Response to Comments for “Implementing marine organic aerosols into the GEOS-Chem model”

B. Gantt et al.

Note that the responses are in bold italic typeset.

D. Lunt:

In my role as Executive editor of GMD, I would like to bring to your attention our Editorial: http://www.geoscientific-model-development.net/gmd_journal_white_paper.pdf

http://www.geosci-model-dev.net/6/1233/2013/gmd-6-1233-2013.html

This highlights some requirements of papers published in GMD, which is also available on the GMD website in the ‘Manuscript Types’ section:

http://www.geoscientific-model-development.net/submission/manuscript_types.html

In particular, please note that for your paper, the following requirements have not been met in the Discussions paper – please correct this in your revised submission to GMD. -“The paper must be accompanied by the code, or means of accessing the code, for the purpose of peer-review. If the code is normally distributed in a way which could compromise the anonymity of the referees, then the code must be made available to the editor. The referee/editor is not required to review the code in any way, but they may do so if they so wish. -“All papers must include a section at the end of the paper entitled "Code availability". In this section, instructions for obtaining the code (e.g. from a supplement, or from a website) should be included; alternatively, contact information should be given where the code can be obtained on request, or the reasons why the code is not available should be clearly stated. ”

We appreciate the reminder for the “Code availability” section, and have added the following to the updated manuscript: “The updated code (GEOS-Chem Fortran and chlorophyll-a NetCDF files) is available upon request. Please contact Matthew S. Johnson at matthew.s.johnson@nasa.gov or https://earthscience.arc.nasa.gov/person/Matthew_S_Johnson for more information.”

Response to Comments for "Implementing marine organic aerosols into the GEOS-Chem model"

B. Gantt et al.

Note that the responses are in bold italic typeset.

Anonymous Referee #1

Gantt et al. have implemented marine organic aerosol (MOA) primary emissions into GEOS-Chem and have used the model to look at MOA concentrations and aging. The article is very well written and clear. This is one of several MOA modeling studies from Gantt and co-authors. I do slightly wonder how much value there is in having this paper in the literature, since Gantt has already implemented MOA emissions into another model (and in GEOS-Chem itself), as have several other groups. However, I think they have presented enough new material, especially the comparisons to recent MOA-specific mass concentration observations and insights into MOA aging, to warrant publication in GMD subject to minor revisions.

Specific comments:

P5968, Line 3-4: Also cite Arnold et al. (2009) here about the SOA/POA contribution to marine organic aerosol?

This has been added to the updated manuscript.

P5969, Line 29: So the main model development step here was just bringing the online MOA emissions into the GEOS-Chem standard code? What exactly did this entail? Is it any different than the previous Gantt implementation into GEOS-Chem?

We appreciate the reviewer's question, and would like to clarify the differences between this effort and that of Gantt et al. (2012). In Gantt et al. (2012), GEOS-Chem was used as a tool to evaluate several different marine POA emission parameterizations with consistent meteorology and chlorophyll-a concentrations. More than 20 tracers were added to GEOS-Chem in Gantt et al. (2012) to enable the comparison, and model inputs such as chlorophyll-a concentrations were in a format (ASCII table requiring the model to be recompiled for every simulation month) that would be difficult for a typical GEOS-Chem modeler to use. This effort uses the top-down approach from Gantt et al. (2012) (which compared most favorably to the observed weekly and monthly mean values of marine organic aerosol from marine sites at Mace Head, Ireland and Amsterdam Island) and implemented the online POA emissions and two MOA tracers in a way easily adaptable for any GEOS-Chem user. In addition to the MOA-specific mass concentration observational comparison and insights into MOA aging, this effort expands upon Gantt et al. (2012) by employing a nested simulation to illustrate the coastal-to-inland concentration gradients. We don't feel that this level of detail is needed for most readers, but have edited the following discussion in the updated manuscript to better highlight these differences: "The overall objective of this study was to expand upon Gantt et al. (2012) by implementing an online marine POA emission parameterization into the current version of GEOS-Chem (v9-02) that can be easily used in the default setting with the following characteristics: 1) adds minimal computational expense, 2) capable of being used for all

GEOS-Chem model domains/simulation periods, and 3) treated with unique tracers capable of explicit atmospheric aging and tracking. During this study the emission parameterization is tested for the global and nested regional model domains and evaluated with new datasets having advanced MOA chemical characterization and widespread global coverage. Finally, the model is used to predict global surface concentrations, ocean-land concentration gradients, and relative contributions of nascent (freshly emitted) and aged marine organic aerosols."

P5973, 1st paragraph, and Fig 1: The concentrations of MOA seem to be larger in the Northern Hemisphere summer (JJA) than the Southern Hemisphere summer (DJF). Of course, this is also the case for the emissions in Fig S1. Why is this exactly? One might expect stronger wind speed in the SH summer months (DJF).

We agree with the reviewer that the summertime differences between the Northern and Southern Hemisphere are somewhat counter-intuitive because of the differential wind speed (and sea spray emission rates). The marine POA emissions (and resulting concentrations) are a function of the sea spray emission rates and OM_{SSA}***. The sea spray emission rates are a function of the 10 meter wind speed and to a lesser degree sea surface temperatures and are higher over the Southern Hemisphere summer. The*** OM_{SSA}***, however, is positively related to chlorophyll-a concentrations and negatively related to 10 meter wind speed using a logistic curve for both relationships. The results shown in Figure 1 and S1 suggests that the higher*** OM_{SSA} ***in the Northern Hemisphere summer has a bigger impact on the emissions and surface concentrations than does the higher sea spray emission rates in the Southern Hemisphere summer. The updated manuscript includes the following discussion: "The summertime MOA concentrations and marine POA emissions predicted by GEOS-Chem were higher in the Northern Hemisphere than in the Southern Hemisphere (see Figures 1 and S1) despite having lower SSA emissions; this was related to the higher*** OM_{SSA} ***in the Northern Hemisphere which is positively related to [chl a] and negatively related to*** U_{10} ***using a logistic curve for both relationships."***

P5975 Line 8: Mention that this is submicron sea salt only.

This has been added to the updated manuscript.

Response to Comments for “Implementing marine organic aerosols into the GEOS-Chem model”

B. Gantt et al.

Note that the responses are in bold italic typeset.

Anonymous Referee #2

Heartfelt apologies for how long it took me to submit this review, especially given how clear and straightforward the paper is. It is within the scope of ACP (GMD), makes a contribution to the field which is of scientific significance, and should be published in ACP (GMD) with only technical corrections.

The sentence starting with “Sea-salt aerosols...” on line 4 of page 5971 should be split into two sentences. In the preceding sentence (“Although marine...”), it might be nice to provide a maximum-minimum range of the different emissions inventories.

The specified sentence has been changed in the updated manuscript, and the emissions estimates have been added.

On line 2 of page 5975, Frankfurt does not have the English/German spelling.

This has been corrected in the updated manuscript.

On page 5976, the words “determined” (line 20) and “particular” (lines 24-25) should perhaps be reconsidered.

The updated manuscript has been changed for clarity and now reads: “During baseline simulations when only terrestrial organic aerosol emissions were included (black circles on Figure 3), GEOS-Chem exhibited a strong model underprediction (normalized mean bias = -79%) and poor correlation (0.16) when compared to observations.” The sentence with “particular” has been removed entirely due to the additional discussion of the seasonal and latitude evaluation.

Please include the R-value and mean bias in the caption for Figure 2.

The R-value of 0.62 and mean bias of -120 ng m^{-3} have been added to the figure caption in the updated manuscript.

I am aware that my comments as a referee have been minor and largely linguistic; however, whenever I made a note on the scientific content, I found that it was addressed elsewhere in the paper. This may be related to Anonymous Referee #1’s statement that Gantt and co-authors have published previously on this subject, but as they note, this paper contains new material in the comparison with observations and the insights to MOA aging.

We appreciate the reviewer’s comment and would refer him/her to comment #2 to Anonymous Referee #1.

Response to Comments for “Implementing marine organic aerosols into the GEOS-Chem model”

B. Gantt et al.

Note that the responses are in bold italic typeset.

Anonymous Referee #3

General comments

This paper presents the implementation of an on-line parameterization of marine primary organic aerosol (POA) into the GEOS-Chem model. The authors have then evaluated the surface concentrations of marine OA (MOA) in comparison to the observational data, and showed some outputs regarding atmospheric aging of MOA. They have also provided some candidates for future field studies on marine OA. The present work may provide valuable information on our understanding of the processes of marine POA. The manuscript fits with the scientific scope of GMD. Although the result presented here is valuable, the authors should provide some more explanations that need to be clarified. I recommend its publication in GMD after some revisions raised below.

Specific comments

(1) I understand that the major focus of this paper is on marine POA, for which the evaluation should be made. However, why was the evaluation made using the observational data obtained at an inland site near Paris in Figure 2? The site might be affected by some other sources such as terrestrial biogenic/anthropogenic sources, which might relate to more complicated processes for OA. The evaluation of the model output with observational data at “clean marine” sites should be more straightforward. The authors should clarify the logic or reasons why they have compared the MOA from the model with OA observed at the terrestrial site.

We acknowledge the reviewer’s concern of evaluating a marine emission source with observations from an inland site, but have included this evaluation because of its uniqueness. The marine-sourced biogenic PMF factor from the HR-ToF-AMS is able to differentiate organic aerosol sources in a way that eliminates terrestrial biogenic/anthropogenic sources from the analysis. This allows for the evaluation of the marine signal after it is transported and deposited from ocean to the Paris site. Along with evaluation of the surface concentrations at clean marine sites, these inland observations provide a more rigorous evaluation of the modelled concentrations in a variety of environments. We have added the following discussion to the updated manuscript: “The high temporally-resolved MOA concentrations derived from HR-ToF-AMS measurements in Paris allowed for an evaluation of model-predicted MOA with two unique characteristics: the observations are 1) at the same hourly time scale of the model output and 2) at an inland site without the influence of terrestrial and anthropogenic sources.”

(2) What is the definition of “MOA” used in this study (or used for the GEOS-Chem)? The definition of MOA might be different from that used in Crippa et al. (2013a). Please clarify this.

The definition of MOA in GEOS-Chem is marine-sourced organic aerosol associated with the organic portion of sea spray aerosol. This definition is different from that of Crippa et al. (2013a) which is the portion of organic aerosol associated with high levels of organic sulfur species formed from marine emissions. The following discussion has been added to the updated manuscript: "In the days immediately following this period (10-11 July), the measured MOA remained high while GEOS-Chem predicted a rapid decrease in concentrations; this discrepancy may be due in part to the different definitions of MOA in GEOS-Chem and Crippa et al. (2013a). The HR-ToF-AMS measurements from Crippa et al. (2013a) do not differentiate between primary and secondary sources of MOA and the current version of GEOS-Chem does not include SOA production from marine-source precursor species. Therefore considerable discrepancies between measurements and model predictions are expected when SOA of marine origin contributes a sizable fraction of MOA mass."

