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## Research Article

# Global Modeling of the Oceanic Source of Organic Aerosols

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The global marine organic aerosol budget is investigated by a 3-dimensional chemistry-transport model considering recently proposed parameterisations of the primary marine organic aerosol (POA) and secondary organic aerosol (SOA) formation from the oxidation of marine volatile organic compounds. MODIS and SeaWiFS satellite data of Chlorophyll-a and ECMWF solar incoming radiation, wind speed, and temperature are driving the oceanic emissions in the model. Based on the adopted parameterisations, the SOA and the submicron POA marine sources are evaluated at about 5 Tg yr<sup>-1</sup> (~1.5 Tg C yr<sup>-1</sup>) and 7 to 8 Tg yr<sup>-1</sup> (~4 Tg C yr<sup>-1</sup>), respectively. The computed marine SOA originates from the dimethylsulfide oxidation (~78%), the potentially formed dialkyl amine salts (~21%), and marine hydrocarbon oxidation (~0.1%). Comparison of calculations with observations indicates an additional marine source of soluble organic carbon that could be partially encountered by marine POA chemical ageing.

## 1. Introduction

Organic aerosol (OA) attracts the attention of the scientific community due to their climate and health relevance [1–4]. Marine OA components are considered as important natural aerosol constituents, which significantly contribute to the global aerosol burden and affect Earth's climate. Observations of OA in the marine atmosphere have shown the existence of significant amounts of primary organic carbon of marine origin [5, 6] in the submicron sea-spray, as well as a small relative contribution to the coarse mode sea-spray [7], over the ocean that seem to be related with the biological activity in the ocean [8].

The ocean also emits a complex mixture of organic gases (VOC) like alkenes, dimethyl sulphide (DMS) [5, 9–11], isoprene, monoterpenes [12–15], and aliphatic amines [7]. A few decades ago, DMS emissions from the oceans have been suggested to control cloudiness in the clean marine environment via sulphate (SO<sub>4</sub><sup>=</sup>) aerosol formation (CLAW hypothesis [16]). DMS oxidation is known to produce SO<sub>4</sub><sup>=</sup> and methane sulphonate (MS<sup>-</sup>), both present in the aerosol phase, at proportions that depend on the meteorological conditions and oxidant levels in the marine environment [17, 18]. Vallina et al. [19] attributed between 35% and 80% of cloud condensation nuclei (CCN) in the Southern Ocean to biogenics of marine origin. They supported the

central role of biogenic DMS emissions in controlling both number and variability of CCN over the remote ocean.  $\text{MS}^-$  containing both sulphur and carbon atoms is also a component of organic aerosol. Other VOCs with identified marine sources that are involved in secondary organic aerosol (SOA) formation are monoterpenes [15] and isoprene [12, 13, 20]. The marine source of monoterpenes has been recently identified [15], but this source requires further investigations for accurate evaluation of its global strength and distribution. Isoprene has been shown to produce secondary organic aerosol both via gas-phase reactions followed by gas-to-particle partitioning of its semivolatile products [21, 22] and cloud processing of organic matter [23, 24]. Isoprene, one of the most important biogenic volatile organic compound (VOC) with large terrestrial emissions  $\sim 600 \text{ Tg yr}^{-1}$  [25], has a comparatively small oceanic source that is highly uncertain and varies from  $0.2\text{--}1.4 \text{ Tg yr}^{-1}$ . Despite its small intensity, this source is expected to have an impact on the marine boundary layer gas-phase chemistry because of isoprene's high reactivity [26, 27].

The formation of SOA over oceans, although expected to be smaller than over land [28, 29], triggers scientific interest due to the potential involvement of SOA in the formation of clouds in the remote marine atmosphere [30] especially where aerosol levels of other components are low. Recently, several studies investigated the intensity of marine sources of OA, with estimates varying by more than an order of magnitude ( $2\text{--}75 \text{ Tg C yr}^{-1}$  [20, 31–34]).

In order to evaluate the marine organic aerosol contribution to the atmosphere, we used the 3-dimensional global chemistry transport model TM4-ECPL. We computed the SOA formation from marine emissions of isoprene, monoterpenes, DMS, and amines, together with the primary organic aerosol (POA) marine emissions. Both primary and secondary OA distributions are calculated online driven by wind speed, temperature, solar radiation, and ocean productivity (represented by chlorophyll-a), as well as atmospheric oxidant levels that are also calculated online [35]. Marine SOA from isoprene, monoterpenes and DMS are formed via gas phase oxidation followed by gas-to-particle conversion and via multiphase chemical processes. As summarized by Ervens et al. [24] and references therein, isoprene chemistry can form SOA via cloud processing that consists of partitioning of isoprene oxygenated products like glyoxal, methylglyoxal, and pyruvic acid to the cloud water and subsequent in cloud oxidation to form glycolic, glyoxylic and oxalic acids. These mechanisms are parameterized in our model based on the linearized relationship recently published by Ervens et al. [24] for stratiform clouds, using the cloud occurrence and lifetime, the liquid water content of clouds, isoprene concentration, and the VOC/NO<sub>x</sub> conditions in each grid and assuming one SOA product from all in-cloud reactions. The participation of aerosol water on gas-to-particle partitioning and multiphase chemistry is not taken into account in the present study. Potential contribution to SOA of amine salts produced by reactions of dimethyl and diethyl amines of marine origin with sulphuric acid is also investigated. The POA submicron marine source is parameterised in the model based on recently published

parameterisations derived from experimental data [8] as described in Vignati et al. [34]. Model results are evaluated against observations in the marine environment.

## 2. Model Description

For the present study, the well documented offline chemistry-transport global model TM4 is used. The model version applied here (TM4-ECPL) contains a comprehensive gas phase chemistry as described by Myriokefalitakis et al. [35] and aerosol parameterisations from Tsigaridis et al. [36] and Tsigaridis and Kanakidou [29] with improvements as described in Section 2.3. TM4-ECPL runs on 31 vertical hybrid layers from the surface to 10 hPa and in two different horizontal resolutions, the low resolution of  $4^\circ \times 6^\circ$  in latitude and longitude and the high resolution of  $2^\circ \times 3^\circ$ . For the present study, the low resolution version of the model with time-step of 1 hour for the chemistry calculations has been used. The model's input meteorology comes from the ECMWF (European Centre for Medium-Range Weather Forecasts) operational forecast data for the period from 2000 to 2008 and is updated every 6 hours.

A complete overview of emissions used in this study can be found in the supplemental material by Myriokefalitakis et al. [35]. Here below, we provide information on the emissions of particular interest for the present study. For the biogenic and anthropogenic VOC, nitrogen oxides ( $\text{NO}_x$ ), carbon monoxide (CO), and all biomass burning trace gas emissions, TM4-ECPL uses the  $1^\circ \times 1^\circ$  gridded emission distributions from the POET database [37] that correspond to the year 2000.

The adopted emissions of primary particles (carbonaceous aerosols, dust, and a small fraction of sulphate  $-2.5\%$ ) in TM4-ECPL are presented in detail in Tsigaridis et al. [36] and Tsigaridis and Kanakidou [29]. Biomass burning emissions of carbonaceous aerosols and black carbon for the respective year are adopted from the Global Fire Emissions Database version 2 [38]. Primary OA from the oceans is parameterised in the model as outlined in Section 2.2.

For most simulations performed for the present study, the sea-salt source has been calculated online driven by the ECMWF wind speed at every time-step, parameterized as suggested by Gong [39] and fitted for accumulation and coarse modes taken into account in TM4-ECPL as described in detail in Vignati et al. [34]. The thus calculated total sea-salt emissions account almost  $6290 \text{ Tg yr}^{-1}$  ( $31 \text{ Tg yr}^{-1}$  in the fine mode) on a global basis for the year 2006, that is slightly higher than the upper limit of the IPCC-TAR fluxes of  $3340 \pm 80\% \text{ Tg yr}^{-1}$ , but lower than the AEROCOM (Aerosol Comparisons between Observations and Models) inventory of about  $7925 \text{ Tg yr}^{-1}$  ( $96.5 \text{ Tg yr}^{-1}$  in the fine mode) for the year 2000 [40]. The AEROCOM 2000 inventory has been also used to evaluate uncertainties. Sea-salt is considered to be present in 2 modes in the online wind driven method (accumulation and coarse) and in 3 modes when using the AEROCOM inventories (Aitken, accumulation, and coarse), while dust is present in 2 modes (accumulation and coarse), which come from the AEROCOM emissions (as described in

TABLE 1: Annual emissions of oceanic species adopted in the model.

