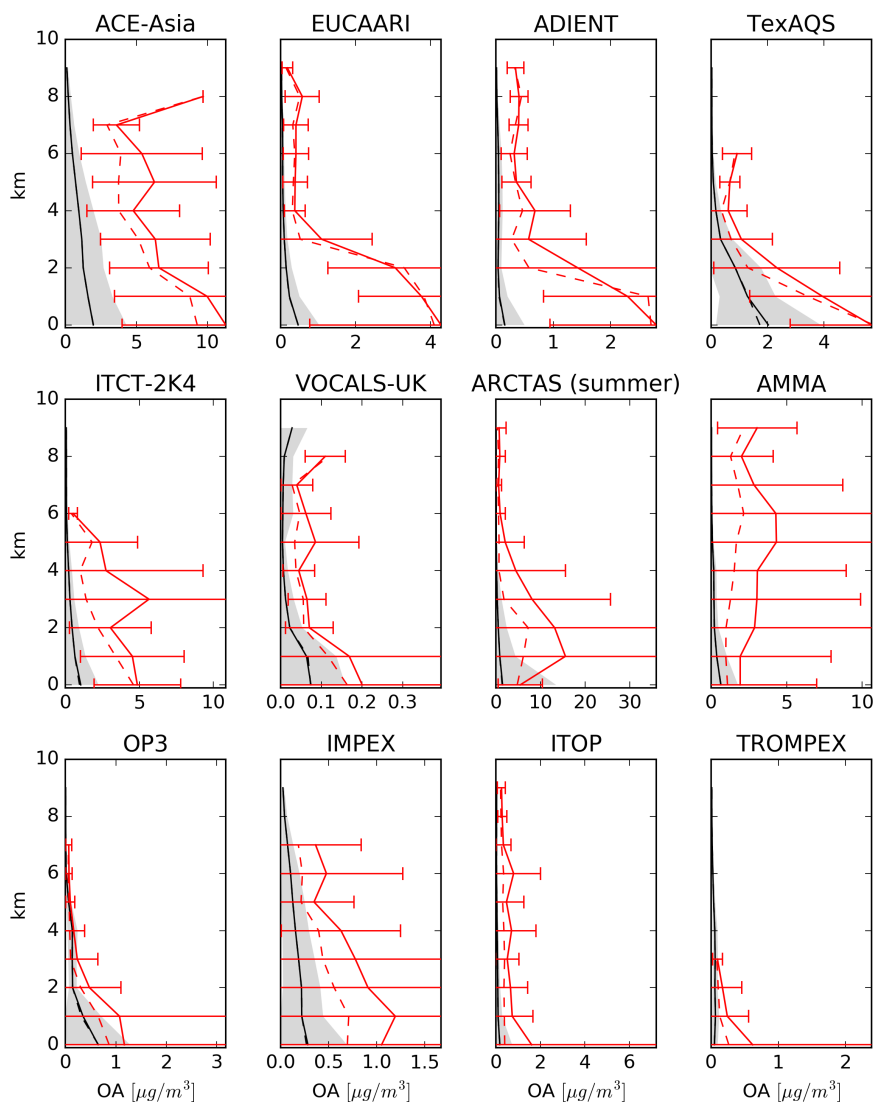
Figure 26. Model results of mean vertical profile of organic aerosol for selected field campaigns in black, and spatio-temporal standard deviation as grey area. The observed mean values are depicted in solid red, with the bars representing the standard deviation of the observations. The observed median is presented as red dashed line.

5 Conclusions

We have presented an evaluation of EMAC with a comprehensive degradation scheme for organics (MOM) in the MECCA chemistry submodel, combined with an explicit estimation of the organic tracers' condensation on aerosols with a VBS approach (ORACLE submodel). We have compared the model results with a large number of in-situ and satellite based remote

sensing observations. The evaluation focuses on carbon monoxide (CO), simple organics and aerosols, which are most influenced by the new scheme. CO is correctly reproduced compared with station measurements, with the correct north-south gradient. Nevertheless, once the model results are compared with the satellite observations from MOPITT, an overestimation of CO over the Amazon basin is apparent, especially in autumn, possibly due to an overestimation of the biomass burning emissions simulated by the model. For alkanes the comparison shows a good agreement, although an oceanic source for the butanes is missing. In contrast, the model underestimates alkenes, and especially C_3H_6, which shows large differences compared to the observations. Model results of oxygenated species show an indifferent picture when compared to observations, depending on the tracer: while methanol is well reproduced, simulated acetone shows large spatial discrepancies compared to the remotely sensed observations. In fact, for the latter, the model misses strong emissions over the boreal forests, while it predicts instead too high total columns over tropical forests (i.e., Amazonia and Central Africa). Formic and acetic acid show similar agreements to the observations, with the main tropical sources well reproduced, but with a strong underestimation elsewhere.