(3) Figure 3: More details on the data sets should be presented without just refereeing Gantt and Meskhidze (2013). Please at least provide locations and time scales for each data used for the comparison with some related references. In addition, what is the definition of "clean marine conditions?"

In the updated manuscript, Figure 3 has been adjusted to include the seasonality and latitudinal zone of the observations and the following discussion has been added to the text: "The seasonal plots in Figure 3 indicate that the reduction in model underprediction at these sites occurred throughout the year. Previous studies showed (see Figure 3 and Figure 1 from Gantt and Meskhidze (2013)) that without the inclusion of MOA emissions, the largest model underpredictions of clean marine organic aerosol (defined as aerosol that contained black carbon concentrations < 0.05 µg m^{-3}) concentrations occurred at remote sites in the Southern Ocean and tropical Pacific."

(4) P.5976, L22-26, "Unlike the direct . . .": I cannot understand the meaning of this sentence.

This statement has been removed in the updated manuscript and replaced with discussion of seasonal and latitude-specific model evaluation given above in response to comment #3.

(5) Figure 5: What are important factors controlling the temporal and spatial distributions of the fractions of marine POA aging? The authors should discuss more on this point.

We have added the following discussion to the updated manuscript: "For all locations, aging of MOA was based on the e-folding time of 1.15 days; therefore, the temporal and spatial distributions of MOA aging were only controlled by the emissions and transport. Regions with high concentrations of low-aged MOA typically occurred over high ocean productivity regions, while high concentrations of aged MOA were predicted over oligotrophic oceanic regions and inland locations."

Implementing marine organic aerosols into the GEOS-Chem model

B. Gantt[1,4], M. S. Johnson[2], M. Crippa[3,5], A. S. H. Prévôt[3], and N. Meskhidze[1]

[1]{Department of Marine, Earth, and Atmospheric Sciences, North Carolina State University, Raleigh, NC, USA}

[2]{Earth ~~Sciences Branch~~Science Division, NASA Ames Research Center, Moffett Field, CA, USA}

[3]{Laboratory of Atmospheric Chemistry, Paul Scherrer Institute, Villigen, Switzerland}

[4]{Now at National Exposure Research Laboratory, Office of Research and Development, US Environmental Protection Agency, Research Triangle Park, NC, USA}

[5]{Now at: European Commission, Joint Research Centre, Institute for Environment and Sustainability, Air and Climate Unit, Ispra, Italy}

Correspondence to B. Gantt (bdgantt@gmail.com)

Abstract

Marine-sourced organic aerosols (MOA) have been shown to play an important role in tropospheric chemistry by impacting surface mass, cloud condensation nuclei, and ice nuclei concentrations over remote marine and coastal regions. In this work, an online marine primary organic aerosol emission parameterization, designed to be used for both global and regional models, was implemented into the GEOS-Chem model. The implemented emission scheme improved the large underprediction of organic aerosol concentrations in clean marine regions (normalized mean bias decreases from -79% when using the default settings to -12% when marine organic aerosols are added). Model predictions were also in good agreement (correlation coefficient of 0.62 and normalized mean bias of -36%) with hourly surface concentrations of MOA observed during the summertime at an inland site near Paris, France. Our study shows that MOA have weaker coastal-to-inland concentration gradients than sea-salt aerosols, leading to several inland European cities having > 10% of their surface submicron organic aerosol mass concentration with a marine source. The addition of MOA tracers to GEOS-Chem enabled us to identify the regions with large contributions of freshly-emitted or

aged aerosol having distinct physicochemical properties, potentially indicating optimal locations for future field studies.

1 Introduction

With the decrease in anthropogenic emissions of particulate matter in many industrialized countries, an increased emphasis has been placed on understanding the inventory of natural aerosol sources (Zare et al., 2014). Natural aerosols also have an important climatic impact, as long term changes in emissions and the feedbacks on meteorology can lead to a global mean radiative perturbation approaching 1 W m^{-2} (Carslaw et al., 2010). Marine-sourced organic aerosols (MOA), which have been observed at concentrations > 1.0 µg m^{-3} (Ovadnevaite et al., 2011) and whose estimated global emissions are comparable to that of fossil fuel burning (Spracklen et al., 2008), are one type of natural aerosol with air quality and climate significance (Gantt and Meskhidze, 2013). For instance, MOA ~~have been shown to~~ affect the surface mass, cloud condensation nuclei, and ice nuclei concentrations in clean marine regions (O'Dowd et al., 2004; Meskhidze et al., 2011; Westervelt et al., 2012; Burrows et al., 2013; Partanen et al., 2014). Uncertainty in the chemical composition of sea spray aerosol (SSA) has also been shown to play an important role in determining their climate impact (Tsigaridis et al., 2013). Therefore, it is important for chemical transport and climate models to take MOA emissions and physicochemical processes into consideration.

With instrumentation such as the high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS), source profiles of ambient organic aerosols can be derived using positive matrix factorization (PMF) ~~technique~~techniques (Lanz et al., 2007; Zhang et al., 2011). Chang et al. (2011) ~~derived~~derives a marine-sourced biogenic PMF factor based on high levels of organic sulfur species observed at several coastal locations affected by marine air masses. Applying HR-ToF-AMS/PMF analysis similar to Chang et al. (2011) to chemically-identify MOA, Crippa et al. (2013a) ~~found~~finds that on average 16% of the total summertime organic aerosol mass ~20 km SW of Paris had a marine source despite being > 150 km from the English Channel and Atlantic Ocean. Concurrent summertime HR-ToF-AMS measurements in the core of the Paris metropolitan area reported by Crippa et al. (2013b) ~~indicated~~indicate that 13% of the total OA had a marine source. Other studies have identified similar MOA-specific HR-ToF-AMS mass spectra in other locations (Ovadnevaite et al, 2011; Schmale et al., 2013) to better understand its sources. Unlike typical organic aerosol observations, these HR-ToF-AMS

Formatted: Header

Formatted: Header

spectra allow for the model evaluation of marine organic aerosol concentrations separate from the surrounding terrestrial/anthropogenic emissions. Although some mathematical mixing between sources cannot be excluded in the HR-ToF-AMS/PMF analysis, Crippa et al. (2013b) obtained similar MOA mass concentrations and percentage contributions when HR-ToF-AMS measurements were combined with that of a high sensitivity proton transfer reaction mass spectrometer (HS-PTR-MS).

Although secondary organic aerosol (SOA) precursors can have a marine source (Shaw et al., 2010), marine primary organic aerosols (POA) have been shown to be the major contributor to organic aerosol mass concentrations over marine regions (Arnold et al., 2009; Gantt and Meskhidze, 2013). The observation of clean marine organic aerosol surface concentrations having the same seasonal cycle as that of surface chlorophyll-*a* concentrations ([chl *a*]) (Cavalli et al., 2004; Sciare et al., 2009) led to the development of marine POA emission parameterizations based on a [chl *a*]-derived organic mass fraction of SSA (OM_{SSA}) (O’Dowd et al, 2008; Vignati et al., 2010). Gantt et al. (2012) ~~compared~~compares several marine POA emission schemes in a global model, finding that the schemes with a strong dependence on [chl *a*] had concentrations most similar to seasonal observations. However, the use of [chl *a*] as a proxy for OM_{SSA} has come into question by several laboratory- and field-based studies showing that oceanic organic carbon concentration might be more closely related to organic enrichment of SSA (Prather et al., 2013; Quinn et al., 2014). Burrows et al. (2014) ~~modelled~~models the organic enrichment of SSA using several classes of organic compounds from a biogeochemical ocean model, finding that OM_{SSA} is related to [chl *a*] only in certain regions. Rinaldi et al. (2013) ~~found~~finds that [chl *a*] was more highly correlated with OM_{SSA} than oceanic organic carbon, but suggested an 8-day time lag to account for biological processes responsible for the production of transferable organic materials during the phytoplankton bloom evolution. Recent field studies have suggested that other physical/biological processes affecting sea spray aerosol production may also be missing in current emission parameterizations, such as the diurnal variability in sea spray aerosol generated from biologically productive waters (Long et al., 2014). Like most global estimates of marine POA emissions, we use satellite-derived [chl *a*] as a proxy for OM_{SSA} due to the lack of consensus of factors driving organic enrichment of sea spray aerosol, strong correlations observed between organic aerosol concentrations and [chl *a*] in clean marine environments, and scarcity of global oceanic datasets for use in chemical transport models.

Formatted: Header

In addition to emissions, the physicochemical treatment of terrestrial and marine organic aerosols in the atmosphere affects their predicted concentrations. A summary of past modeling studies showed that the aging of marine and terrestrial organic aerosols (calculated either by e-folding times, microphysics, or oxidant/sulfate concentrations) is highly variable spatially and temporally with global averages ranging from ~1 to 5 days (Huang et al., 2013). Spracklen et al. (2008) ~~found~~finds that doubling the marine organic aerosol e-folding time for conversion from hydrophobic to hydrophilic in GEOS-Chem (thus decreasing the aerosol aging process) from 1.2 to 2.4 days increased surface MOA concentrations by ~15% globally due to decreased in-cloud scavenging. Westervelt et al. (2012), on the other hand, did not predict significant differences in surface concentrations after changing the aging timescale of marine organic aerosols from 1.5 to 4.5 days in the GISS II-prime model. Huang et al. (2013) found that several detailed aging schemes (including oxidant and condensation-coagulation aging) for terrestrial carbonaceous aerosols in GEOS-Chem led to a variable hydrophobic to hydrophilic conversion lifetime, ranging from < 1 to 8+ days. Modeling studies have typically treated the chemistry and physics of marine organic aerosols within the atmosphere like that of terrestrial organic aerosols due to the lack of understanding of marine boundary layer aerosol processes (Meskhidze et al., 2013).

In this study, we ~~use~~used the GEOS-Chem model to quantify the contribution of ~~marine POA~~organics associated with submicron SSA emissions to ~~the~~ global ~~surface organic aerosol mass concentration~~MOA concentrations. GEOS-Chem is a global chemical transport model widely used for simulating aerosol and gas emission processes, atmospheric chemistry, regional and global scale pollution transport, and for providing boundary conditions to regional chemical transport models (CTMs). Global emissions estimates of marine POA and inter-comparison of multiple emission parameterizations has been previously performed using older versions of GEOS-Chem (Spracklen et al., 2008; Lapina et al., 2011; Gantt et al., 2012); these studies had variable success replicating the observed surface organic aerosol concentrations in clean marine environments. Nevertheless, analysis of model results indicates that addition of marine primary organic source brought model results closer to observations. Despite these previous studies, the current version of the GEOS-Chem model does not include online marine POA emissions or MOA tracers in the default settings. The overall objective of this study ~~is~~was to ~~implement~~expand upon Gantt et al. (2012) by implementing an online marine POA emission parameterization into the current version of GEOS-Chem (v9-02) that can be easily used in the default setting with the following characteristics: 1) adds minimal computational expense, 2) capable of being used for all GEOS-Chem model domains/simulation periods, and 3) treated with unique tracers capable of explicit atmospheric aging and tracking. During this study the emission parameterization is tested for the global and nested regional model domains and evaluated with new datasets having advanced ~~organic~~MOA chemical characterization and widespread global coverage. Finally, the model is used to predict global surface concentrations, ocean-land concentration gradients, and relative contributions of nascent (freshly emitted) and aged marine organic aerosols.