Oceanic tracer	Emissions (Tg yr <sup>-1</sup> )
Isoprene	1.0
Monoterpenes	0.2
POA	7-8*
DMS	19.5**
C <sub>2</sub> H <sub>2</sub>	1.0
C <sub>2</sub> H <sub>4</sub>	1.2
C <sub>3</sub> H <sub>6</sub>	1.3
C <sub>3</sub> H <sub>8</sub>	1.1
Sea-Salt	6290*
Amines	0.8 <sup>#</sup>

\* Calculated by the model for 2006; \*\*TgS yr<sup>-1</sup>; <sup>#</sup>TgN yr<sup>-1</sup>.

Tsigaridis et al. [36]) updated to interannual dust inventory for the years 2000–2007. All other aerosol components are considered to be present in the accumulation mode only.

**2.1. VOC Marine Emissions.** Annual mean distribution of light alkenes marine emissions (Table 1) are taken from POET database in  $1^\circ \times 1^\circ$  grid [37]. DMS, isoprene, and monoterpenes oceanic emissions, which are of particular interest for the present study as secondary sources of OA in the marine environment, are parameterized interactively as a product of piston velocity and surface seawater concentration. Piston velocity is calculated as a function of wind speed, temperature and the Schmidt number [45]. DMS surface seawater concentration distribution is taken from Kettle et al. [11]. For isoprene and monoterpenes their surface seawater distributions are assumed proportional to the product of chlorophyll-a (Chl-a) distribution and the logarithm of the square of the incoming solar radiation at the earth’s surface. The incoming solar radiation at surface is taken from the ECMWF data and is used as substitute for the ambient light intensity that has been suggested by Gantt et al. [20] to drive the isoprene emission rates in the marine environment. However, our approach does not account for different phytoplankton groups that have been shown to produce biogenic volatile organic compounds at different rates [13–15, 20]. Chl-a is taken from observations by the satellite-based sensors moderate resolution imaging spectroradiometer (MODIS) (Figure 1) and sea-viewing wide field-of-view sensor (SeaWiFS). SeaWiFS and MODIS global monthly data products have been generated by the NASA ocean biology processing group (OBPG) and ingested into the GES-DISC interactive online visualization and analysis infrastructure (Giovanni) system, developed by the Goddard Earth Sciences Data and Information Services Center (GES DISC/DAAC) [46]. There are missing data in the MODIS/SeaWiFS Chl-a daily products on high spatial resolution ( $9\text{ km} \times 9\text{ km}$ ) that have been neglected when producing the  $1^\circ \times 1^\circ$  monthly product. The  $1^\circ \times 1^\circ$  daily products have been produced as the composite of the high resolution daily  $9\text{ km} \times 9\text{ km}$  data. They have been further averaged over a calendar month to provide the monthly data at  $1^\circ \times 1^\circ$  on a global scale [47, 48]. Absence of data at the

$1^\circ \times 1^\circ$  monthly constructed database, as is the case for polar regions, is translated by the model to absence of chl-a in the corresponding model grid. The thus derived substitute of the isoprene emissions is scaled to the global value of  $1\text{ Tg yr}^{-1}$  for the year 2006 that is a central in the range of published global marine isoprene source estimates ([12, 13, 20] and references therein). The distribution of isoprene emission rates in the model is depicted in Figures 1(c) and 1(d). Driven by wind speed, Chl-a and solar incoming radiation, isoprene emissions in TM4-ECPL show high levels in the extratropics and particularly during summer-time as well as in the tropical region where incoming solar radiation maximizes. This pattern is similar with the more accurate computations by Gantt et al. [20]. Based on the measured emission rates from various studied phytoplankton species of monoterpenes ( $0.3$  to  $225.9\text{ nmol g}^{-1}[\text{Chl-a}]^{-1}\text{ day}^{-1}$  [15]) and of isoprene ( $1.21$ – $9.66\text{ }\mu\text{mol g}^{-1}[\text{Chl-a}]^{-1}\text{ day}^{-1}$  [13] or even up to  $24\text{ }\mu\text{mol g}^{-1}[\text{Chl-a}]^{-1}\text{ day}^{-1}$ , measured for diatoms at high light intensity [20]), annual global marine emissions of monoterpenes of up to  $0.4\text{ Tg yr}^{-1}$  are derived. In the present study  $0.2\text{ Tg yr}^{-1}$  of monoterpenes marine emissions have been adopted and distributed as those of isoprene.

Observations in the marine environment indicate that dimethyl and diethyl ammonium salts of biogenic origin are present in the marine OA and could account for about 20% of the observed nitrogen in the inorganic form of ammonium [7]. On the other hand, Gibb et al. [49] evaluated a net flux of methylamines from the atmosphere into the sea water in the NW Arabian Sea based on atmospheric and sea water observations. They mentioned, however, that this observation should not be extrapolated to the global ocean. Therefore, in the present study, we also explore the amines contribution to the marine SOA. For this, amines emissions are arbitrary taken to about one tenth of the ammonia emissions from the oceans as distributed in the GEIA database (<http://www.mnp.nl/geia/data/Ammonia/> [50]). Thus, the marine amines emissions of  $0.8\text{ TgN yr}^{-1}$  are adopted for this explorative simulation.

**2.2. Primary Marine Organic Aerosol Emissions.** The oceanic source of primary submicron OA has been calculated based on the parameterisation proposed by O’Dowd et al. [8] and updated by Vignati et al. [34] that provides the POA as a mass fraction of the submicron sea-salt aerosol source, based on the surface ocean Chl-a.

In the present study, the monthly average oceanic Chl-a concentrations are derived from satellite-based MODIS observations in  $1^\circ \times 1^\circ$  horizontal grid resolution (Figures 1(a) and 1(b) for two different seasons). Alternatively, we calculated this fraction based on SeaWiFS Chl-a product as in Vignati et al. [34]. Sea-salt emissions are parameterized as detailed in Vignati et al. [34] accounting for particles radius increases with Chl-a due to added organic material from the oceans.

In TM4-ECPL, marine submicron POA is considered to be emitted entirely as insoluble but internally mixed with sea-salt as determined by O’Dowd et al. [8], in contrast to terrestrial POA from combustion and fossil fuel sources that