The aerosols at the surface are well reproduced by the model, both with respect to composition and total amount. The annually averaged simulated AODs show a very good agreement with the AERONET station observations, but with some deficiencies in the representation of the short term variability. The agreement of the fine particulate mass ($PM_{2.5}$) near the surface is also quite good, with most of the simulated values within a factor of 2 to the observations. The evaluation of the aerosol chemical composition shows a high level of agreement for near-surface sulphate and some more deviations for NH_4^+ and nitrate, which are both overestimated by the model, especially the latter (even though the observations are characterized with a high level of uncertainty). The mechanically produced primary aerosol species (dust and seasalt) show a reasonable agreement with the observations with some substantial overestimation of the simulated chloride concentrations indicating a too weak acid displacement process over the continents.

Finally, the comparison of OA shows a good agreement with station observations, while the vertical distribution of the simulated values are largely underestimated, when compared with aircraft measurements, analogously to other global atmospheric chemistry models of similar complexity, although significant improvement in this direction has been recently published (Pai et al., 2020).

6 Outlook

The presented model evaluation is useful for identifying areas for further model improvements. A few possible directions are discussed next.

Emissions have always been a critical point for simulating tropospheric chemistry. It has already shown in many studies that even anthropogenic emissions of alkanes need to be improved as severely underestimated in many inventories (e.g. Emmons et al., 2015; Tilmes et al., 2016), mostly coming from erroneous speciation of the total VOC emissions (Dalsøren et al., 2018)

Residential wood burning and/or biofuel use (e.g., for heating) that often contribute significantly to both POA and SOA formation over urban areas are strongly underestimated in the emission inventories (Tsimpidi et al., 2016; Denier Van Der Gon

et al., 2015). In addition, global models lack OA emissions from residential and commercial cooking activities that can be an
605 important source of OA (Mohr et al., 2012; Sun et al., 2011; Ge et al., 2012; Hayes et al., 2013). Underestimation of cold-start
vehicle emissions (Weilenmann et al., 2009) can also lead to significant underestimation of OA formation from the transport
sector (e.g., during wintertime).

As seen in this study, the model results underestimate selected VOCs in boreal regions. The thawing of permafrost is poten-
tially an additional emission source of organic compounds at high latitudes in the northern hemisphere (Li et al., 2020), which
610 has not been considered yet. However, an estimate with global data sets is still missing. Furthermore, the emission of VOCs
from biomass burning is likely strongly underestimated. In fact, overwintering fires in boreal forest (Scholten et al., 2021),
which smoulder through the non-fire season, are normally not detected by satellite observations and therefore are missing in
our used emissions dataset. Moreover, peat fires are not easily detected from space, but are characterized by larger emission
factors for many VOCs. They are important for simulating air composition during peat fires in Indonesia (Rosanka et al.,
615 2021c) and likely critical for resolving the model biases at high latitudes, where most of peatland is located and could be fur-
ther released by permafrost thawing. Ramo et al. (2021) also found that small undetected fires enhance the estimated amount
of emitted carbon from biomass burning in sub-Saharan Africa by 31-101% . Finally, soil temperature and soil wetness play
an important role in the estimation of the online emissions of biogenic VOCs, and it is therefore important to have a correct
simulation of the surface properties by the underlying climate model.

620 Furthermore, dry deposition is a relevant process also affecting VOCs in the lower troposphere (Khan et al., 2015). The
inclusion of the additional uptake at the plant cuticle leads to a better representation (Karl et al., 2004; Müller et al., 2018;
Emmerichs et al., 2021) and would likely reduce the overestimation of species like acetaldehyde in the Tropics, as shown here.
In the Amazon forest, the missing storage capacity of soil water leading to too high temperatures (Hagemann and Stacke, 2015)
additionally causes an underestimation of dry deposition (Emmerichs et al., 2021), while temperature-dependent processes like
625 VOC emissions are overestimated.