Formatted: Header

2 Model ~~Configuration~~configuration

2.1 GEOS-Chem

We ~~use~~used v9-02 of the global CTM GEOS-Chem (http://geos-chem.org/) with 2° × 2.5° (latitude – longitude) horizontal resolution and 47 vertical hybrid sigma-pressure levels, driven by Goddard Earth Observing System (GEOS)-5 assimilated meteorology from the NASA Global Modeling Assimilation Office (GMAO). The model ~~is~~was run with a full chemistry configuration, which includes H_2SO_4-HNO_3-NH_3 aerosol thermodynamics (ISORROPIA II) coupled to an O_3-NO_x-hydrocarbon-aerosol chemical mechanism (Bey et al., 2001; Park et al., 2004; Fountoukis and Nenes, 2007). Terrestrial emissions of carbonaceous aerosols ~~are~~were based on Bond et al. (2007) (biofuel and fossil fuel) and daily wildfire emissions from version 3 of the Global Fire Data (GFED3) database (van der Werf et al., 2010). Secondary organic aerosol formation ~~is~~was included in our simulations based on Pye et al. (2010). Although marine-source SOA have been shown to contribute to the organic aerosol mass concentration in some regions (Decesari et al, 2011; Fu et al., 2013; Hu et al., 2013), we ~~do~~did not consider oceanic emissions of SOA precursors because they have uncertain global emission inventories ranging from 0.32-11.6 Tg C yr^{-1} for isoprene and 0.013- 29.5 Tg C yr^{-1} for α-pinene (Sinreich et al., 2010; Luo and Yu, 2010; Miyazaki et al., 2014~~),~~). Furthermore, marine-source SOA formation mechanisms ~~that~~ are not well known (Bikkina et al., 2014~~),~~) and when modelled have been estimated to contribute less than primary sources to the organic aerosol budget in many marine regions (Arnold et al., 2009; Fu et al., 2013). Sea-salt aerosols in the model ~~are~~were emitted in two size bins (fine mode ranging from 0.02 to 1.0 µm in diameter and coarse mode ranging from 1.0 to 16.0 µm in diameter) as a function of a power relationship with 10 meter winds speeds (U_{10}) following the formulation of Gong (2003) and includes the 3rd order polynomial dependence on sea surface temperature (SST) as described by Jaeglé et al. (2011). Within this model setup, we ~~introduce~~introduced a hydrophilic and hydrophobic tracer for

Formatted: Subscript

Formatted: Subscript

Formatted: Subscript

Formatted: Subscript

Formatted: Subscript

Formatted: Subscript

Formatted: Header

marine POA. The differences between the hydrophilic and hydrophobic tracers ~~involve~~involved depositional processes: scavenging in convective updrafts and rainout only occurs for hydrophilic tracers (Liu et al., 2001). Dry deposition in the model ~~is~~was based on the resistance-in-series scheme described in Wesely (1989), with the surface resistances for aerosols following the work of Zhang et al. (2001). A detailed description of the various marine POA emission schemes and model treatment of the marine POA tracers is given in Sect. 2.2. A year-long GEOS-Chem simulation for 2009 ~~is~~was performed for the global domain, with a nested simulation of the European domain (0.5° × 0.67°) performed for July 2009 in order to show ocean-continental concentration gradients and compare with novel measurements of marine organic aerosol collected near Paris, France. 3-hr dynamic boundary conditions for the nested model run ~~are~~were prescribed from the global GEOS-Chem simulation.

2.2 Marine POA ~~Emission~~emission

Submicron marine POA emissions implemented into GEOS-Chem ~~are~~were based on the top-down parameterization developed by Gantt et al. (2012), which compared several marine POA emission schemes using an older version of GEOS-Chem (v8-01-01). The top-down parameterization from Gantt et al. (2012) updated the Gantt et al. (2011) emission scheme by: 1) increasing the OM_{SSA} dependence on [chl *a*] and U_{10} to strengthen the correlation between model-predicted and observed organic aerosol surface concentrations at Mace Head, Ireland and Amsterdam Island over several years, and 2) scaling the total marine POA mass emission rate (E_{POA}) to minimize the bias of GEOS-Chem-predicted surface concentrations with seasonal observations at Mace Head and Amsterdam Island. In addition to improving the prediction of seasonal observations, we ~~use~~used the Gantt et al. (2012) top-down parameterization because it ~~yielded~~yields better predictions of both monthly and seasonal concentrations of organic aerosol over coastal regions, and hourly surface concentrations during a MOA plume event (Ovadnevaite et al., 2011). The Gantt et al. (2012) top-down emission parameterization ~~was~~is given as follows:

$$OM_{SSA}(\mathrm{chl}\ a, U_{10}, D_p) = \frac{\left(\frac{1}{1+\exp(3(-2.63[\mathrm{chl}\ a])+3(0.18(U_{10}))}\right)}{1+0.03\exp(6.81D_p)} + \frac{0.03}{1+\exp(3(-2.63[\mathrm{chl}\ a])+3(0.18(U_{10}))} \qquad (1)$$

$$E_{POA}(\mathrm{chl}\ a, U_{10}, D_p) = 6\times V_{SSA}\times OM_{SSA}\times\rho_{SSA} \qquad (2)$$

where D_p is the sea spray particle dry diameter (μm), V_{SSA} is the volume emissions (cm^3 m^{-2} s^{-1}) of sea spray aerosol according to the Gong et al. (2003) source function with SST dependence of Jaeglé et al. (2011), ρ_{SSA} is the apparent density (g cm^{-3}) of the sea spray aerosol calculated as a function of the organic and sea-salt mass fractions, E_{POA} has units of molecules cm^{-2} s^{-1} after conversion from g m^{-2} s^{-1} using a molecular weight of carbon, and [chl *a*] and U_{10} have units of mg m^{-3} and m s^{-1}, respectively.

The daily-average [chl *a*] used in this study to calculate marine POA emissions in GEOS-Chem ~~is~~was from temporally-interpolated, monthly-average MODIS/Aqua-derived [chl *a*] at 1/12° horizontal resolution that is spatially-averaged online to fit the global and European domains. Although the year 2009 was simulated for this study due to the availability of inland marine organic aerosol measurements (Crippa et al., 2013a), model-ready MODIS/Aqua [chl *a*] inputs were generated for 2005-2011 and can easily be expanded to include additional years/satellite datasets. Similar to terrestrial primary organic aerosols in GEOS-Chem, marine POA ~~are~~were emitted as hydrophobic and converted to hydrophilic in the atmosphere with an e-folding time of 1.15 days (Cooke et al., 1999). This ~~is~~was consistent with the observation that freshly-emitted submicron marine primary organic aerosols are water insoluble colloids and aggregates (Facchini et al., 2008; Collins et al., 2013) but can become more water soluble through atmospheric aging (Rinaldi et al., 2010; Decesari et al., 2011). Marine POA ~~is~~was emitted as an external mixture with sea-salt aerosols based on evidence that organics exist separately from sea-salt in aerosols below 200 nm in diameter (Bigg and Leck, 2008; Prather et al., 2013), although the implementation of MOA tracers allows for future changes in the chemical treatment.

3 Results

3.1 Seasonal ~~Concentrations~~concentrations

Figure 1 shows surface averaged (~100 meters above ground level) MOA mass concentrations (left column) and the contribution of marine-source organic aerosol to total (terrestrial + marine) submicron organic aerosol surface mass (right column) predicted by GEOS-Chem. ~~Simulations show that vast~~Vast regions of the Northern Atlantic, Northern Pacific, and Southern Oceans ~~have~~had summertime concentrations (up to 1000 ng m^{-3}) up to a factor a 5 higher than the wintertime concentrations (< 200 ng m^{-3}) due primarily to the increase in emissions (see Figure S1) associated with the seasonal cycle of [chl *a*]. This strong seasonal

Formatted: Header

Formatted: Header

cycle of organic aerosol concentrations ~~is~~was consistent with long-term observations at several mid-latitude coastal locations (Cavalli et al., 2004; Spracklen et al., 2008; Sciare et al., 2009) having summertime organic aerosol concentrations a factor of 2 to 5 higher compared to wintertime. Similarly, the MOA factor observed in Paris in the summertime by Crippa et al. (2013a,b) was not detected in the wintertime (Crippa et al., 2013b,c) because the contribution to total OA was below the detection limit of ~ 20 ng m^{-3} (DeCarlo et al., 2006). ~~According to Figure 1, equatorial oceanic regions reveal~~The summertime MOA concentrations and marine POA emissions predicted by GEOS-Chem were higher in the Northern Hemisphere than in the Southern Hemisphere (see Figures 1 and S1) despite having lower SSA emissions; this was related to the higher OM$_{SSA}$ in the Northern Hemisphere which is positively related to [chl *a*] and negatively related to U$_{10}$ using a logistic curve for both relationships. According to Figure 1, equatorial oceanic regions revealed little seasonal variation in marine organic aerosol concentrations, with low concentrations over oligotrophic oceans and high concentrations over productive coastal regions throughout the year. Inland regions far from the ocean ~~have~~had very low MOA concentrations (< 50 ng m^{-3}) throughout the year, while coastal areas typically have concentrations up to 200 ng m^{-3}.

Figure 1 (right column) shows that marine-source organic aerosols typically ~~contribute~~contributed > 80% of the total (terrestrial + marine) submicron organic aerosol burden over remote oceanic regions such as the Southern Ocean and Equatorial Pacific for much of the year. In coastal regions downwind of terrestrial aerosol sources, the ratio of marine-source to total submicron organic aerosols (F$_{MOA}$) ~~is~~was much lower (< 40%) than remote marine regions. Figure 1 also shows that the seasonal cycle of F$_{MOA}$ for many inland and coastal regions (i.e., Arctic Ocean coastline, European continent) ~~is~~was different from that of surface concentrations (left column) because of the strong seasonal cycle of terrestrial organic aerosol concentrations from biomass burning and SOA formation. Compared to a previously-published map of F$_{MOA}$ from the TM4-ECPL model (see Figure 4c in Myriokefalitakis et al., 2010), GEOS-Chem ~~predicts~~predicted higher values (up to 20% vs. < 5%) widespread over terrestrial regions. Similarly, GEOS-Chem ~~predicts~~predicted higher F$_{MOA}$ than Myriokefalitakis et al. (2010) over most remote oceanic regions (> 60% vs. 10-50%). These discrepancies ~~are~~were likely caused by a number of differences including marine POA emission schemes (Gantt et al. (2012) vs. Vignati et al. (2010)), SOA formation mechanisms, atmospheric aging schemes of hydrophobic POA, and the inclusion of supermicron terrestrial organic aerosols in F$_{MOA}$ by Myriokefalitakis et al. (2010).