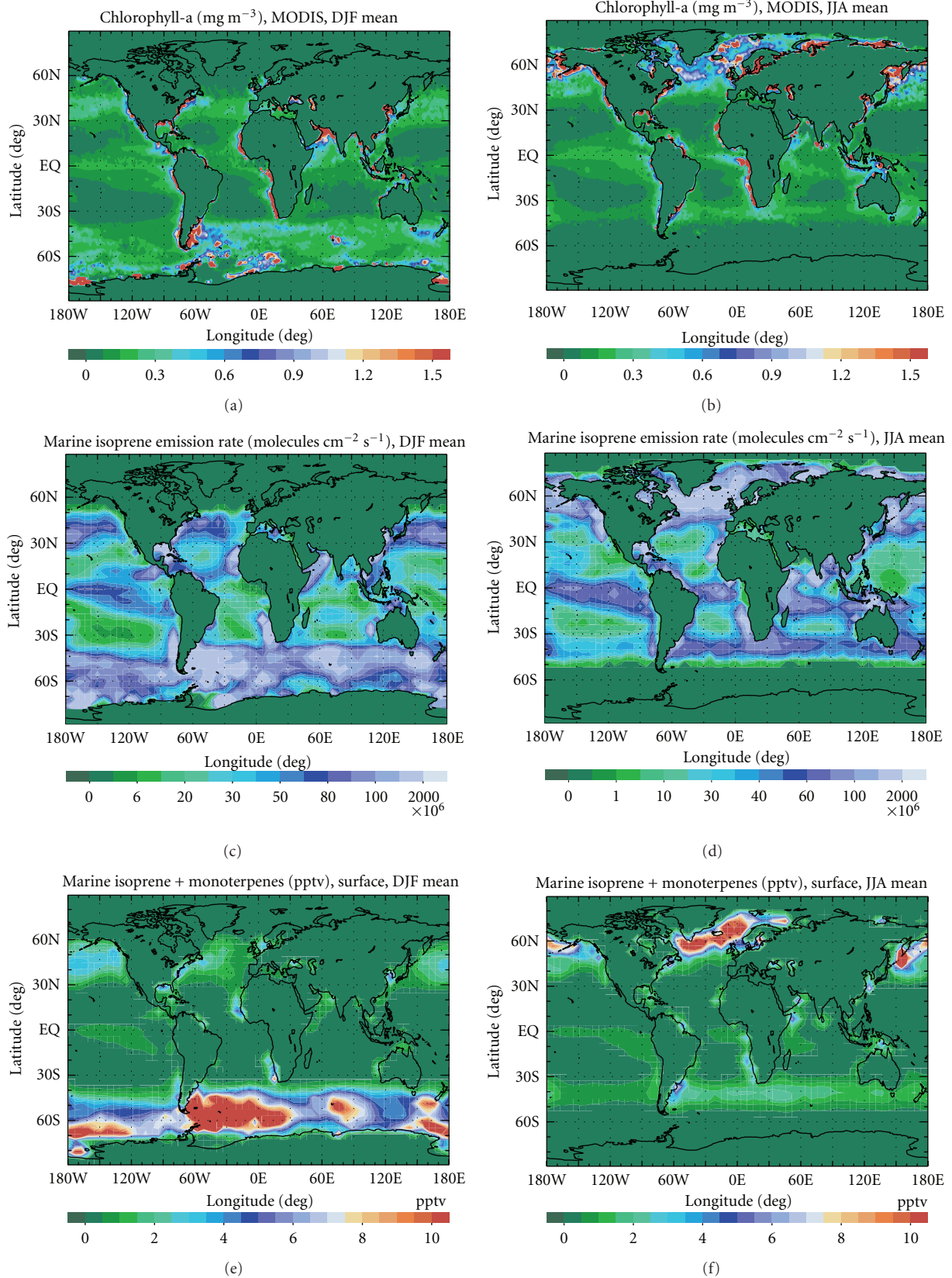


FIGURE 1: Seasonal mean surface distribution of Chl-a in  $\text{mg m}^{-3}$  as retrieved from MODIS (see text) (a) for DJF and (b) for JJA; Marine isoprene emission rate in  $\text{molecules cm}^{-2} \text{s}^{-1}$  (c) for DJF (d) for JJA; Sum of marine isoprene and monoterpenes concentrations in pptv computed by the model (e) for DJF and (f) for JJA; for the year 2006.

are considered to be emitted by 50% as hydrophilic [51]. Ageing of insoluble POA of continental origin is taken into account as described by Tsigaridis and Kanakidou [28] and corresponds to a global mean turnover time of about 1 day. Finally, based on Facchini et al. [52], we adopted coarse mode marine POA source as suggested by Gantt et al. [20].

*2.3. Secondary Organic Aerosol Formation Pathways Considered in the Model.* TM4-ECPL considers sulphur and ammonia chemistry and the oxidation of C<sub>1</sub>–C<sub>5</sub> volatile organic compounds (VOC) including isoprene, glyoxal as well as a highly simplified terpenes and aromatic chemistry, described in detail by Myriokefalitakis et al. [35]. All major aerosol components including secondary ones (sulphate, nitrates, methane sulphonate, and other organics) are computed online together with the gas-phase chemistry and aerosol associated water; details are given in Tsigaridis et al. [36] and references therein.

Compared to earlier OA modelling studies [13, 32, 33], the marine POA and SOA are calculated at every model time-step. Precisely, marine SOA is produced from the oxidation of isoprene and monoterpenes of marine origin and from DMS oxidation by hydroxyl radicals (with methanesulphonate (MS<sup>-</sup>) being a minor oxidation product). A potential reaction of amines of marine origin with sulphuric acid [7, 53] has been also investigated. Thus, for isoprene and DMS, explicit oxidation schemes are considered in TM4-ECPL that affect oxidants and organic compound levels at every model time-step. MS<sup>-</sup>, that is also a SOA component, is considered to be produced via both gas and aqueous phase reactions based on the parameterisation of Mihalopoulos et al. [54].

For the SOA formation from isoprene and monoterpenes, the gas-phase oxidation two-product model has been adopted. In addition to the earlier studies by Tsigaridis and Kanakidou [29] and references therein, the applied updated SOA two-product yield parameterisation also accounts for the NO<sub>x</sub>-dependent SOA formation from isoprene oxidation. This parameterisation is based on VOC/NO<sub>x</sub> threshold values proposed in literature as indicated in Table 3 together with the input parameters adopted for these parameterisations. This approach for simplification purposes assumes that only hydrogen peroxy (HO<sub>2</sub>)/organic peroxy (RO<sub>2</sub>) or NO reactions occur depending on the VOC/NO<sub>x</sub> ratio [55]. Unpublished results by Tsigaridis and coworkers indicate that an overestimate by less than 10% in the low NO<sub>x</sub> environment, as is the case of the marine atmosphere, is associated with this approach. In the model, isoprene is also considered to produce SOA via cloud processing, parameterized based on the linearised relationship recently published by Ervens et al. [24] for stratiform clouds.

Finally, in an explorative simulation on the role of amines, biogenic marine amines are represented in the model by one gas-phase surrogate species considered to be a 50 : 50 mixture of dimethyl and diethyl amines with average properties. For simplicity, their oxidation by OH radical is assumed to produce only gas phase products, namely formic and acetic acids, formaldehyde, and acetaldehyde and to

proceed with a rate of  $K_{OH} = 3.5 \times 10^{-12}$  molecules<sup>-1</sup> cm<sup>3</sup> s<sup>-1</sup> (mean between ethylamine and dimethylamine reaction rates with OH radical [49, 64]). Also, for simplicity, reactions with O<sub>3</sub> which are at least 5 times less effective than those with OH in removing dimethyl amine from the gas phase have been neglected here. This assumption can lead to less than 20% overestimate of the importance of the amines reactions with OH radical. In the absence of available kinetic and thermodynamic data [7], dialkyl amines uptake on sulphate aerosol is assumed to proceed similarly to ammonia. Note that recently amines of biogenic origin in the nucleation mode in the marine environment have been suggested to enhance sulphuric acid water nucleation by Kurtén et al. [65]. Although largely uncertain, our simulations will provide a first estimate of the order of magnitude of the levels of the potentially formed amine salts that are here represented by one particulate phase surrogate species. SOA formation in the troposphere from other amine oxidation pathways [53] has been neglected in the present study. A Henry law coefficient of 39 M atm<sup>-1</sup> given by Sander [66] for diethylamine has been adopted.

*2.4. The Simulations.* In order to investigate the oceanic source of OA and especially the distribution and global budget of secondary and primary components, we performed various TM4-ECPL simulations. The two simulations discussed here are Simulation S1 and Simulation S2.

Simulation S1, used as the base case, accounts for marine SOA formation from isoprene, monoterpenes and DMS oxidation and tentatively by amines reactions with sulphuric acid as described in Section 2.3. The levels of each marine SOA component are individually computed and stored to allow detailed SOA budget analysis. The model also takes into account Chl-a monthly distributions from MODIS retrievals and computes on line the sea-salt emissions in the accumulation and coarse modes and POA marine emissions in the sub micron mode as a fraction [34] of sea-salt emissions in the accumulation mode. Simulation S1 has been performed for the period 2000–2008.

Simulation S2 is as S1, but it is based on monthly distributions of Chl-a from SeaWiFS retrievals and is used to evaluate uncertainties associated in the OA submicron source with the adopted Chl-a retrievals. This simulation has been performed for 2006.