Another source of uncertainty is related to the scavenging efficiency of gas-phase OA precursors. The water solubility of
these oxidized organic vapors is largely unknown and is typically considered uniform for all organic compounds in modeling
studies even though they become increasingly more hydrophilic during their atmospheric lifetime (Hodzic et al., 2014; Tsimpidi
et al., 2017).

630 The extension of MOM for the oxidation of additional VOCs has the potential to reduce the negative model biases for some
oxygenated volatile organic compounds (OVOCs) and enhance the predicted OA levels. For instance, with an emission strength
of more than $40 \, \mathrm{Tg \, yr^{-1}}$, anthropogenic C_5- and higher hydrocarbons can be a significant source of OVOCs like acetaldehyde
and acetone (Pozzer et al., 2010). Further improvements are expected from an extended representation of the emission and
oxidation of known biogenic VOCs with more than 5 carbon atoms. Moreover, the emissions of aromatic compounds from
635 biogenic sources could be as large as $40 \, \mathrm{Tg \, yr^{-1}}$ (Misztal et al., 2015). So far only a small emission of toluene is considered
and a more comprehensive representation of biogenic aromatics would likely lead to further improvements.

The formation of SOA in most models relies on the reaction of its gas-phase precursors with reactive atmospheric radicals
(e.g., $\mathrm{OH, O_3, NO_3}$) and their chemical aging is usually considered by the further photo-oxidation of the semivolatile products

solely in the gas phase. However, SOA is also subject to oxidation in the aqueous phase through superficial and bulk interactions
640   with gas-phase oxidants (George and Abbatt, 2010). Therefore, fundamental processes of SOA formation in the aqueous
phase (e.g., from isoprene epoxydiols (Nguyen et al., 2009) and glyoxal (Fu et al., 2008)) are typically missing from the
conventionally used parameterizations. In addition, the uptake of small carbonyls (e.g., aldehydes and acids) to the aqueous
phase and their subsequent oxidation and oligomerization has been recently linked to significant increases of SOA mass during
pollution events (Gkatzelis et al., 2021).

645   Recently, MOM has been coupled to the detailed Jülich Aqueous-phase Mechanism of Organic Chemistry (JAMOC, Rosanka
et al., 2021a) for cloud droplets. An explicit treatment of multiphase chemistry of OVOC has already been used for assess-
ing the global role of clouds as a sink of ozone (Rosanka et al., 2021b). By comparing EMAC's prediction of total methanol
columns to IASI satellite retrievals (comparable to Sect. 4.2.3 and Fig. 6), they find that EMAC's tendency to overestimate
methanol is partially reduced by the additional cloud sink. This suggests that the missing representation of in-cloud OVOC
650   chemistry introduces a significant bias in the present study, and therefore a more detailed multi-phase chemistry should be
included for future studies. Furthermore, JAMOC is limited to the oxidation of OVOCs containing up to four carbon atoms
(Rosanka et al., 2021a), and an expansion to larger species (i.e. containing more than four carbon atoms) is thus desirable, in
order to improve the representation of these OVOCs in EMAC when using MOM. Finally, based on the results of Franco et al.
(2021), more detailed in-cloud chemistry could improve the representation of acids (such as acetic and formic acid), which is
655   clearly underestimated here where cloud chemistry is important.

Code and data availability.   The Modular Earth Submodel System (MESSy) is continuously further developed and applied by a consortium
of institutions. The usage of MESSy and access to the source code is licensed to all affiliates of institutions which are members of the MESSy
Consortium. Institutions can become a member of the MESSy Consortium by signing the MESSy Memorandum of Understanding. More
information can be found on the MESSy Consortium Website (http://www.messy-interface.org). The code presented here has been based on
660   MESSy version 2.54 and is available in the official release of version 2.55.

Author contributions.   A.P., A.P.T. and V.A.K. planned the research. A.P. designed, coded, prepared the input files and performed the model
simulation. A.P., V.K., S.G., S.F.R., B.F. S.R., T.E., D.T., H.T., V.F. and A.P.T. wrote the manuscript. D.T. developed MOM and integrated it
into MECCA. S.G. implemented extended budgeting of species turnover. A.P.T and V.A.K. modified ORACLE to accommodate the organic
tracers from the MOM chemical mechanism. M.C., D.G. and J.K. provided the emissions for the simulations. A.P., S.F.R, V.K and D.A. have
665   contributed to the evaluation. C.H. provided observational data for the comparison. P.J. and H.T. contributed to model development of the
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