Formatted: Header

The nested GEOS-Chem simulation in this study ~~highlights~~illustrated the MOA concentration gradient from coastal to inland regions. Figure 2a shows a sharp concentration gradient over Europe, decreasing from 1000 to 200 ng m^{-3} within ~250 km of the northern Atlantic Ocean coastline. Three major cities roughly 25, 200, and 370 km from the coast, Amsterdam, Dusseldorf, and Frankfurt, ~~have~~had monthly-average surface concentrations of marine organic aerosol decreasing exponentially from 670 to 280 to 180 ng m^{-3} for July 2009, respectively (see Figure 2). For these three cities, the modelled F$_{MOA}$ ~~decreases~~decreased from 37 to 12 to 8%, respectively. Although Dusseldorf and ~~Frankfort have~~Frankfurt had significantly lower F$_{MOA}$ than Amsterdam, these inland cities still ~~have~~had ~10% of their submicron organic aerosol mass contributed by a marine source. GEOS-Chem ~~predicts~~predicted that of the ten largest cities in Europe, three (Istanbul, London, and Madrid) have marine-source organic aerosols making up > 10% of the total (terrestrial + marine) surface organic aerosol concentration. The coastal gradient of marine organic aerosol concentrations ~~is~~was not as sharp as that of submicron sea-salt aerosol (see Figure S2) due to the poor in-cloud scavenging of hydrophobic nascent marine organic aerosol. Relatively weak concentration gradients between the ocean and land over the western coast of Ireland ~~suggest~~suggested that measurements at Mace Head, Ireland are likely to be characteristic of the open ocean (Rinaldi et al., 2009~~; O'Dowd et al., 2013).~~). The sharpest marine organic aerosol concentration gradients in Figure 2a ~~occur~~occurred in mountainous regions of Norway due to the steep terrain.

3.2 Comparison with ~~Surface Observations~~surface observations

The time series in Figure 2b shows a comparison of hourly marine organic aerosol surface concentrations near Paris, France during July 2009 from the observations made by Crippa et al. (2013a) and GEOS-Chem predictions. ~~High~~The high temporally-~~ and chemically~~ resolved MOA concentrations derived from HR-ToF-AMS measurements ~~from the HR-ToF-AMS allow~~in Paris allowed for ~~the~~an evaluation of ~~the~~ model-predicted MOA ~~concentrations on an~~ with two unique characteristics: the observations are 1) at the same hourly time scale~~.~~ of the model output and 2) at an inland site without the influence of terrestrial and anthropogenic sources. Figure 2b shows that with a few exceptions, GEOS-Chem ~~is~~was able to capture both the magnitude and temporal variability of marine organic aerosol concentrations (correlation coefficient = 0.62 and normalized mean bias = -36%). The period of highest observed and GEOS-Chem predicted MOA concentrations (6-9 July) also had low black carbon concentrations (< 1 µg m^{-3}) and air masses originating in the North Atlantic Ocean. Back

Formatted: Header

trajectories (not shown) were derived from NOAA's hybrid single-particle Lagrangian integrated trajectory (HYSPLIT) model (Draxler and Rolph, 2014). In the days immediately following this period (10-11 July), the ~~observed~~measured MOA ~~concentrations remain~~remained high while GEOS-Chem ~~predicts~~predicted a rapid decrease in concentrations; this discrepancy may be due ~~to additional MOA formation processes missing in~~ in part to the ~~model such as marine emissions~~different definitions of MOA in GEOS-Chem and Crippa et al. (2013a). The HR-ToF-AMS measurements from Crippa et al. (2013a) do not differentiate between primary and secondary sources of MOA and the current version of GEOS-Chem does not include SOA ~~precursors~~production from marine-source precursor species. Therefore considerable discrepancies between measurements and model predictions are expected when SOA of marine origin contributes a sizable fraction of MOA mass. Doubling the hydrophobic to hydrophilic conversion timescale in GEOS-Chem from the baseline value of 1.15 days to 2.3 days ~~results~~resulted in slightly improved MOA predictions near Paris (correlation coefficient = 0.64 [vs. 0.62 for 1.15 day aging] and normalized mean bias = -26% [vs. -36%]).~~ It's worth noting that Crippa et al. (2013a) suggested a possible secondary origin of this HR-ToF-AMS marine factor due to the high degree of oxygenation and strong correlation to methanesulfonic acid concentrations, although resuspended oxidized primary organic material from the ocean could not be excluded as a source.~~

In addition to the comparison with hourly concentrations of AMS-derived marine organic aerosol at an inland site, we have also evaluated terrestrial and total organic aerosol concentrations predicted by GEOS-Chem to a recently-published compilation of surface organic aerosol concentrations in clean marine conditions (defined as having black carbon concentrations < 0.05 µg m^{-3}) from Gantt and Meskhidze~~,~~ (2013). Figure 3 shows a scatterplot of the observational data ~~compare~~compared to GEOS-Chem surface concentrations matched by ~~the~~ location and month ~~of the measurement (albeit for~~ (s) but representing different years~~).~~ (observations span 1973-2009 while GEOS-Chem predictions are for 2009). During baseline ~~GEOS-Chem~~ simulations~~,~~ when only terrestrial organic aerosol emissions ~~are~~were included (black circles on Figure 3), GEOS-Chem exhibited a strong model underprediction (normalized mean bias = -79%) and poor correlation (0.16) ~~was determined.~~when compared to observations. Including ~~marine organic aerosols~~MOA in the comparison (red circles on Figure 3) substantially reduced the model bias (normalized mean bias = -12%) and ~~slightly~~ improved the correlation (0.28). ~~Unlike~~The seasonal plots in Figure 3 indicate that the ~~direct spatiotemporal comparison with~~reduction in model underprediction at these sites occurred throughout the

Formatted: Header

~~Crippa et al. (2013a) dataset,~~year. Previous studies showed (see Figure 3 and Figure 1 from Gantt and Meskhidze (2013)) that without the ~~weak model correlation with~~inclusion of MOA emissions, the ~~extensive dataset~~largest model underpredictions of clean marine organic aerosol (defined as aerosol that contained black carbon concentrations ~~is not surprising because particular observations spanning several decades (1973 to 2009) are compared to monthly-averaged GEOS-Chem predictions for 2009~~< 0.05 µg m^{-3}) concentrations occurred at remote sites in the Southern Ocean and tropical Pacific.

3.3 Marine ~~Organic Aerosol Aging~~organic aerosol aging

The atmospheric aging of organic aerosols, especially those with a marine source, is not well understood and is an active area of research. In GEOS-Chem, we ~~model~~modelled the aging of MOA based on the e-folding conversion from nascent (hydrophobic) to aged (hydrophilic) in a way similar to terrestrial primary organic aerosols. Tracking the nascent and aged fractions of marine organic aerosol concentrations ~~provides~~provided a distribution of their physicochemical characteristics, which could help in identifying locations for future field campaigns. The percentage of aged marine organic aerosol (hydrophilic/(hydrophilic + hydrophobic) × 100) in Figure 4 shows a strong ocean-continental gradient, with an aged fraction of 40 to 60% over the open ocean increasing to nearly 100% over the continents. As expected, the aged fraction ~~is~~was typically inversely related to the marine POA emission rate (Figure S1). Gradients between mostly nascent and mostly aged MOA ~~occur~~occurred over oceanic regions as well; the European region inset of Figure 4 shows the aged fraction increasing from < 40% in productive waters off the coast of Ireland to 80% in oligotrophic waters off the coast of Spain. For the Gantt and Meskhidze (2013) clean marine organic aerosol dataset, 45% of the average MOA mass was predicted by GEOS-Chem to be aged.

In addition to having MOA with a range of atmospheric ages, optimal locations for future field campaigns should have concentrations greater than the detection limit of instrumentation capable of routine monitoring such as the Aerosol Chemical Speciation Monitor (200 ng m^{-3} for 30 min signal averaging; Ng et al., 2011). Figure 5 segregates areas in which marine organic aerosol mass concentration greater than 200 ng m^{-3} ~~are~~were found in both low- and highly-aged regimes (arbitrarily chosen as < 40% and > 60% aged, respectively) as predicted by GEOS-Chem. For all locations, aging of MOA was based on the e-folding time of 1.15 days; therefore, the temporal and spatial distributions of MOA aging were only controlled by the emissions and transport. Regions with high concentrations of low-aged MOA typically ~~occur along coastal~~

Formatted: Header

~~areas~~occurred over high ocean productivity regions, while ~~regions with~~ high concentrations of aged MOA ~~are located either inland (where MOA can be difficult to differentiate from terrestrial organic aerosols) or~~were predicted over oligotrophic oceanic regions ~~(where few studies have been conducted).~~and inland locations. As many ~~previously conducted~~past field campaigns focused on the physical and chemical characteristics of marine organic aerosols have taken place in biologically-productive coastal areas (Cavalli et al., 2004; Decesari et al., 2011; Russell et al., ~~2011~~2010), nascent MOA have likely been sampled more frequently than aged aerosols. Regions identified as having a high concentration of aged MOA such as the Equatorial Atlantic Ocean and eastern Equatorial Pacific Ocean would be good candidates for field campaigns as they likely have MOA with physicochemical characteristics different than that of nascent aerosols. Figure 5 also identifies regions like the Arabian Sea and Bay of Biscay that ~~have~~had a seasonal cycle of low- and highly-aged regimes, making them good candidates for long-term field studies.