### 3. Results and Discussion

*3.1. Global Distributions and Seasonal Variability.* The computed global distributions of marine POA, SOA from marine isoprene and monoterpenes, MS<sup>-</sup> from DMS oxidation and potentially formed amine sulfates are calculated by TM4-ECPL every time-step, monthly mean values are stored and analyzed here below. The annual mean surface distributions of the respective marine OA components for the first model level (simulation S1) for the year 2006 are shown in Figures 2(c)–2(g) together with the sea-salt distribution in the accumulation mode (Figure 2(b)). The computed annual mean distribution of the fraction of marine POA (%OA)

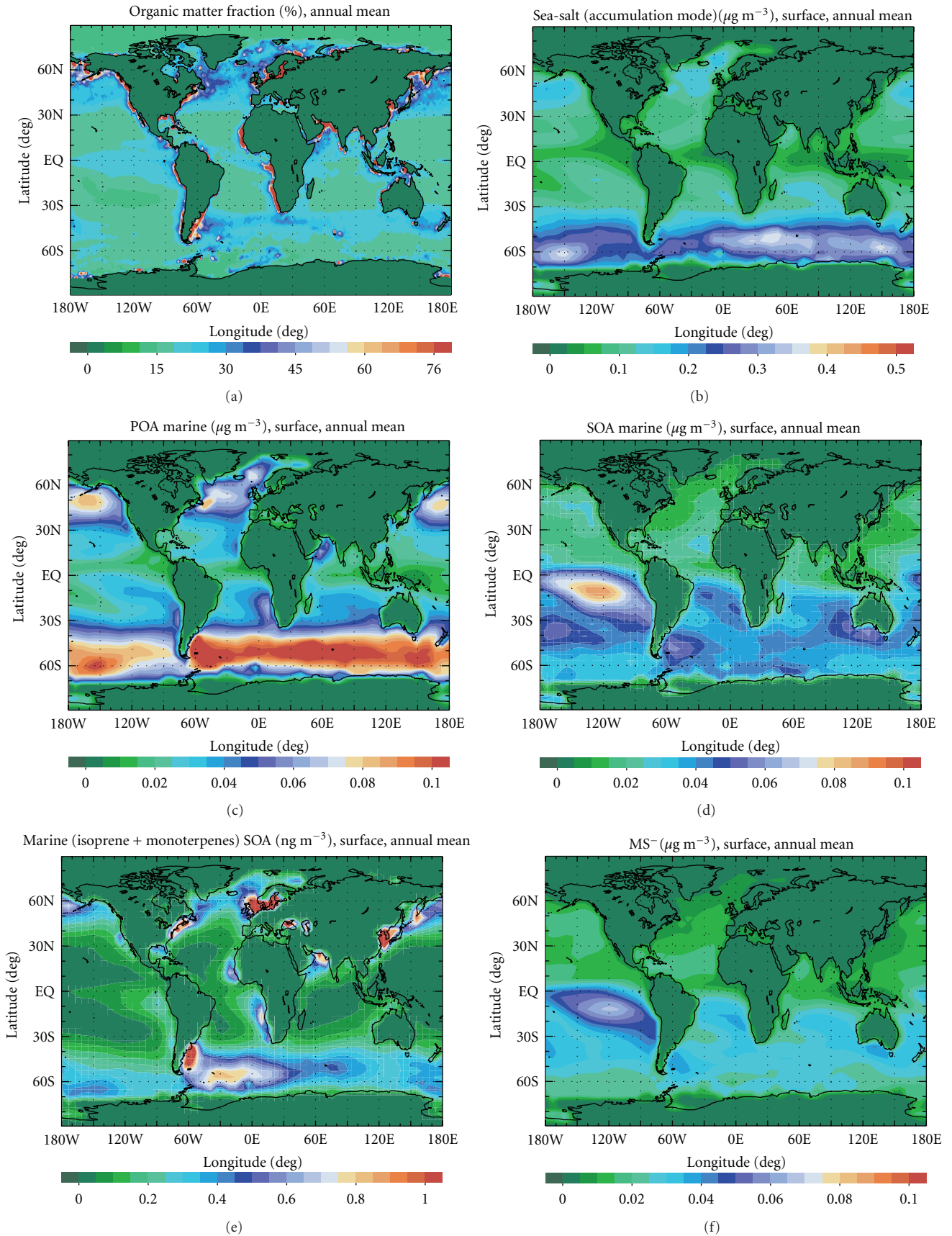


FIGURE 2: Continued.

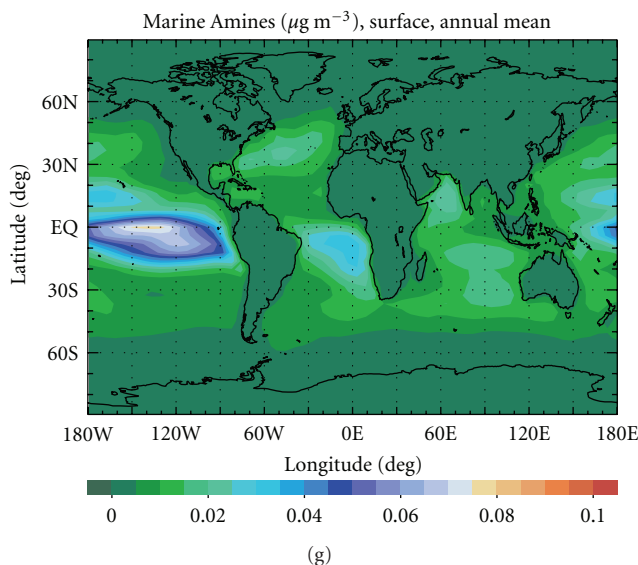


FIGURE 2: Annual mean surface distributions of (a) mass fraction of Marine OA to submicron sea-spray aerosol (in percent) calculated based on Chl-a as described by Vignati et al. [34]; (b) sea-salt in the accumulation mode; (c) Marine POA; (d) total marine SOA (from  $\text{MS}^-$ , isoprene and monoterpenes); (e) SOA from marine isoprene and monoterpenes; (f) SOA from  $\text{MS}^-$ , (g) SOA from marine Amines. Aerosol components are given in  $\mu\text{g m}^{-3}$ , except for SOA from marine isoprene and monoterpenes which is given in  $\text{ng m}^{-3}$ .

TABLE 2: Isoprene and monoterpene surface concentrations (in pptv) in the marine boundary layer Comparison between observations and TM4-ECPL monthly mean model results in the corresponding  $4^\circ \times 6^\circ$  (latitude  $\times$  longitude) model grid.

Location	Month	Model (pptv)	Observations (pptv)	Reference
Isoprene				
N. Atlantic Ocean	Jul. 2004	0.06	$2.8 \pm 0.8$	[56]
Norwegian Sea	Aug. 1999	2.4	$1.9 \pm 0.8$	[57]
NW Pacific Ocean	May 2001	2.5	7.2–110	[58]
Indian Ocean ( $50^\circ\text{S}$ – $20^\circ\text{S}$ & $50^\circ\text{E}$ – $80^\circ\text{E}$ )	Dec. 2004	2–9	20–340	[59]
Southern Ocean* ( $69^\circ\text{S}$ , $39^\circ 35'\text{E}$ – $45^\circ\text{S}$ , $105^\circ\text{E}$ )	Dec. 1997	1.4	13 ( $< 0.1$ –57)	[60]
Straits of Florida ( $24^\circ\text{N}$ , $80^\circ\text{W}$ )	Sep. 1993	127	5–11	[61]
Hao atoll ( $18^\circ\text{S}$ , $140^\circ\text{W}$ )	Jun. 1990	0.6	$< 2$	[12]
Syowa Station ( $69^\circ 00'\text{S}$ , $39^\circ 35'\text{E}$ )	Dec. 1997	0.2	0.1–57	[60]
Southern Ocean	Jan.-Feb. 2007	10.4	26–187*	[15]
Monoterpenes				
Southern Ocean	Jan.-Feb. 2007	$1.4 \pm 0.9$	5 – 125*	[15]
Indian Ocean ( $50^\circ\text{S}$ – $20^\circ\text{S}$ & $50^\circ\text{E}$ – $80^\circ\text{E}$ )	Dec. 2004	23	$56 \pm 20$	[59]

\* Range of average observations for far away before the bloom and in situ bloom cases,  $35^\circ 49'\text{S}$ ,  $20^\circ 22'\text{E}$  to  $52^\circ 17'\text{S}$ ,  $67^\circ 73'\text{W}$ .

associated with the submicron sea-salt aerosol is depicted in Figure 2(a) and maximizes near the coasts at upwelling areas as well as in the north and south Atlantic midlatitudes and in the southern Indian Ocean. The marine POA submicron source distribution (Figure 2(c)) is the product of the distributions of submicron sea-salt (Figure 2(b)) and of %OA fraction. Whereas the marine submicron POA maximizes over the oceans in the  $30^\circ$ – $60^\circ$  latitude band in both hemispheres with the highest levels calculated for the southern hemisphere, SOA from isoprene and monoterpenes exhibit high levels in the high productivity regions mainly in the northern hemisphere and at the south east coast of South America as well as secondary marine maxima

in the southern tropics. It is worth mentioning that the few pptv isoprene calculated by the model for the remote marine boundary layer are close to the low values of the observations summarized in Table 2. The concentrations of isoprene reflect its emission distribution and its oxidation by hydroxyl and nitrate radicals and ozone. Thus, they maximize over the extra-tropical oceans (Figures 1(e) and 1(f)) and present secondary maxima over the tropics in areas of relatively high Chl-a exposed to intensive incoming solar radiation. The monthly mean calculated marine isoprene concentrations near the surface are in general lower than the observed levels that correspond to a short (a few minutes to  $< 1$  h) daytime period (Table 2), like for instance the



TABLE 3: Properties of the SOA species used by the two-product model for SOA formation.

<sup>1</sup> SOA <sub><i>i</i></sub>	$\alpha_i$	$K_i$ (m <sup>3</sup> $\mu$ g <sup>-1</sup> )	$\Delta H$ (kJ mol <sup>-1</sup> )	Reference
isoprene-p1N	0.0021	1.6200	42	[22]
isoprene-p2N	0.4975	0.0086	42	[22]
isoprene-p1H	0.0288	1.6200	42	[22]
isoprene-p2H	0.2320	0.0086	42	[22]
a-pinene-p1N	0.0138	0.0637	38	[62]
a-pinene-p2N	0.4610	0.0026	38	[62]
a-pinene-p1H	0.1920	0.0637	38	[62]
a-pinene-p2H	0.2150	0.0026	38	[62]
b-pinene-p1N	0.0260	0.1950	40	[62]
b-pinene-p2N	0.4580	0.0030	40	[62]
b-pinene-p1H	0.3617	0.1950	40	[62]
b-pinene-p2H	0.2262	0.0030	40	[62]
toluene-p1N	0.0348	0.0403	40	[63]
toluene-p2N	0.1178	0.0010	40	[63]
toluene-p1H	0.0710	0.0530	40	[63]
toluene-p2H	0.1380	0.0019	40	[63]
xylene-p1N	0.0240	0.2290	60	[63]
xylene-p2N	0.1520	0.0040	60	[63]
xylene-p1H	0.0490	0.3010	60	[63]
xylene-p2H	0.1780	0.0080	60	[63]

<sup>1</sup>Nomenclature of species was chosen as follows: first 3 or 4 capital letters denote the parent VOC. The letter “p”, followed by the number 1 or 2, denotes the product number. In case there is an additional letter “N” or “H”, it denotes formation under low and high VOC/NO<sub>x</sub> ratio conditions, respectively. For the intermediate case of aromatic oxidation ( $5.5 < \text{VOC/NO}_x < 8$  in ppbC/ppb; [63]), the average parameters of high-to-low VOC/NO<sub>x</sub> were used.

100–200 pptv observed in the Indian Ocean during summer by Colomb et al. [59]. Differences between model results and observations like those shown in Table 2 are expected and justified both by the low spatial resolution of our model as well as the expected high temporal and spatial variability of isoprene and monoterpenes concentrations in the marine environment.

MS<sup>-</sup> shows a smoother geographical distribution with high levels all over the southern ocean and a regional maximum in the tropical Pacific. The highest levels of amine sulphates, tentatively calculated, seem to occur over the tropical oceans (Figure 2(g)) following the adopted ocean emission distribution of gaseous amines and the surface concentrations of sulphuric acid.

Figures 3(a), 3(b), 3(c), and 3(d) depict the seasonality of marine POA and SOA (excluding the amine salt contribution), respectively, as calculated by the model for simulation S1. Both primary and secondary OA sources are computed to exhibit a strong seasonality driven by biological activity, represented in the model by Chl-a, and wind speed (both for SOA and POA) as well as surface solar radiation, temperature and oxidant levels (for SOA). In Figures 3(e) and 3(f), the fraction of marine OA to the marine submicron aerosol mass is depicted and indicates contributions of at least 10% over the oceans that maximise in the tropics to about 20%–25% (attributed to the SOA patterns) and in the extratropical oceans with more than 50% contribution mainly attributed to the marine POA. As

expected, the OA contribution to the sub micron marine aerosol exhibits large seasonal patterns in the extra tropical areas.

The relative importance between primary and secondary marine submicron OA source can be seen from Figures 4(a) and 4(b) that depict the contribution of marine POA and marine SOA to the marine OA (sum of the two components), respectively, on an annual mean basis. These figures clearly demonstrate the dominance of SOA in the tropics compared to the POA that dominates the marine OA in the extra-tropical oceans.

The ratio of marine OA to total (marine and terrestrial) OA at surface is depicted in Figure 4(c). According to TM4-ECPL model calculations, marine OA is a significant fraction of surface OA concentrations over the oceans with the greatest contribution to the total OA load in the North Atlantic, North Pacific, and the Southern Ocean (between 30° and 60°S). At this latitude zone, marine SOA is also the major component of total SOA (Figure 4(d)). Regions of continental outflow are subject to less than 40% marine contribution to the total OA whereas in the Southern Ocean’s this fraction reaches 90%. The relative importance of marine OA to the other marine fine aerosol components, the sea-salt in the accumulation mode and the marine sulphate are depicted in Figures 4(e) and 4(f), respectively. These figures indicate the dominance of marine SOA over the sea-salt submicron aerosol in the tropics and that of marine POA over sulphate aerosol in the extratropical oceanic regions.

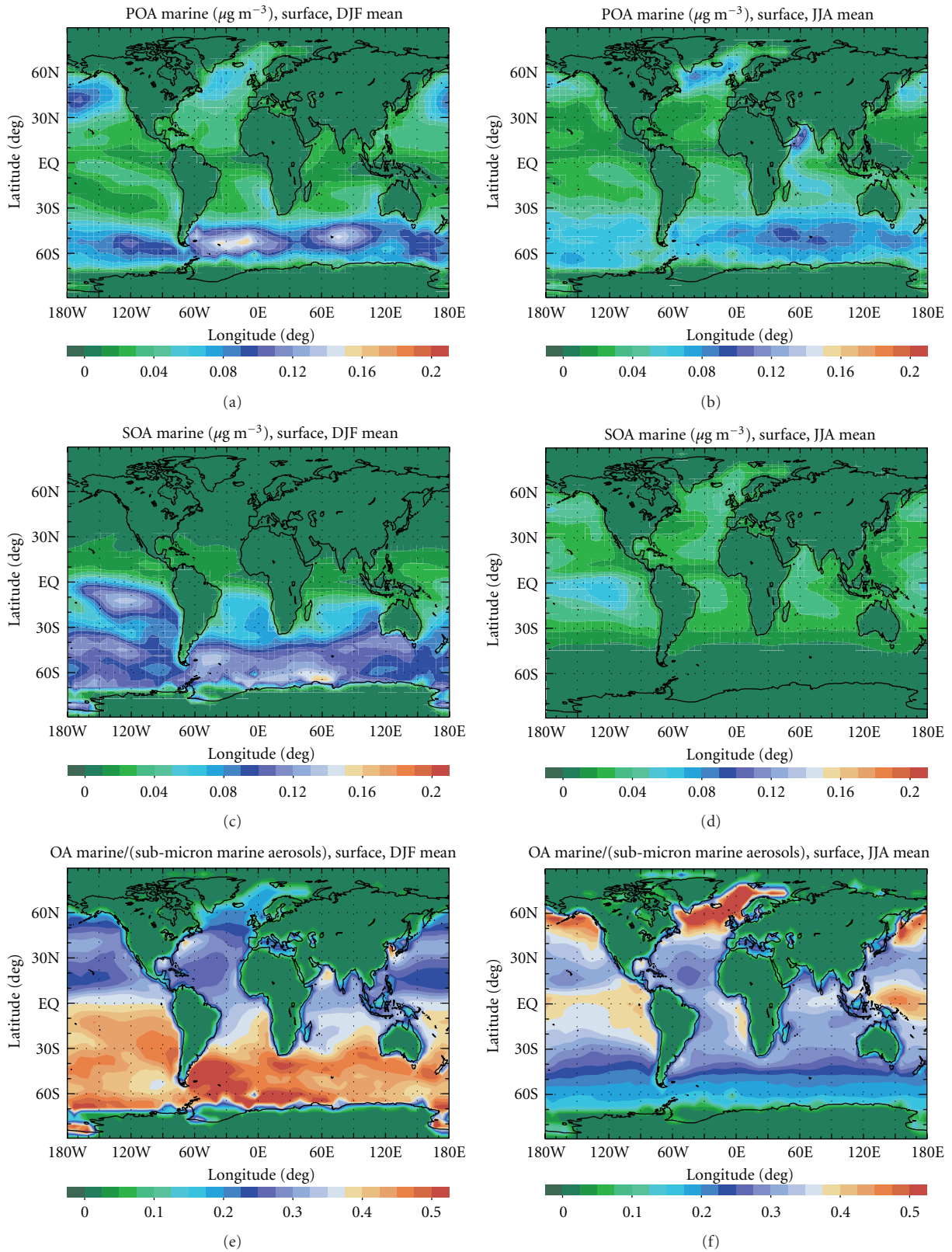


FIGURE 3: Calculated mean surface distributions for S1 of ((a), (b)) marine submicron POA ((c), (d)) marine SOA in  $\mu\text{g m}^{-3}$ ; ((e), (f)) mass ratio of marine OA (POA+SOA) to marine sub micron aerosol (sum of OA,  $\text{SO}_4^-$  and sea-salt in the accumulation mode) for DJF ((a), (b), and (c)) and JJA ((b), (d), and (f)) 2006.