4 Conclusions

In this work, an online emission parameterization of submicron marine POA has been implemented into the GEOS-Chem model and evaluated with novel datasets of episodic events and global surface concentrations. This computationally-inexpensive marine POA emission scheme includes marine organic aerosol tracers that are independent from terrestrial tracers and treats their hydrophilic-hydrophobic conversion in the atmosphere. The flexibility of this implementation for multiple years/model domains allows for users to apply these emissions in the default setting of GEOS-Chem with minimal effort. The comparison with HR-ToF-AMS MOA observations shows that GEOS-Chem replicates the variability (correlation coefficient = 0.62) and magnitude (normalized mean bias = -36%) of summertime concentrations at an inland site near Paris, France. When GEOS-Chem is compared to globally-distributed organic aerosol observations in clean marine conditions, the underprediction for the default setting of only simulating terrestrial emissions (normalized mean bias = -79%) is reduced with the inclusion of marine POA emissions (normalized mean bias = -12%). In addition to improving the predictions of organic aerosol surface concentrations, the inclusion of marine emissions allows for the prediction of the global distribution of nascent and aged MOA. With the increasing focus on background aerosol concentrations at remote marine, coastal, and inland sites, this

Formatted: Header

emission parameterization has the flexibility and ease of use to be considered for the default setting of global chemical transport/climate models such as GEOS-Chem.

This implementation of marine POA emissions in GEOS-Chem ~~leads to improve predictions~~improves the prediction of clean marine organic aerosol concentrations, although additional drivers of marine POA emissions not considered here (such as oceanic organic carbon, sunlight, and/or organic composition) may be needed to refine the emission scheme in the future (Prather et al, 2013; Quinn et al., 2014; Long et al., 2014). The physicochemical treatment of marine organic aerosol aging identical to that of terrestrial organic aerosols also has large uncertainties, as the processes affecting aerosols in the marine boundary layer have a low level of understanding (Meskhidze et al., 2013). Marine emissions of SOA precursors may also be needed to further reduce the model underprediction of clean marine organic aerosol concentrations. Regardless of future refinements, this implementation of MOA into GEOS-Chem addresses a missing aerosol source, improves the prediction of clean marine and inland marine-sourced organic aerosol concentrations, and enables the model to indicate potential locations for future field studies focused on sampling marine organic aerosols.

Acknowledgements

This research was supported by the Office of Science (BER), US Department of Energy grant No. DEFG02-08ER64508, National Science Foundation grant No. ATM-0826117, and National Aeronautics & Space Administration (NASA) through grant no NNX11AG72G. The measurements in Paris were conducted in the MEGAPOLI project, mainly financially supported by the European Community's Framework Program FP/2007-2011 under grant agreement no. 212520. The authors would like to thank Dr. Daniel Jacob and the Harvard University Atmospheric Chemistry Modeling Group for providing the base GEOS-Chem model used during our research. Resources supporting this work were provided by the NASA High-End Computing (HEC) Program through the NASA Advanced Supercomputing (NAS) Division at NASA Ames Research Center. B.G. ~~was~~is supported by an appointment to the Research Participation Program at the Office of Research and Development, U.S. EPA, administered by ORISE.

Code Availability

Formatted: Header

The updated code (GEOS-Chem Fortran and chlorophyll-*a* NetCDF files) is available upon request. Please contact Matthew S. Johnson at matthew.s.johnson@nasa.gov or https://earthscience.arc.nasa.gov/person/Matthew_S_Johnson for more information.

Formatted: Header

References

Arnold, S. R., Spracklen, D. V., Williams, J., Yassaa, N., Sciare, J., Bonsang, B., Gros, V., Peeken, I., Lewis, A. C., Alvain, S., and Moulin, C.: Evaluation of the global oceanic isoprene source and its impacts on marine organic carbon aerosol, Atmos. Chem. Phys., 9, 1253-1262, doi:10.5194/acp-9-1253-2009, 2009.

Bey, I., Jacob, D. J., Yantosca, R. M., Logan, J. A., Field, B., Fiore, A. M., Li, Q., Liu, H., Mickley, L. J., and Schultz, M.: Global modeling of tropospheric chemistry with assimilated meteorology: Model description and evaluation, J. Geophys. Res., 106, 23073–23095, 2001.

Bigg, E. K. and Leck, C.: The composition of fragments of bubbles bursting at the ocean surface, J. Geophys. Res., 113, D11209, doi:10.1029/2007JD009078, 2008.

Bikkina, S., Kawamura, K., Miyazaki, Y., and Fu, P.: High abundances of oxalic, azelaic, and glyoxylic acids and methylglyoxal in the open ocean with high biological activity: Implication for secondary SOA formation from isoprene, Geophys. Res. Lett., 41, doi:10.1002/2014GL059913, 2014.

Bond, T. C., Bhardwaj, E., Dong, R., Jogani, R., Jung, S., Roden, C., Streets, D. G., and Trautmann, N. M.: Historical emissions of black and organic carbon aerosol from energy-related combustion, 1850–2000, Global Biogeochem. Cy., 21, GB2018, doi:10.1029/2006GB002840, 2007.

Burrows, S. M., Hoose, C., Poschl, U., and Lawrence, M. G.: Ice nuclei in marine air: biogenic particles or dust?, Atmos. Chem. Phys., 13, 245–267, doi:10.5194/acp-13-245-2013, 2013.

Burrows, S. M., Ogunro, O., Frossard, A. A., Russell, L. M., Rasch, P. J., and Elliott, S. M.: A physically~~-~~ based framework for ~~modelling~~modeling the organic fractionation of sea spray aerosol from bubble film Langmuir equilibria, Atmos. Chem. Phys~~. Discuss~~., 14, ~~5375-5443~~13601-13629, doi:10.5194/~~acpd~~acp-14-~~5375~~13601-2014, 2014.

Carslaw, K. S., Boucher, O., Spracklen, D. V., Mann, G. W., Rae, J. G. L., Woodward, S., and Kulmala, M.: A review of natural aerosol interactions and feedbacks within the Earth system, Atmos. Chem. Phys., 10, 1701-1737, doi:10.5194/acp-10-1701-2010, 2010.

Cavalli, F., Facchini, M. C., Decesari, S., Mircea, M., Emblicia, L., Fuzzi, S., Ceburnis, D., Yoon, Y. J., O'Dowd, C. D., Putaud, J.-P., and Dell'Acqua, A.: Advances in characterization of size resolved organic matter in marine aerosol over the North Atlantic, J. Geophys. Res., 109, D24215, doi:10.1029/2004JD005137, 2004.

Chang, R. Y.-W., Leck, C., Graus, M., Müller, M., Paatero, J., Burkhart, J. F., Stohl, A., Orr, L. H., Hayden, K., Li, S.-M., Hansel, A., Tjernström, M., Leaitch, W. R., and Abbatt, J. P. D.: Aerosol composition and sources in the central Arctic Ocean during ASCOS, Atmos. Chem. Phys., 11, 10619-10636, doi:10.5194/acp-11-10619-2011, 2011.

Collins, D. B.; Ault, A. P.; Moffet, R. C.; Ruppel, M. J.; Cuadra-Rodriguez, L. A.; Guasco, T. L.; Corrigan, C. E.; Pedler, B. E.; Azam, F.; Aluwihare, L. I.; Bertram, T. H.; Roberts, G. C.; Grassian, V. H.; Prather, K. A.: Impact of marine biogeochemistry on the chemical mixing state and cloud forming ability of nascent sea spray aerosol. J. Geophys. Res.-Atmos., 118, (15), 8553-8565, 2013.

Cooke, W. F., Liousse, C., Cachier, H., and Feichter, J.: Construction of a 1×1 fossil fuel emission data set for carbonaceous aerosol and implementation and radiative impact in theECHAM-4 model, J. Geophys. Res., 104, 22137–22162, 1999.

Crippa, M., El Haddad, I., Slowik, J. G., DeCarlo, P. F., Mohr, C., Heringa, M. F., Chirico, R., Marchand, N., Jean, S., Baltensperger, U., Prévót, A. S. H.: Identification of marine and continental aerosol sources in Paris using high resolution aerosol mass spectrometry, J. Geophys. Res. 118, 1–19, doi:10.1002/jgrd.50151, 2013a.

Crippa, M., Canonaco, F., Slowik, J. G., El Haddad, I., DeCarlo, P. F., Mohr, C., Heringa, M. F., Chirico, R., Marchand, N., Temime-Roussel, B., Abidi, E., Poulain, L., Wiedensohler, A., Baltensperger, U., and Prévôt, A. S. H.: Primary and secondary organic aerosol origin by combined gas-particle phase source apportionment, Atmos. Chem. Phys., 13, 8411-8426, doi:10.5194/acp-13-8411-2013, 2013b.

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

DeCarlo, P. F., Kimmel, J. R., Trimborn, A., Northway, M. J., Jayne, J. T., Aiken, A. C., Gonin, M., Fuhrer, K., Horvath, T., Docherty, K. S., Worsnop, D. R., and Jimenez, J. L.: Field-

Formatted: Header

Formatted: Header

deployable, high-resolution, time-of-flight aerosol mass spectrometer, Anal. Chem., 78, 8281–8289, 2006.

Decesari, S., Finessi, E., Rinaldi, M., Paglione, M., Fuzzi, S., Stephanou, E., Tziaras, T., Spyros, A., Ceburnis, D., O’Dowd, C. D., Dall’Osto, M., Harrison, R., Allan, J., Coe, H., and Facchini, M. C.: Primary and secondary marine organic aerosols over the North Atlantic Ocean during the MAP experiment, J. Geophys. Res., 116, D22210, doi:10.1029/2011JD016204, 2011.

Draxler, R. R. and Rolph, G. D.: HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website, available at: http://ready.arl.noaa.gov/HYSPLIT.php (last access: June, 2014), NOAA Air Resources Laboratory, Silver Spring, MD, 2014.

Facchini, M. C., Rinaldi, M., Decesari, S., Carbone, C., Finessi, E., Mircea, M., Fuzzi, S., Ceburnis, D., Flanagan, R., Nilsson, E., de Leeuw, G., Martino, M., Woeltjen J., and O’Dowd, C. D.: Primary sub-micron marine aerosol dominated by insoluble organic colloids and aggregates, Geophys. Res. Lett., 35, L17814, doi:10.1029/2008GL034210, 2008.

Fountoukis, C. and Nenes, A.: ISORROPIA II: a computationally efficient thermodynamic equilibrium model for K+–Ca2+–Mg2+–NH4+–Na+–SO42−–NO3−–Cl−–H2O aerosols, Atmos. Chem. Phys., 7, 4639-4659, doi:10.5194/acp-7-4639-2007, 2007.

Fu, P. Q., Kawamura, K., Chen, J., Charrière, B., and Sempéré, R.: Organic molecular composition of marine aerosols over the Arctic Ocean in summer: contributions of primary emission and secondary aerosol formation, Biogeosciences, 10, 653-667, doi:10.5194/bg-10-653-2013, 2013.

Gantt, B., Meskhidze, N., Facchini, M. C., Rinaldi, M., Ceburnis, D., and O’Dowd, C. D.: Wind speed dependent size-resolved parameterization for the organic mass fraction of sea spray aerosol, Atmos. Chem. Phys., 11, 8777–8790, doi:10.5194/acp-11-8777-2011, 2011.

Gantt, B., Johnson, M. S., Meskhidze, N., Sciare, J., Ovadnevaite, J., Ceburnis, D., and O’Dowd, C. D.: Model evaluation of marine primary organic aerosol emission schemes, Atmos. Chem. Phys., 12, 8553–8566, doi:10.5194/acp-12-8553-2012, 2012.

Gantt, B. and Meskhidze, N.: The physical and chemical characteristics of marine primary organic aerosol: a review, Atmos. Chem. Phys., 13, 3979-3996, doi:10.5194/acp-13-3979-2013, 2013.

Formatted: Header

Gong, S.: A parameterization of sea-salt aerosol source function for sub- and super-micron particles, Global Biogeochem. Cy., 17, 1097–1103, 2003.

Hu, Q., Xie, Z., Wang, X-M., Kang H., He, Q-F., Zhang P.: Secondary organic aerosols over oceans via oxidation of isoprene and monoterpenes from Arctic to Antarctic, Sci. Rep., 3, 2280, doi:10.1038/srep02280, 2013.

Huang, Y., Wu, S., Dubey, M. K., and French, N. H. F.: Impact of aging mechanism on model simulated carbonaceous aerosols, Atmos. Chem. Phys., 13, 6329-6343, doi:10.5194/acp-13-6329-2013, 2013.

Jaeglé, L., Quinn, P. K., Bates, T. S., Alexander, B., and Lin, J.-T.: Global distribution of sea salt aerosols: new constraints from in situ and remote sensing observations, Atmos. Chem. Phys., 11, 3137–3157, doi:10.5194/acp-11-3137-2011, 2011.

Lanz, V. A., Alfarra, M. R., Baltensperger, U., Buchmann, B., Hueglin, C., and Prévôt, A. S. H.: Source apportionment of submicron organic aerosols at an urban site by factor analytical modelling of aerosol mass spectra, Atmos. Chem. Phys., 7, 1503-1522, doi:10.5194/acp-7-1503-2007, 2007.

Lapina, K., Heald, C. L., Spracklen, D. V., Arnold, S. R., Allan, J. D., Coe, H., McFiggans, G., Zorn, S. R., Drewnick, F., Bates, T. S., Hawkins, L. N., Russell, L. M., Smirnov, A., O'Dowd, C. D., and Hind, A. J.: Investigating organic aerosol loading in the remote marine environment, Atmos. Chem. Phys., 11, 8847–8860, doi:10.5194/acp-11-8847-2011, 2011.

Long, M. S., Keene, W. C., Kieber, D. J., Frossard, A. A., Russell, L. M., Maben, J. R., Kinsey, J. D., Quinn, P. K., and Bates T. S.: Light-enhanced primary marine aerosol production from biologically productive seawater, Geophys. Res. Lett., 41, doi:10.1002/2014GL059436, 2014.

Luo, G. and Yu, F.: A numerical evaluation of global oceanic emissions of α-pinene and isoprene, Atmos. Chem. Phys., 10, 2007-2015, doi:10.5194/acp-10-2007-2010, 2010.

Meskhidze, N., Xu, J., Gantt, B., Zhang, Y., Nenes, A., Ghan, S. J., Liu, X., Easter, R., and Zaveri, R.: Global distribution and climate forcing of marine organic aerosol: 1. Model improvements and evaluation, Atmos. Chem. Phys., 11, 11689–11705, doi:10.5194/acp-11-11689-2011, 2011.

Meskhidze, N. Petters, M. D., Tsigaridis, K., Bates, T., O'Dowd, C., Reid, J., Lewis, E. R., Gantt, B., Anguelova, M. D., Bhave, P. V., Bird, J., Callaghan, A. H., Ceburnis, D., Chang, R., Clarke, A., de Leeuw, G., Deane, G., DeMott, P. J., Elliot, S., Facchini, M. C., Fairall, C. W., Hawkins, L., Hu, Y., Hudson, J. G., Johnson, M. S., Kaku, K. C., Keene, W. C., Kieber, D. J., Long, M. S., Martensson, M., Modini, R. L., Osburn, C. L., Prather, K. A., Pszenny, A., Rinaldi, M., Russell, L. M., Salter, M., Sayer, A. M., Smirnov, A., Suda, S. R., Toth, T. D., Worsnop, D. R., Wozniak, A., and Zorn, S. R.: Production mechanisms, number concentration, size distribution, chemical composition, and optical properties of sea spray aerosols, Atmos Sci Let, 14(4), 207-213, doi:10.1002/asl2.441, 2013.

Miyazaki, Y., Sawano, M., and Kawamura, K.: Low-molecular-weight hydroxyacids in marine atmospheric aerosol: evidence of a marine microbial origin, Biogeosciences~~ Discuss.,~~, 11, ~~5743-5763~~4407-4414, doi:10.5194/~~bgd~~bg-11-~~5743~~4407-2014, 2014.

Myriokefalitakis, S., Vignati, E., Tsigaridis, K., Papadimas, C., Sciare J., Mihalopoulos, N., Facchini, M.C., Rinaldi, M., Dentener, F. J., Ceburnis, D., Hatzianastasiou, N., O'Dowd, C. D., van Weele, M., and Kanakidou, M.: Global modelling of the oceanic source of organic aerosols, Adv. Meteorol., 2010, 939171, 16 pp., doi:10.1155/2010/939171, 2010.

Ng, N. L., Herndon, S. C., Trimborn, A., Canagaratna, M. R., Croteau, P., Onasch, T. M., Sueper, D., Worsnop, D. R., Zhang, Q., Sun, Y. L., and Jayne, J. T.: An Aerosol Chemical Speciation Monitor (ACSM) for routine monitoring of atmospheric aerosol composition, Aerosol Sci. Technol., 45, 770–784, 2011.

O'Dowd, C. D., Facchini, M. C., Cavalli, F., Ceburnis, D., Mircea, M., Decesari, S., Fuzzi, S., Yoon, Y. J., and Putaud, J. P.: Biogenically driven organic contribution to marine aerosol, Nature, 431, 676–680, 2004.

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

Ovadnevaite, J., O'Dowd, C., Dall'Osto, M., Ceburnis, D., Worsnop, D. R., and Berresheim, H.: Detecting high contributions of primary organic matter to marine aerosol: a case study, Geophys. Res. Lett., 38, L02807, doi:10.1029/2010GL046083, 2011.

Park, R. J., Jacob, D. J., Field, B. D., Yantosca, R. M., and Chin, M.: Natural and transboundary pollution influences on sulfate-nitrate-ammonium aerosols in the United States: implications for policy, J. Geophys. Res., 109, D15204, doi:10.1029/2003JD004473, 2004.

Formatted: Header

Formatted: Header

Partanen, A.-I., Dunne, E. M., Bergman, T., Laakso, A., Kokkola, H., Ovadnevaite, J., Sogacheva, L., Baisnée, D., Sciare, J., Manders, A., O'Dowd, C., de Leeuw, G., and Korhonen, H.: Global modelling of direct and indirect effects of sea spray aerosol using a source function encapsulating wave state, Atmos. Chem. Phys~~. Discuss~~., 14, ~~4537-4597~~11731-11752, doi:10.5194/~~acpd~~acp-14-~~4537~~11731-2014, 2014.

Prather, K. A., Bertram, T. H., Grassian, V. H., Deane, G. B., Stokes, M. D., DeMott, P. J., Aluwihare, L. I., Palenik, B. P., Azam, F., Seinfeld, J. H., Moffet, R. C., Molina, M. J., Cappa, C. D., Geiger, F. M., Roberts, G. C., Russell, L. M., Ault, A. P., Baltrusaitis, J., Collins, D. B., Corrigan, C. E., Cuadra-Rodriguez, L. A., Ebben, C. J., Forestieri, S. D., Guasco, T. L., Hersey, S. P., Kim, M. J., Lambert, W. F., Modini, R. L., Mui, W., Pedler, B. E., Ruppel, M. J., Ryder, O. S., Schoepp, N. G., Sullivan, R. C., and Zhao, D.: Bringing the ocean into the laboratory to probe the chemical complexity of sea spray aerosol, P. Natl. Acad. Sci. USA, 110, 7550–7555, doi:10.1073/pnas.1300262110, 2013.

Pye, H. O. T., Chan, A. W. H., Barkley, M. P., and Seinfeld, J. H.: Global modeling of organic aerosol: the importance of reactive nitrogen (NOx and NO3), Atmos. Chem. Phys., 10, 11261-11276, doi:10.5194/acp-10-11261-2010, 2010.

Quinn, P. K., Bates, T. S., Schulz, K. S., Coffman, D. J., Frossard, A. A., Russell, L. M., Keene, W. C., and Kieber, D. J.: Contribution of sea surface carbon pool to organic matter enrichment in sea spray aerosol, Nat. Geosci., 7, 228–232, doi:10.1038/ngeo2092, 2014.

Rinaldi, M., Facchini, M. C., Decesari, S., Carbone, C., Finessi, E., Mircea, M., Fuzzi, S., Ceburnis, D., Ehn, M., Kulmala, M., de Leeuw, G., and O'Dowd, C. D.: On the representativeness of coastal aerosol studies to open ocean studies: Mace Head – a case study, Atmos. Chem. Phys., 9, 9635-9646, doi:10.5194/acp-9-9635-2009, 2009.

Rinaldi, M., Decesari, S., Finessi, E., Giulianelli, L., Carbone, C., Fuzzi, S., O’Dowd, C. D., Ceburnis, D., and Facchini,M. C.: Primary and secondary organic marine aerosol and oceanic biological activity: Recent results and new perspectives for future studies, Adv. Meteorol., 2010, 310682, doi:10.1155/2010/310682, 2010.

Rinaldi, M., Fuzzi, S., Decesari, S., Marullo, S., Santoleri, R., Provenzale, A., von Hardenberg, J., Ceburnis, D., Vaishya, A., O’Dowd, C. D., and Facchini, M. C.: Is chlorophyll-a the best surrogate for organic matter enrichment in submicron primary marine aerosol?, J. Geophys. Res. Atmos., 118, 4964–4973, doi:10.1002/jgrd.50417, 2013.

Formatted: Header

Russell, L. M., Hawkins, L. N., Frossard, A. A., Quinn, P. K., and Bates, T. S.: Carbohydrate-like composition of submicron atmospheric particles and their production from ocean bubble bursting, P. Natl. Acad. Sci. USA, 107, 6652–6657, doi:10.1073/pnas.0908905107, 2010.

Schmale, J., Schneider, J., Nemitz, E., Tang, Y. S., Dragosits, U., Blackall, T. D., Trathan, P. N., Phillips, G. J., Sutton, M., and Braban, C. F.: Sub-Antarctic marine aerosol: dominant contributions from biogenic sources, Atmos. Chem. Phys., 13, 8669-8694, doi:10.5194/acp-13-8669-2013, 2013.