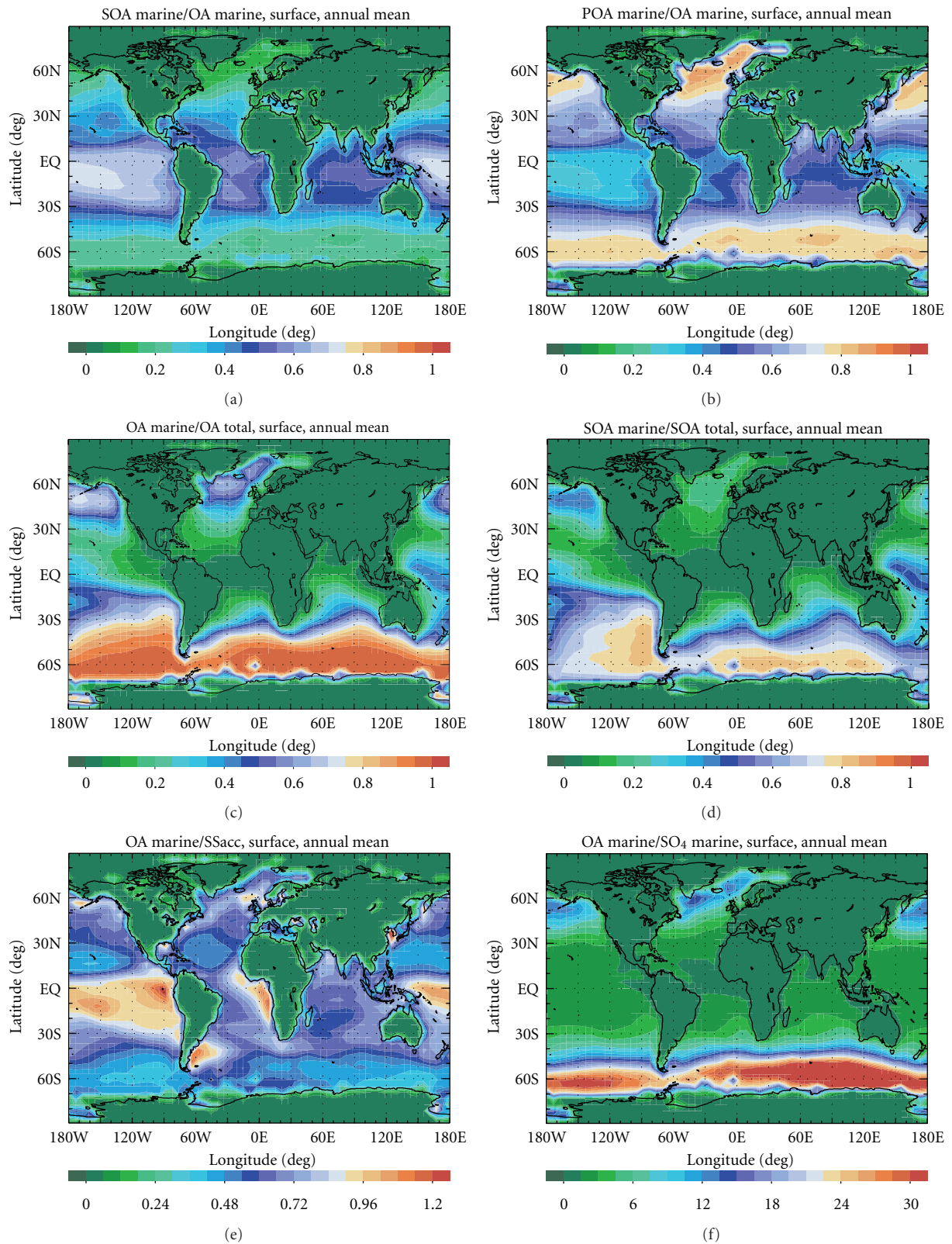
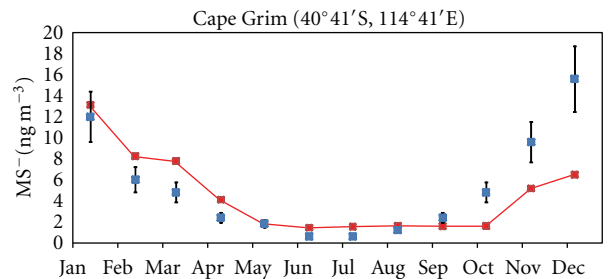
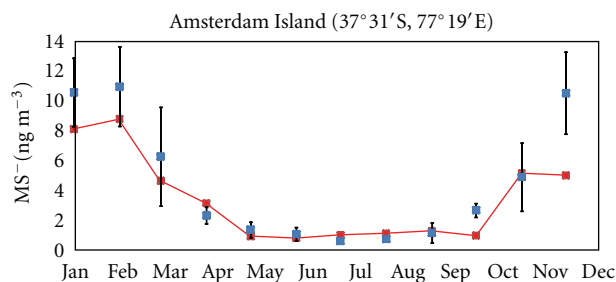


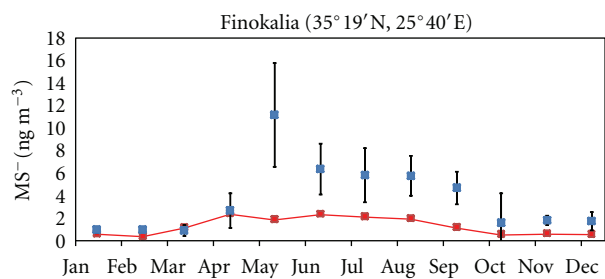
FIGURE 4: Calculated mean fraction of (a) marine SOA to total marine OA, (b) marine POA to total marine OA, (c) marine OA to total OA, (d) marine SOA to total SOA, (e) marine OA to sea-salt in the accumulation mode, (f) marine OA to marine sulphate. For clarity values over entirely land covered model grids have been omitted.



(a)



(b)

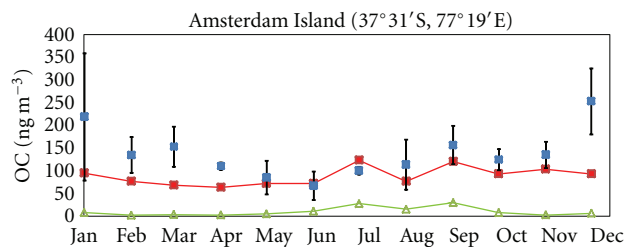


(c)

FIGURE 5: Comparison of methanesulphonate ( $MS^-$ ) observations with model results. Observed (filled squares with standard deviation bars) and model  $MS^-$  (solid line red squares) at: (a) Cape Grim ( $40^\circ 41'S$ ,  $114^\circ 41'E$ ; [17]) (b) Amsterdam Island ( $37^\circ 31'S$ ,  $77^\circ 19'E$ ; [41]), (c) Finokalia ( $35^\circ 19'N$ ,  $25^\circ 40'E$ ; [42]). All values are in  $ng\ m^{-3}$ .

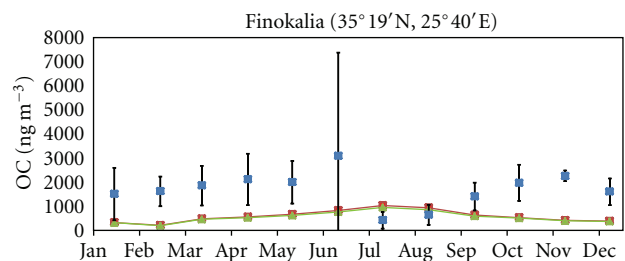
3.2. Comparison of Aerosol Simulations with Observations. Model results are compared with few recent observations of organic aerosol and particulate  $MS^-$  over oceanic locations available in literature.

Figure 5 depicts the comparison between model results and observed annual cycle of  $MS^-$ . TM4-ECPL is able to reasonably simulate concentrations and seasonal variation of  $MS^-$  at these oceanic locations. The concentrations of  $MS^-$  show strong seasonal dependence with the maximum values of  $MS^-$  observed during the warm season. At Amsterdam Island [41] and Cape Grim [17] sites, both of them located in the South Hemisphere, the maximum  $MS^-$  concentrations are observed and calculated during December to February ( $\sim 12\ ng\ cm^{-3}$  in February and  $\sim 16\ ng\ cm^{-3}$  in December, respectively). At Finokalia station located in the eastern

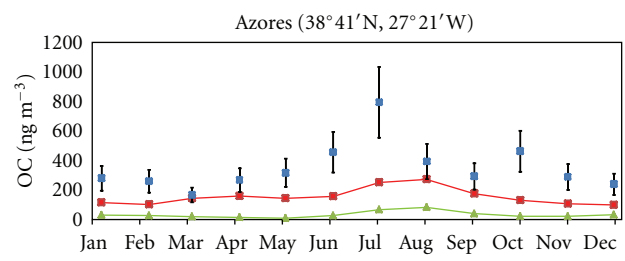


(a)

—■— TM4 OC  
—▲— TM4 OC-no marine sources  
—■— Obs. OC



(b)



(c)

FIGURE 6: Comparison of particulate Organic Carbon (OC) observations with model results. Observed OC (blue squares with standard deviation bars), modelled OC-S1 accounting for the oceanic sources of OA (red line—squares), and neglecting the marine OA sources (green line—triangles) at marine locations. (a) Amsterdam Island ( $37^\circ 31'S$ ,  $77^\circ 19'E$ ; [41]) and (b) Finokalia ( $35^\circ 19'N$ ,  $25^\circ 40'E$ ; [42] and [43]), (c) Azores ( $38^\circ 41'N$ ,  $27^\circ 21'W$ ; from Pio et al. [44]). All values are in  $ng\ m^{-3}$ .

Mediterranean the maximum concentrations are observed [42] and calculated during May and October (with maximum value of  $\sim 14\ ng\ cm^{-3}$ ), when the oxidation of  $MS^-$  precursors (DMSO, gaseous MSA, DMS) by OH radicals in the aqueous phase is significant and wet removal is low. Comparing Figures 5(b) and 7(a), it appears that  $MS^-$  contributes less than 15% to the observed WSOC in the remote marine atmosphere.

Figure 6 compares the observed concentrations of organic aerosols with model results from simulation S1 (all sources) when the oceanic components of OA are neglected. TM4-ECPL underpredicts the observed OC concentrations at various oceanic stations (see figure caption for details). At these sites the highest concentrations are observed during summer, but the model best simulates the OC concentrations

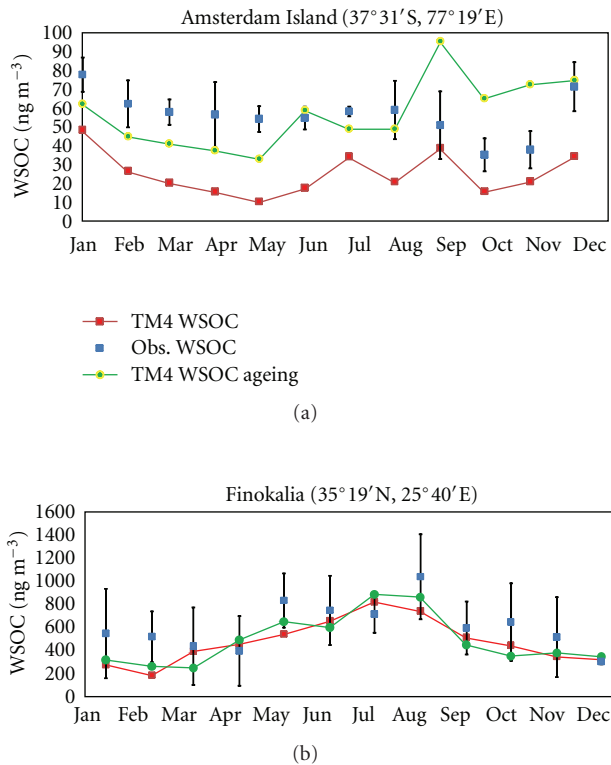


FIGURE 7: Comparison of water-soluble organic carbon (WSOC) observations with model results. Observed WSOC (blue squares with standard deviation bars) and modelled WSOC-S1 (red line—squares) and WSOC when ageing of marine POA is taken into account (circles and green line) at (a) Amsterdam Island (37°31'S, 77°19'E) [41] and (b) Finokalia (35°19'N, 25°40'E) [42]. All values are in ng m<sup>-3</sup>.

during winter. In order to investigate the uncertainties of marine sources on OC concentrations, the measured values are compared with the OC concentrations computed when accounting and when neglecting the oceanic source of OA. Based on these comparisons, among the studied locations, Amsterdam Island is the station the most affected by the marine OA source (Figure 6(a)). We find that a wintertime mean background level of about 25 ng cm<sup>-3</sup> of OC at Amsterdam island can be attributed to other sources of OC than the ocean that corresponds to about 10% of the total OA in agreement with our calculations depicted in Figure 4. Note, however, that Amsterdam Island is located at the north edge of a highly biologically active zone over the Southern Ocean. The underestimation of OC concentrations by the model might be associated either with the coarse resolution of the model that prohibits accounting for the sharp latitudinal gradients in the biological activity in the surrounding area or with a possible underestimation of marine sources associated with the specific phytoplankton species distribution. The contribution of the various SOA components (from isoprene and monoterpenes, MS<sup>-</sup> and amine salts) that are part of the water soluble organic carbon (WSOC) has been further investigated for this

location. Figure 7 compares the WSOC observations with TM4-ECPL model results. It appears that although the model simulates reasonably well the observations of OC at Amsterdam island (Figure 6(a)), the model underestimate WSOC observations at this remote ocean monitoring station as shown in Figure 7(a). This could indicate a potentially missing marine source of WSOC in our model. This is not the case for the remote coastal monitoring station of Finokalia in the Mediterranean (Figure 7(b)) where model results compare well with observations, indicating that for continentally affected marine locations the model captures well the WSOC since any potentially missing marine sources of WSOC would be minor contributors to the observed WSOC. To further investigate potentially missing formation pathways for WSOC, we have performed an additional simulation considering that the marine POA is subject to chemical ageing as in the case of anthropogenic POA [28], converted thus to WSOC. Because marine POA is associated with the short lived sea-salt aerosol and thus experiences a short lifetime, this conversion is not expected to significantly affect total marine OA but mainly increase WSOC levels. Indeed, as shown in Figure 7(a) for Amsterdam island, observed and modeled WSOC agree reasonably well when ageing of marine POA is taken into account. These results point to the chemical ageing of marine POA as a significant source of WSOC in the remote marine atmosphere.

The model aerosol optical depth (AOD) derived as explained in Tsigaridis et al. [36] has been confronted with MODIS retrievals for AOD in the fine mode. The selected oceanic regions for this comparison are shown in Figure 8(a) and the annual mean computed AOD are compared with the MODIS AOD in Figure 8(b). On average, the model AOD distribution presents similar pattern with the MODIS retrievals except over the Pacific tropical oceanic regions (30° N–30° S) where the model underestimates the fine fraction of AOD by a factor of 2. This underestimate over the tropical Pacific Ocean might be related to missing secondary organic aerosol sources in our model. Indeed, as shown in Figures 3(e) and 3(f) organic aerosols tend to significantly contribute to fine aerosol values over these marine regions. Furthermore, Figure 4 shows that the major contribution of marine SOA (Figure 4(a)) is at the tropic regions (30° N–30° S) and that of marine POA (Figure 4(b)) in the extratropics.

In addition to the direct interactions with radiation, aerosols affect climate via their impact on CCN. CCN activity is characterised by the critical size to which a particle activates and depends among other on the mass of the particle that affects its size, on the hygroscopicity and the surface tension of its components. Thus, OA mass of marine origin, if not contributing to new nuclei as suggested by Kurtén et al. [65] for amine salts, will increase the existing submicron particles helping them to reach a critical size faster than in the absence of these OA. In this respect, the insoluble organic fraction of the aerosol is expected to provide droplet growth kinetic delays [67] whereas the water soluble organic mass is behaving approximately similar to sulphate aerosols.