Sciare, J., Favez, O., Sarda-Estève, R., Oikonomou, K., Cachier, H., and Kazan, V.: Long-term observations of carbonaceous aerosols in the Austral Ocean atmosphere: Evidence of a biogenic marine organic source, J. Geophys. Res., 114, D15302, doi:10.1029/2009JD011998, 2009.

Shaw, S. L., Gantt, B., and Meskhidze, N.: Production and emissions of marine isoprene and monoterpenes, A review, Adv. Meteorol., 24, 408696, doi:10.1155/2010/408696, 2010.

Sinreich, R., Coburn, S., Dix, B., and Volkamer, R.: Ship-based detection of glyoxal over the remote tropical Pacific Ocean, Atmos. Chem. Phys., 10, 11359-11371, doi:10.5194/acp-10-11359-2010, 2010.

Spracklen, D. V., Arnold, S. R., Carslaw, K. S., Sciare, J., and Pio, C.: Globally significant oceanic source of organic carbon aerosol, Geophys. Res. Lett., 35, L12811, doi:10.1029/2008GL033359, 2008.

Tsigaridis, K., Koch, D., and Menon, S.: Uncertainties and importance of sea spray composition on aerosol direct and indirect effects, J. Geophys. Res., 118, 220–235, doi:10.1029/2012JD018165, 2013.

van der Werf, G. R., Randerson, J. T., Giglio, L., Collatz, G. J., Mu, M., Kasibhatla, P. S., Morton, D. C., DeFries, R. S., Jin, Y., and van Leeuwen, T. T.: Global fire emissions and the contribution of deforestation, savanna, forest, agricultural, and peat fires (1997–2009), Atmos. Chem. Phys., 10, 11707-11735, doi:10.5194/acp-10-11707-2010, 2010.

Vignati, E., Facchini, M. C., Rinaldi, M., Scannell, C., Ceburnis, D., Sciare, J., Kanakidou, M., Myriokefalitakis, S., Dentener, F., and O’Dowd, C. D.: Global scale emission and distribution of seaspray aerosol: sea-salt and organic enrichment, Atmos. Environ., 44, 670–677, 2010.

Wesely, M. L. (1989), Parameterization of surface resistances to gaseous dry deposition in regional-scale numerical-models, Atmos. Environ., 23(6), 1293–1304, doi:10.1016/0004-6981(89)90153-4.

Westervelt, D. M., Moore, R. H., Nenes, A., and Adams, P. J.: Effect of primary organic sea spray emissions on cloud condensation nuclei concentrations, Atmos. Chem. Phys., 12, 89–101, doi:10.5194/acp-12-89-2012, 2012.

Zare, A., Christensen, J. H., Gross, A., Irannejad, P., Glasius, M., and Brandt, J.: Quantifying the contributions of natural emissions to ozone and total fine PM concentrations in the Northern Hemisphere, Atmos. Chem. Phys., 14, 2735-2756, doi:10.5194/acp-14-2735-2014, 2014.

Zhang, L. M., S. L. Gong, J. Padro, and L. Barrie (2001), A size-segregated particle dry deposition scheme for an atmospheric aerosol module, Atmos. Environ., 35(3), 549–560, doi:10.1016/S1352-2310(00)00326-5.

Zhang, Q., Jimenez, J., Canagaratna, M., Ulbrich, I., Ng, N., Worsnop, D., and Sun, Y. L.: Understanding atmospheric organic aerosols via factor analysis of aerosol mass spectrometry: a review, Analytical and Bioanalytical Chemistry, 401, 3045–3067, doi:10.1007/s00216-011-5355-y, 2011.

Formatted: Header

Formatted: Header

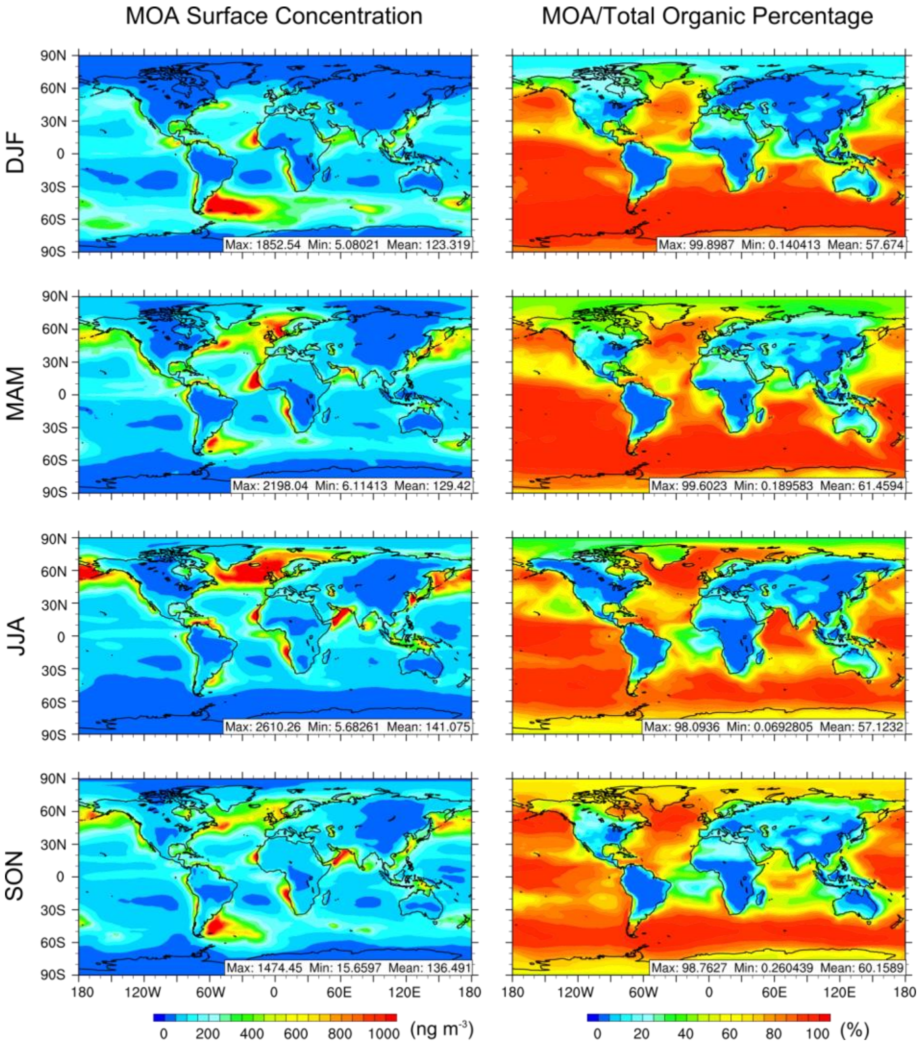


Figure 1. Seasonally-averaged submicron MOA surface concentrations and percentages of total submicron organic aerosol (marine + primary anthropogenic + biomass burning + secondary) with a marine source as predicted by GEOS-Chem for 2009.

Formatted: Header

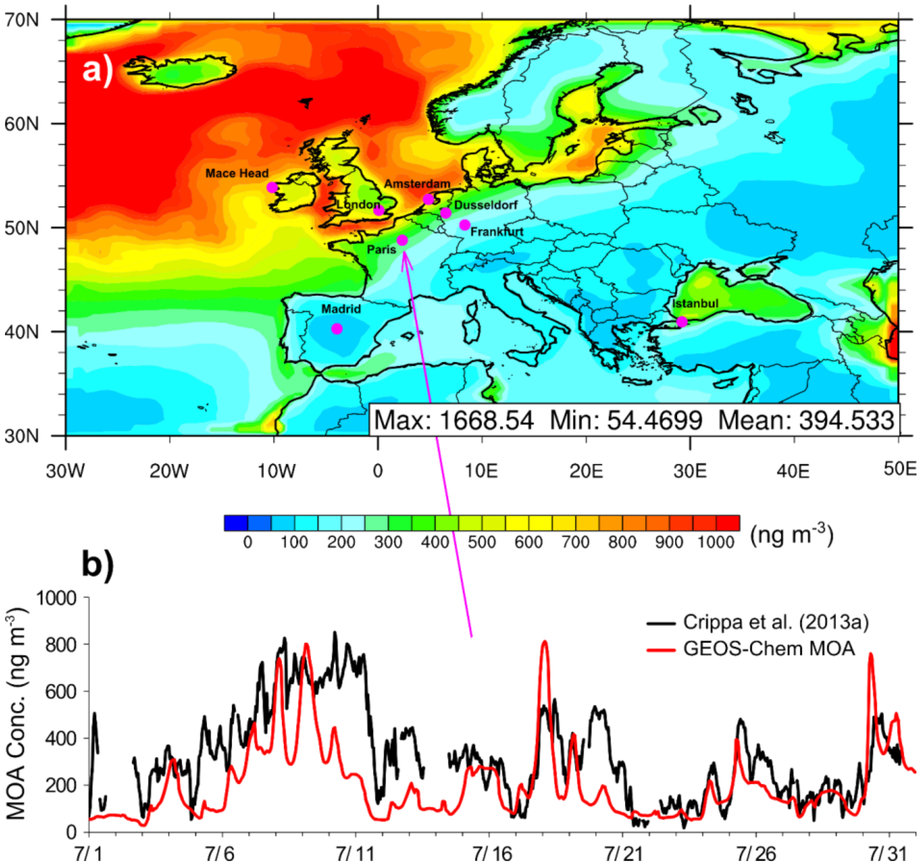
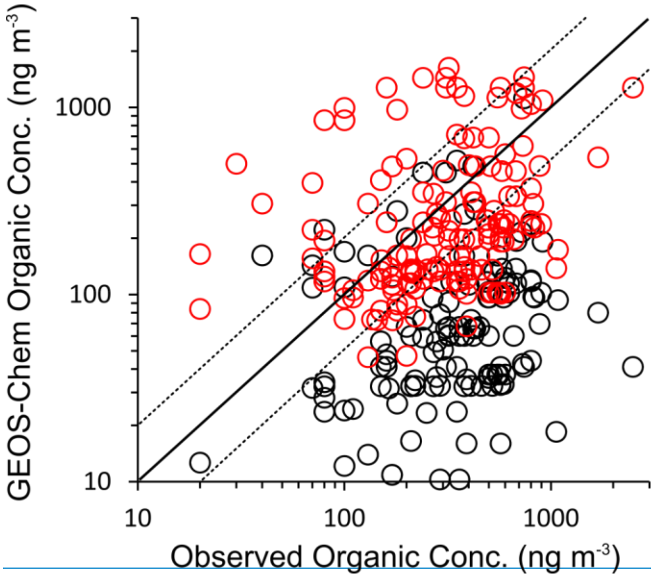


Figure 2. a) Average submicron surface concentration of MOA for July 2009 in the nested Europe GEOS-Chem domain and the b) time series of the observed and predicted marine organic aerosol concentration near Paris, France as reported by Crippa et al. (2013a). Evaluation of the GEOS-Chem MOA with the Crippa et al. (2013a) observations gives a correlation coefficient of 0.62, mean bias of -120 ng m^{-3}, and normalized mean bias of -36%.