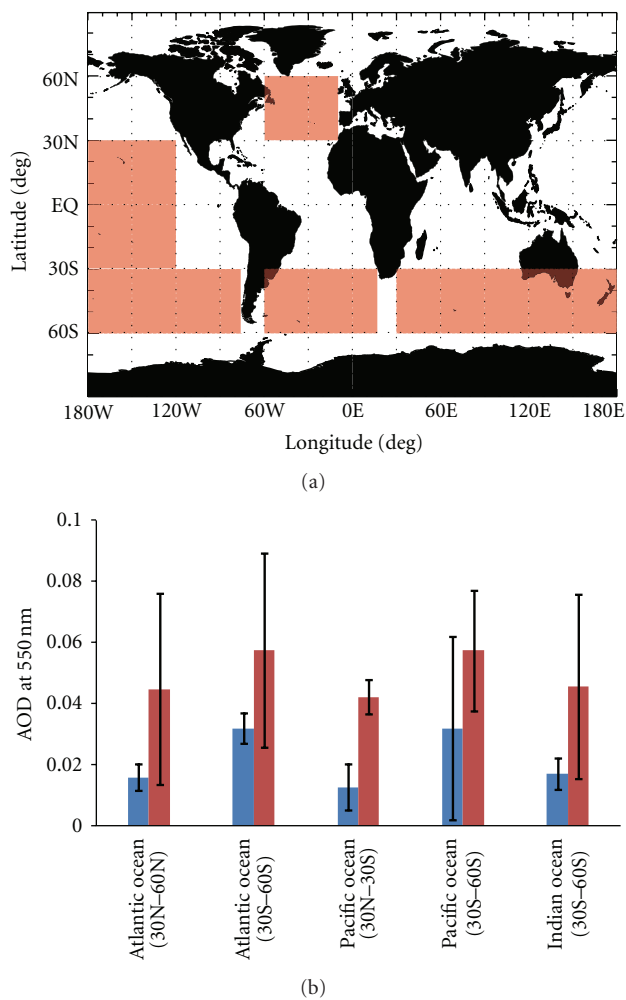


FIGURE 8: Comparison of MODIS AOD retrievals with model results. Retrieved MODIS AOD (red bars), modeled total AOD-S1 (blue bars), at selected marine locations: Atlantic Ocean (60 N,60 W-0 N,10 W), Atlantic Ocean (30 S,60 W-60 S,15 E), Pacific Ocean (30 S,180 W-60 S,75 W), Pacific Ocean (30 N,180 W-30 S,120 W) and Indian Ocean (30 S,30 E-60 S,180 E).

**3.3. Budget Calculations.** Based on the adopted parameterizations of marine sources of DMS, marine amines, isoprene and monoterpenes emissions as well as the parameterizations of SOA formation from the oxidation of these marine precursors TM4-ECPL evaluates the marine SOA global annual chemical production at about  $5.1 \text{ Tg yr}^{-1}$ . Approximately,  $0.1 \text{ Tg yr}^{-1}$  originate from oceanic monoterpenes and isoprene oxidation,  $4.0 \text{ Tg yr}^{-1}$  from  $\text{MS}^-$  and  $1.0 \text{ Tg yr}^{-1}$  in case of from marine amines when they are taken into account for SOA production. Marine SOA is removed via dry and wet deposition. As a result the global annual burden on marine SOA in the model domain equals about  $0.06 \text{ Tg yr}^{-1}$  for SOA mainly (78%) from  $\text{MS}^-$ .

The global annual oceanic POA emissions in the accumulation mode are calculated to be  $7 \text{ Tg yr}^{-1}$  based on MODIS Chl-a retrievals for the year 2006. By adopting Chl-a distribution retrieved from SeaWiFS observations in the

model leads to about  $1 \text{ Tg yr}^{-1}$  higher marine source of POA than estimated based on the MODIS Chl-a retrievals. As discussed in Vignati et al. [34] the calculated POA marine emissions are associated with an uncertainty of about a factor of 4, mainly attributed to that in the submicron sea-salt emissions. In addition, at least an overall 45% of uncertainty is associated with low spatial resolution estimates of POA source; the low resolution always overestimates the POA source compared to the high resolution simulation. Comparison of model results with observations indicates an additional marine source of soluble organic carbon that could be partially encountered by marine POA chemical ageing.

A large fraction of oceanic OA is removed from the atmosphere through wet ( $9.7 \text{ Tg yr}^{-1}$ ) and dry ( $2.4 \text{ Tg yr}^{-1}$ ) deposition. A small fraction of marine sub-micron POA is also removed via sedimentation, following the fate of sea-salt aerosols. The global annual burden of marine OA equals  $0.12 \text{ Tg}$  with a lifetime of about 4 days. Note, however, that the model POA emissions from terrestrial sources in the model domain, amount  $42 \text{ Tg yr}^{-1}$  for the year 2006. That is about 8 times higher than the marine sources estimated in the present study. Moreover, the SOA formation from terrestrial sources in the model domain amounts about  $42 \text{ Tg yr}^{-1}$ , which is about 8 times higher than marine SOA production.

## 4. Conclusions

The global 3-dimensional chemistry/transport model TM4-ECPL has been adapted to simulate the temporal and spatial distribution of primary and secondary marine organic aerosols. The annual global source of marine SOA is estimated at about  $5.1 \text{ Tg yr}^{-1}$ . Monoterpenes and isoprene oxidation is calculated to produce about  $0.1 \text{ Tg yr}^{-1}$ ,  $\text{MS}^-$  contribution to SOA is  $4 \text{ Tg yr}^{-1}$  and in the case of taking into account marine alkyl amine salts marine SOA production is increasing by  $1 \text{ Tg yr}^{-1}$ . On the global scale, most of marine SOA (~78%) originates from the dimethylsulfide oxidation to methanesulfonic acid seconded by alkyl amines salts (~21%). Note that these results depend on the adopted parameterisations of marine sources of DMS, marine amines, and marine volatile organic compounds as well as the parameterizations of SOA formation from the oxidation of these marine precursors. For instance, if the oceanic source of isoprene and monoterpenes is one and two orders of magnitude larger, respectively, as evaluated by Luo and Yu [68], then the contribution of these compounds to the marine SOA formation could be significant. The annual global marine source of POA is evaluated at about 7 to  $8 \text{ Tg POA yr}^{-1}$  with an additional uncertainty of a factor of 4 associated with our calculations. The lowest estimates are issued when the sea-salt source is calculated on line by TM4 driven by wind speed whereas about 4 times higher estimates are derived using the AEROCOM derived sea-salt emission inventory [40] that differs from the online estimates to the size distribution of the emissions. In addition, Chlorophyll-a distributions derived from MODIS lead to slightly lower ( $\sim 1 \text{ Tg yr}^{-1}$ ) marine POA emission estimates than those

from SeaWiFS. The primary marine source estimate is about 10% the terrestrial POA emissions. Primary submicron and secondary OA sources are calculated to be of about the same order of magnitude in terms of mass. DMS is strongly contributing to the SOA source from known precursors on global scale. However, regionally and seasonally, isoprene and monoterpenes could significantly contribute to marine SOA formation. According to our model simulations that are based on the present understanding of marine SOA formation, organosulfates are the major marine SOA components. Unidentified potential source of VOC or missing SOA formation processes, like for instance aerosol water chemistry that is here neglected, in the marine atmosphere could account for additional marine SOA.

The present study elucidates the importance of interactions between nitrogen, sulphur, and carbon cycle for the organic aerosol mass in the atmosphere. Further investigations are needed to improve our knowledge on such processes and in particular to properly account for organic nitrogen formation and amines which appear to be a large fraction of marine organic aerosols.

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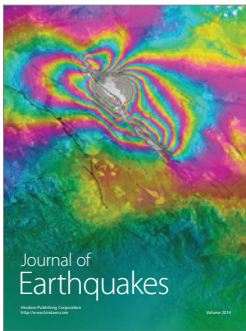
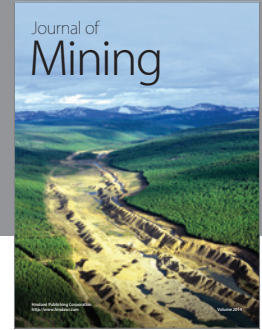
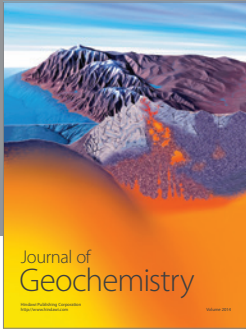
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