Formatted: Header



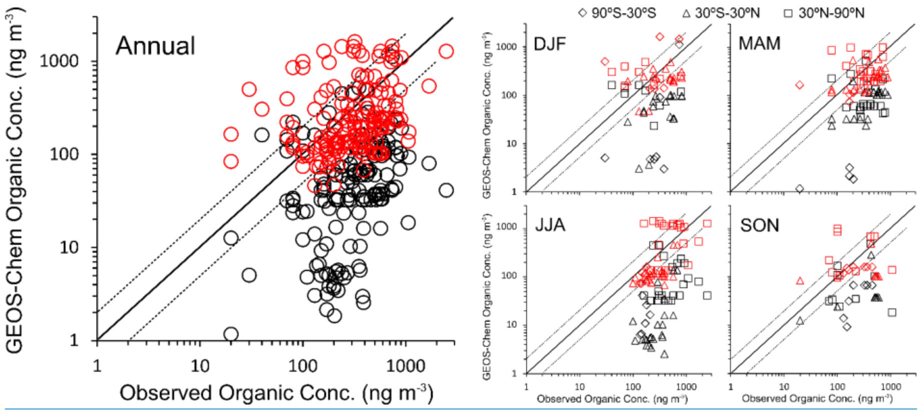


Figure 3. Global comparison of observed clean marine organic aerosol concentrations ~~(see~~compiled by Gantt and Meskhidze~~,~~ (2013~~ for details~~) and GEOS-Chem-predicted terrestrial (black) and total (marine + terrestrial, in red) submicron organic aerosol concentrations. ~~Concentrations are matched by location and month(s), but represent different years (observations span 1973-2009 while GEOS-Chem predictions are for 2009).~~ The solid and dotted lines represent the 1:1 line and 1:2 and 2:1 lines, respectively.

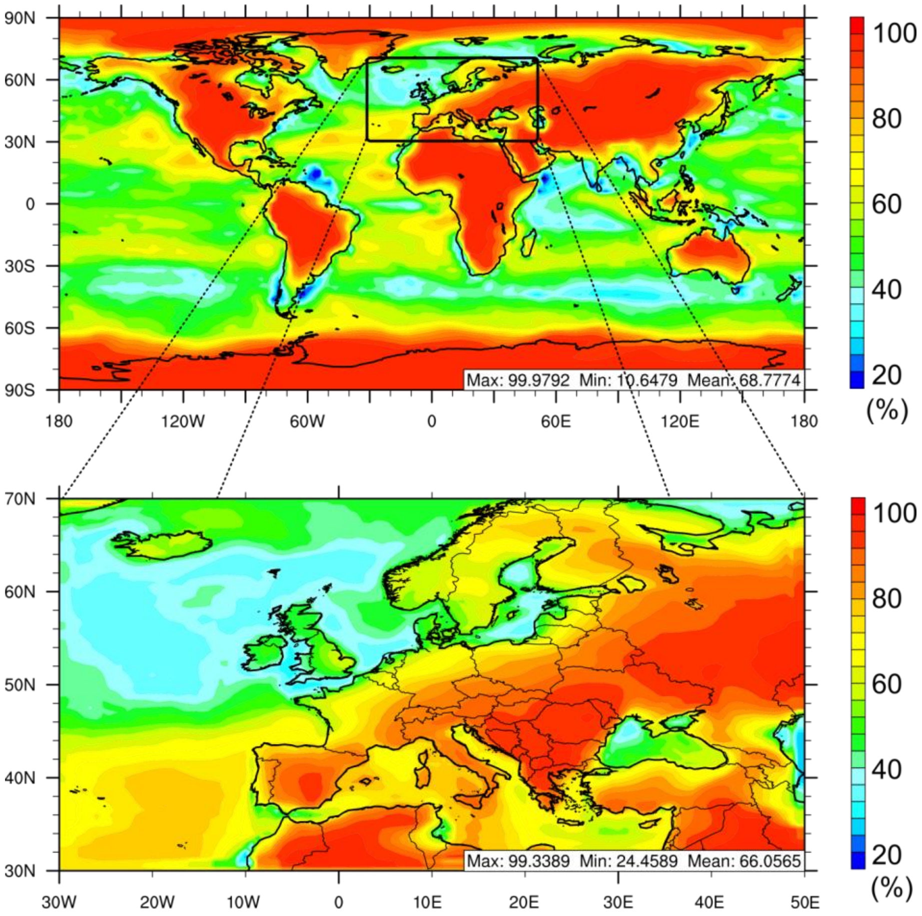


Figure 4. Percentage of the submicron MOA concentration predicted by GEOS-Chem to be hydrophilic (aged) for July 2009.

Formatted: Header

Formatted: Header

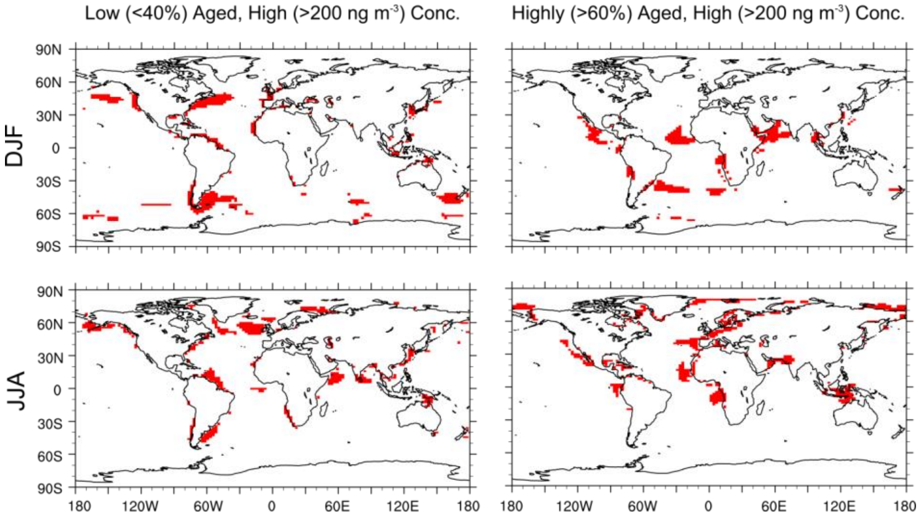


Figure 5. Regions (in red) with GEOS-Chem predicted seasonal submicron MOA concentrations > 200 ng m^{-3} for both low-aged (left column, < 40% hydrophilic marine organic aerosol) and highly-aged (right column, > 60% hydrophilic marine organic aerosol) regimes.

Formatted: Header

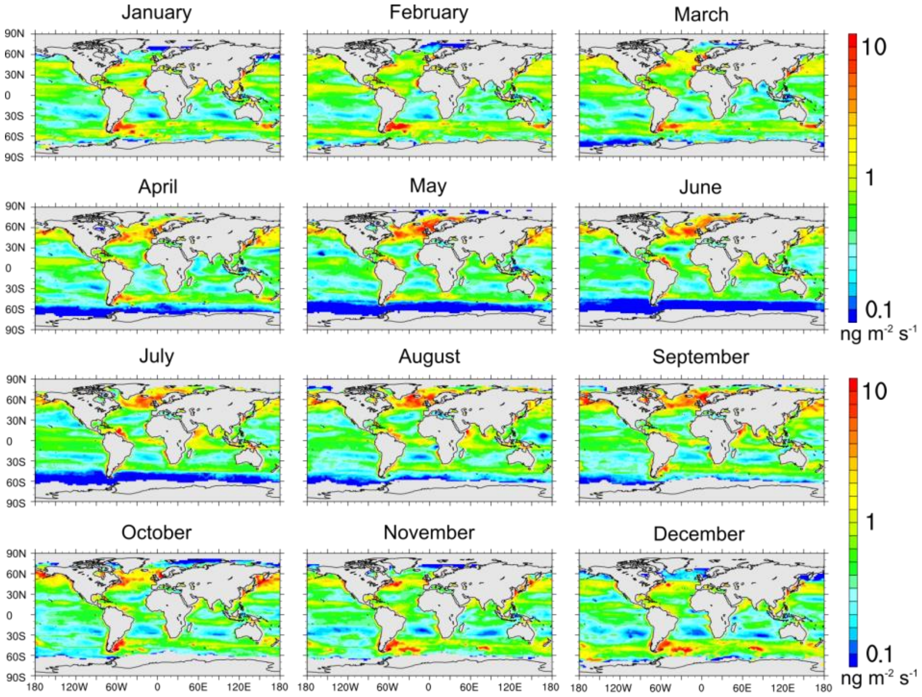


Figure S1. Monthly-average GEOS-Chem marine POA emissions for 2009.

Formatted: Header

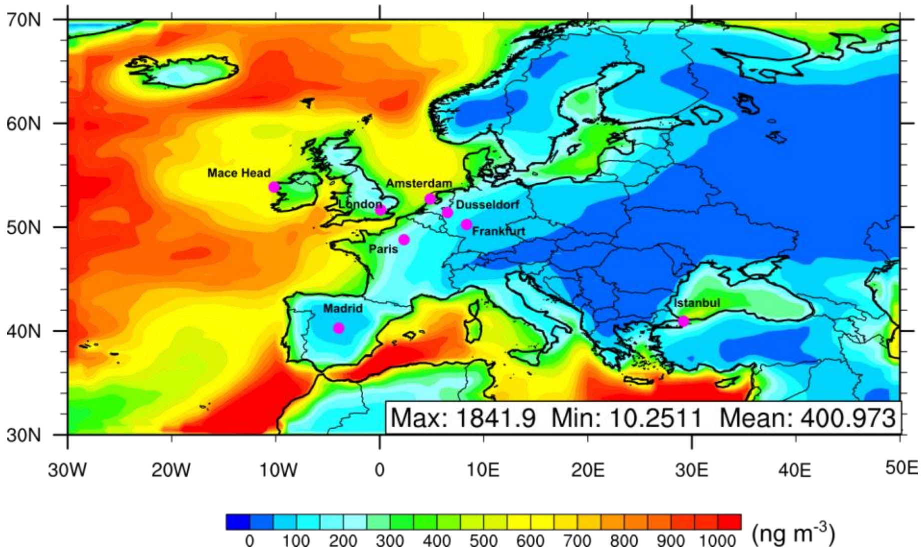


Figure S2. Average surface concentration of submicron sea-salt aerosol for July 2009 in the nested Europe GEOS-Chem domain.